



Synthesis, Characterization and Thermal Study of some new Organochalcogenide compounds containing arylamide group

A. F. Hassan^a, A. T. Abdulwahid^a, M. Y. Al-Luaibi^{*a}, and S. N. Al-Jadaan^b

^aDepartment of Chemistry, College of Sciences, University of Basrah, Basrah, Iraq

^bDepartment of Pharmaceutical Chemistry, College of Pharmacy, University of Basrah, Basrah, Iraq



Abstract

Two Series of organochalcogen compounds were prepared. The first series was prepared by the reaction of 2-chloro-N-arylacetamide (where aryl is benzyl, phenyl, *o*-toluene, or *p*-toluene) with sodium hydrogen selenide (prepared *in situ*) to give diorganyl selenide compounds (R₂Se). The second series was prepared by reaction of N-benzyl-2-chloro-N-(2-chloroacetyl) acetamide with sodium chalcogenate, Na₂E (where E= S, Se, and Te) to give the corresponding cyclic chalcogenide compounds. Diiodo derivatives of cyclic selenide and telluride were also prepared. The thermal stability of the new selenium compounds (R₂Se) were decomposed at 300°C. Thermogram showed a phase transfer point between 120-150°C indicating that these compounds may act as liquid crystal compounds. All new compounds were characterized by CHN elemental analysis, UV-Visible, FT-IR and ¹H NMR spectroscopic data.

Keywords: 2-chloro-N-arylacetamide, selenium, tellurium, organochalcogen compounds, heterocycles.

1. Introduction

Selenium and tellurium are rare elements, and they are regarded as toxic metalloids although they have a role in some biological applications [1,2]. Both elements are reported to be essential elements[3]. Organo chalcogenides, diorgano dichalcogenides, and selenazoles are well known compounds and they are widely studied for their biological activities [4]. Thus, several methods were used to prepare such compounds. The most used method involving chalcogenide reagents is the nucleophilic substitutions using organic halides with disodium or sodium hydrogen chalcogenide [5].

In this paper, a series of new organochalcogenide compounds containing an amide group were prepared in the hope to use them as antioxidants and

antibacterial agents. Furthermore, their thermal properties will be discussed.

2. Materials

All materials and solvents used in this study were of analytical reagent grade (Sigma, Aldrich, and British Drug House companies).and used as supplied.

3. Experimental

3.1. Synthesis of compound

3.1.1. Synthesis of 2-Chloro-N-phenylacetamide

A mixture of aniline (3.72 g; 4 mmol) and potassium carbonate (5.52 g; 4 mmol) in 70 ml of acetone was stirred for 10 min. Chloroacetylchloride

*Correspondence: majeedalluaibi7@gmail.com. (Majeed Y. Alluaibi) ORCID ID, <https://orcid.org/0000-0003-2219-7716>

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(6.5 ml; 8 mmol) was added dropwise. The reaction and stirred for two hours, filtered. The acetone was removed under vacuum. To the filtrate 30 ml of dis. water was added. A white ppt. formed, filtered, dried then recrystallized from ethanol[6], the product was obtained in 75 % yield, m.p. 167-168 °C.

The following compounds were prepared by the same procedure described,

o-CH₃PhNHCOCH₂Cl, m.p. 146-147 °C and *p*-CH₃PhNHCOCH₂Cl, m.p. 157-158 °C; PhCH₂NHCOCH₂Cl, m.p. 98 °C.

3.1.2. Synthesis of Bis-(*N*-(*o*-tolyl)acetamide) selenide (I)

To a suspended solution of selenium powder (0.115 g; 3.05 mmol) in 25 ml of H₂O has added a solution of NaBH₄ (0.116 g; 1.45 mmol) in 25 ml of H₂O under Argon atmosphere. A vigorous reaction occurs with the evolution of hydrogen gas. Selenium powder was consumed in less than 10 min. A colorless solution of NaHSe was formed[7]. To the resulting solution was added a solution of 2-chloro-*N*-phenylacetamide (0.5 g; 2.96 mmol) in 30 ml of ethanol under Argon atmosphere. After about 30 min. a violet solution was formed and filtered. To this solution 50 ml of H₂O was added, the resulting solution extracted with CH₂Cl₂. The solvent was evaporated by a rotary evaporator. A violet solid was obtained, collected by filtration, dried then recrystallized from ethanol[8]. A violet precipitate was obtained in 82 % yield, m.p 204-205 °C.

3.1.3. Synthesis of *N*-Benzyl-2-chloro-*N*-(2-chloroacetyl)acetamide (compound (V))

The compound was prepared according to a similar method described for compound I by using phenylmethanamine (4.28 g; 40 mmol). A Yellowish-white precipitate was obtained in 82 % yield, m.p 90-92 °C.

3.1.4. Synthesis of *N*-Benzyl-2-iodo-*N*-(2-iodoacetyl)acetamide)

The compound was prepared by the addition of (0.3 g; 2 mmol) to compound (V) (0.26 g; 1 mmol). A deep brown crystals was formed, recrystallized from ethanol.

3.1.5. Synthesis of 4-Benzylselenomorpholine-3,5-dione (VI)

This compound was prepared by reacting of *N*-benzyl-2-chloro-*N*-(2-chloroacetyl)acetamide (0.77 g; 2.96 mmol) in 30 ml of ethanol with aqueous of NaHSe by the same above method. A yellowish-white solid was obtained. Recrystallization by ethanol gave the compound in 82 % yield, m.p. 89-90 °C.

3.1.6. Synthesis of 4-Benzylthiomorpholine-3,5-dione (VII)

To an aqueous solution of Na₂S.2H₂O (0.34 g; 2.96 mmol) was added a solution of *N*-benzyl-2-chloro-*N*-(2-chloroacetyl)acetamide (0.77 g; 2.96 mmol) in 30 ml of ethanol under Argon atmosphere. After about 30 min. a Pale-yellow solution formed, filtered, 50 ml of dis.H₂O was added, the resulting solution extracted with three portion of CH₂Cl₂. The solvent evaporated to a minimum amount, a Pale yellow precipitate was collected, dried and recrystallized from ethanol. A pale-yellow solid was obtained in 82 % yield, m.p 138-140°C.

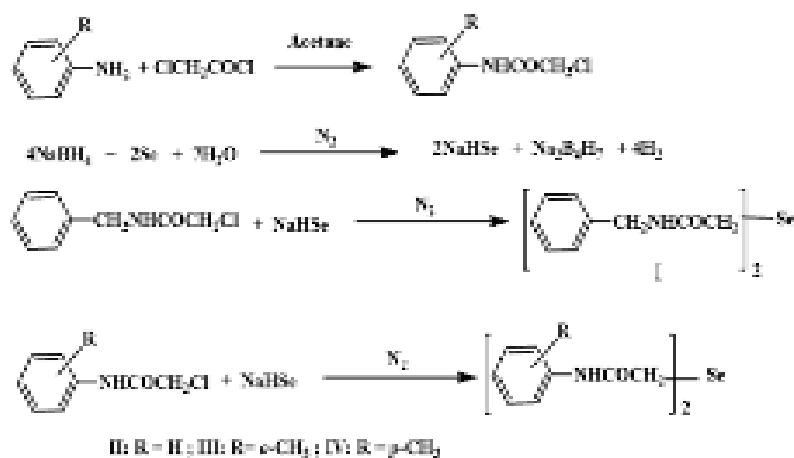
3.1.7. Synthesis of 4-Benzyl-1,1-diiodo-114-telluromorpholine-3,5-dione (IX)

A mixture of *N*-benzyl-2-chloro-*N*-(2-chloroacetyl)acetamide (0.28 g; 1 mmol) and excess of sodium iodide (1.2g ; 8 mmol) and Te powder (0.63 g; 5 mmol) in 50 ml of 2-ethoxy ethanol was stirred for 3h at room temperature. The solution turned to deep red color and filtered. The solvent was removed under vacuum. Reddish-brown crystals obtained and recrystallized from chloroform[8]. Reddish-brown solid was obtained in 82 % yield, m.p 101-103 °C.

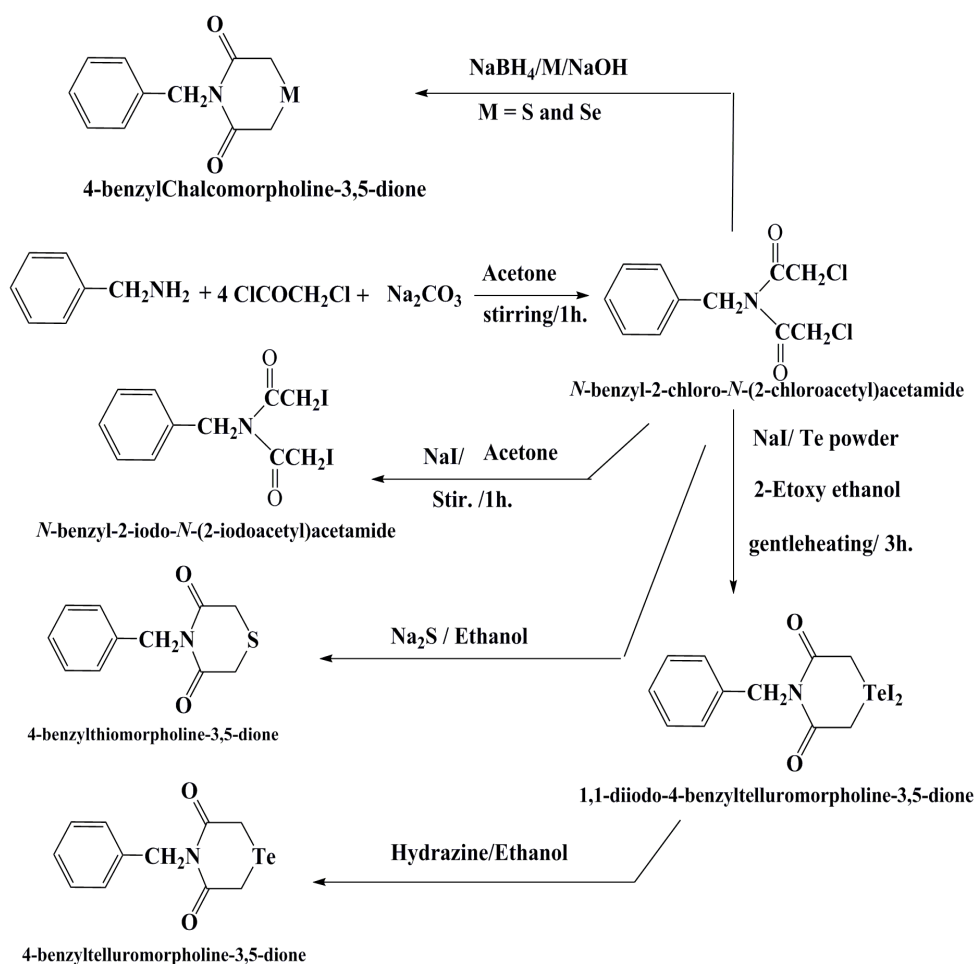
3.1.8. Synthesis of 4-Benzyltelluromorpholine-3,5-dione (VIII)

4-Benzyl-1,1-diiodo-114-telluromorpholine-3,5-dione (IX) (1.596 g, 2.8 mmol) of was dissolved in 40 mL of hot ethanol and heated under reflux for 1 h. A solution of hydrazine hydrate in 30 mL of ethanol was added dropwise to the refluxing solution until the evolution of nitrogen was ceased. The solution was filtered hot, poured into 600 mL of water and then extracted several times by diethyl ether. The combined ether extracts were dried over CaCl₂ and evaporated to dryness by a rotary evaporator. The residue was recrystallized from petroleum ether[8] (60/80). Yield

82% , Yeiowished white solid, mp 103°C.
Physical properties of new compounds are listed in Table 1 and the synthesis of compounds are shows in scheme 1 and 2.



Scheme 1. Synthesis of compounds I-IV



Scheme 2. Synthesis of chalcogenide compounds V-XI .

4. Results and Discussion

The FTIR spectra for organoselenides have been studied, were analyzed in terms of functional groups determination. The infrared data proved that Se powder reacts in a basic NaBH₄ solution with alkyl halides to produce the corresponding organoselenium compounds. Se-C stretching vibrations were observed around 493- 528 cm⁻¹[9,10]. No evidence for a NH₂ bond was found, while N-H bands appeared as very strong single bands at about 3150 – 3420 cm⁻¹ which gave the first evidence about the suggestion of the first step of reactions. Other unsymmetrical stretching vibrations for C=O, C-Har., C-Hale. and C=C bonds were found at expected regions[10,11], Table 2.

¹H NMR spectra of the new selenide compounds have been measured to determine their structures in solution. The ¹H NMR chemical shift values were found to be particularly useful in distinguishing between selenides. The downfield chemical shifts of 8.53 – 10.13 ppm are characteristic of the NH groups, while the chemical shifts at about 7.3 – 7.56 ppm due to the aromatic rings in the organic part of selenides. The methyl and methylene groups appeared in the upper field at chemical shifts (2.007- 4.27) ppm[10-12]. The ¹H NMR spectra showed the disappearance of NH frequencies at their expected region that the most effective evidence for double substitutions of the

two hydrogens on nitrogen in compounds V-IX, Table 3 and the expected structures for new compounds are shown in Fig 1.

4.1. Thermogravimetric analysis (TGA)

TGA analysis depends on the amount of weight change of a material as a function of temperature, or a time in an inert atmosphere of nitrogen or argon gases.

Thermal gravimetric analysis can be interfaced with a mass spectrometer RGA to identify and measure the vapors generated, a more sensitive results could be gains when the mass spectroscopy heating is used in an ultrahigh vacuum system so, composite materials can be found accurately. In the present study, all prepared compounds show good thermal stability up to 300°C or more while their dissociation occurs with two steps in addition to a phase transfer step that appeared at about 120°C- 150°C. Increasing temperature led to melting point followed by loosing of a small part such as NH, CH₂NH, or methyl groups

in toluene compounds. The residues are largely selenium metal or amide group, The TG and DTG grums for new organoselenium compounds are shown in Fig. 2 and the expected thermal decomposition pathway for some new selenium compounds are shown in Scheme 3- a,b,c, and d.

Table 1. Physical properties and C H N data for comps.

Compd. No.	Chemical structure	m.p °C	Color	yield%	Elemental analysis Calculated (Found)		
					C%	H%	N%
I	(Ph NHC(O)CH ₂) ₂ Se	204 - 205	violet	82	55.34(55.58)	4.64(4.80)	8.06(7.87)
II	(<i>p</i> -CH ₃ Ph NHC(O)CH ₂) ₂ Se	151	Yellowish-white	54	57.60 (58.24)	5.37(5.87)	7.46(8.28)
III	(<i>o</i> -CH ₃ Ph NHC(O)CH ₂) ₂ Se	179	violet	79	57.60 (57.46)	5.37 (5.67)	7.46 (7.78)
IV	(Ph CH ₂ NHC(O)CH ₂) ₂ Se	150	yellowish-white	50	57.60(55.80)	5.37 (5.58)	7.46 (6.68)
V	Ph CH ₂ N(COCH ₂ Cl) ₂	90-92	Yellowish-white	82	50.79(50.58)	4.26(4.85)	5.38(5.697)
VI	Ph CH ₂ N(COCH ₂) ₂ Se	89-90	Yellowish-white	82	49.27	49.27	5.22
VII	Ph CH ₂ N(COCH ₂) ₂ S	138-140	Pale yellow	82	59.71 (59.82)	5.01 (4.81)	6.33 (6.874)
VIII	Ph CH ₂ N(COCH ₂) ₂ Te	105	Yellowish-white	82	41.70(41.545)	3.50(3.64)	4.42(4.627)
IX	Ph CH ₂ N(COCH ₂) ₂ TeI ₂	101-103	Reddish-brown	82	23.15	1.94	2.45

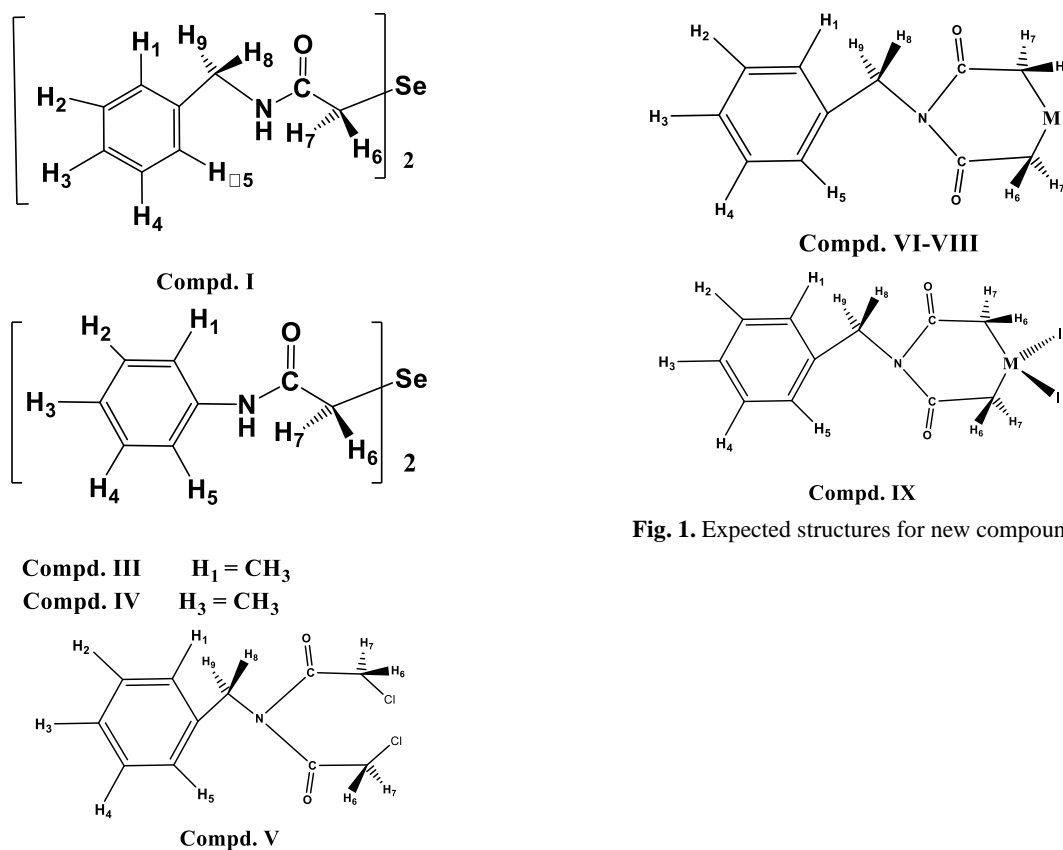


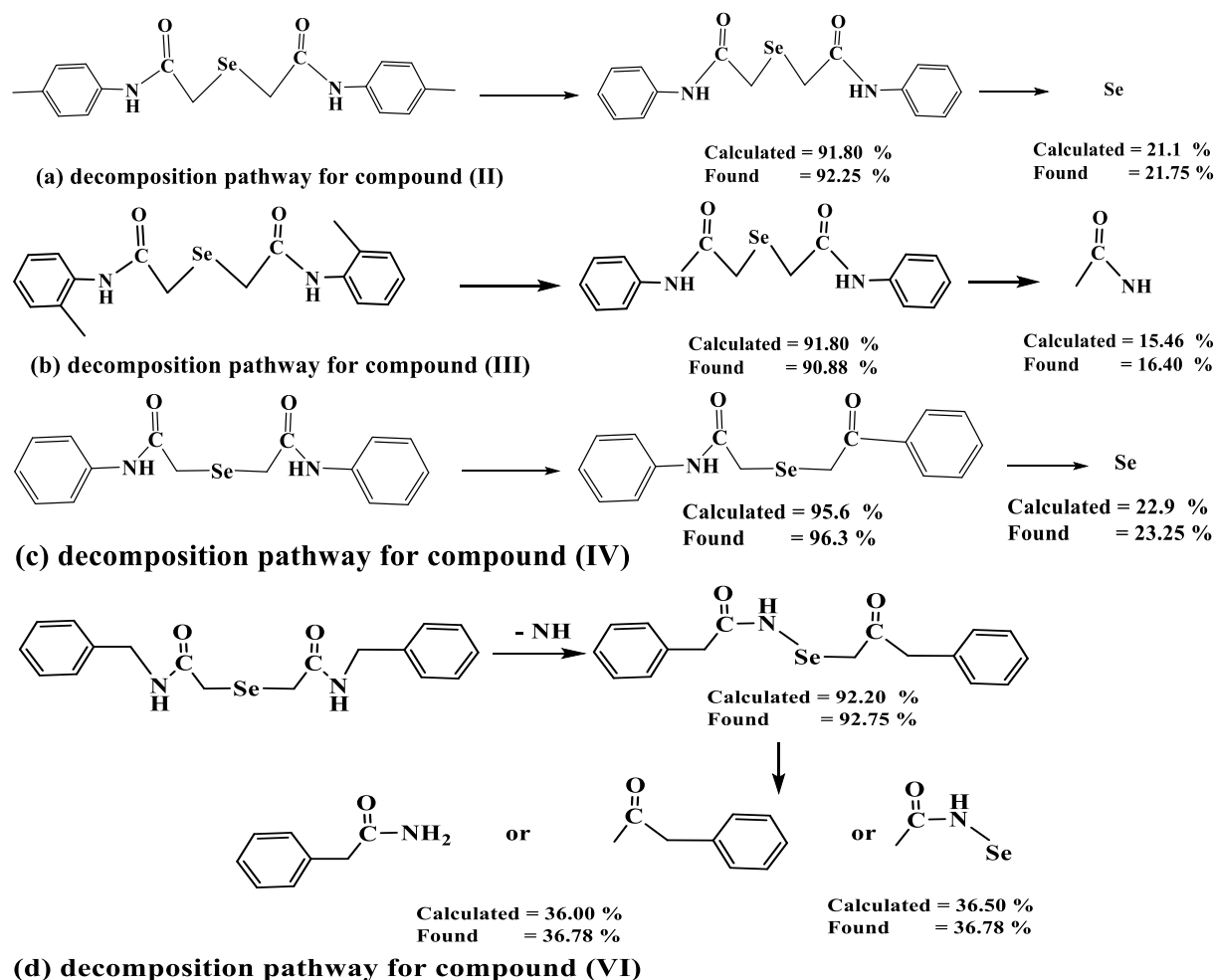
Fig. 1. Expected structures for new compounds

Table 2. UV-Vis. and IR Data for new comps.

Compd. No	UV- Visible Spectra (nm)				Infrared Spectra for main bands(cm^{-1})				
	Band I	Band II	Band III	Band IV	C=O	N=H	C-H _{ale.}	C=C	M-C M= S, Se or Te
I	404	302	260	-	1662	3248	2862	1554	493
II	-	294	246	-	1662	3290	2862	1550	501, 528
III	-	-	246	-	1643	3271	2920	1589	505
IV	360	290	240	-	1600	3483	2866	1550	528
V	-	-	-	-	1658	3286	2950	1556	-
VI	225	370	460	670	1641	3282	2950	1552	505
VII	-	-	246	-	1647	3286	2914	1525	720
VIII	360	290	240	680	1643	3280	2950	1552	500
IX	360	290	240	670	1620	3255	2925	1558	515

Table 3. ^1H NMR data for new compounds

Compd. No.	^1H NMR spectra (ppm) DMSO- d_6 solvent .TMS = 0ppm
I	8.53 (s) NH ; 7.23 - 7.31 (m) ph- protons ; 4.23- 4.27 (s) H_8, H_9 ; 3.35- 3.37 (s) H_6, H_7 .
II	10.13 (s) NH ; 7.56- 7.58 (d) H_1, H_5 ; 7.25- 7.31 (t) H_2, H_4 ; 7.03- 7.06 (t) H_3
III	9.47 (s) NH ; 7.05- 7.43 (m) H_3, H_4 ; 7.45 (d) H_2, H_5 ; 2.78 (s) H_6, H_7 ; 2.215 (s) H_1
IV	10.03 (s) NH ; 7.43 - 7.45 (d) H_1, H_5 ; 7.06- 7.10 (t) H_2, H_4 ; 2.24 (s) H_6, H_7 ; 2.007 (s) H_3
VI	7.22- 7.36 (m) phen; 4.90 H_8, H_9 ; 4.25-4.37 (d) H_6, H_6' ; 3.69 (d) H_7, H_7' ; 2.088 (s) H_1
VII	7.23- 7.37 (m) phen ; 4.90 H_8, H_9 ; 4.26-4.28 (d) H_6, H_6' ; 3.5 (d) H_7, H_7'
VIII	7.24- 7.42 (m) phen; 4.90 H_8, H_9 ; 4.26-4.37 (d) H_6, H_6' ; 3.69 (d) H_6, H_6' ; 2.088 (s) H_1
IX	7.24- 7.42 (m) phen ; 4.90 H_8, H_9 ; 4.29-4.3 (d) H_6, H_6' ; 3.69 (d) H_6, H_6' ; 2.089 (s) H_1



Scheme 3 Expected thermal decomposition pathway for some new selenium compounds(II,III,IV and VI)

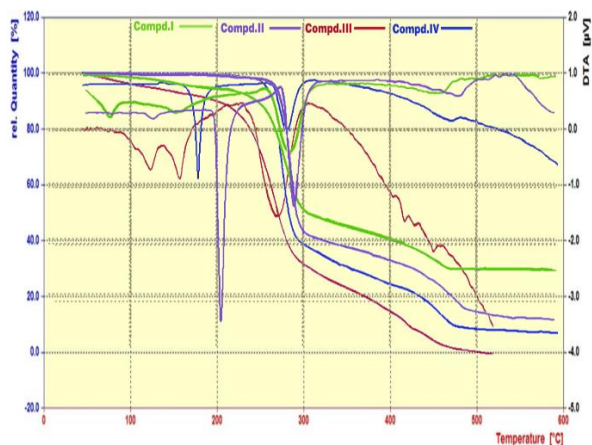


Fig. (2) TG and DTG grums for the new organoselenium compounds.

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