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Synthesis of New Seleno-Schiff Base Compounds

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ABSTRACT

Many organoselenium compounds can be prepared by using Potassium Selenocyanate (KSeCN) such as organoselenonitrile and diorgano diselane which is easily prepared by the alkaline hydrolysis of organoselenonitrile. That afforded a variety of new selenocarbonyl compounds which is condensation with different anime compounds to synthesis new Schiff base compounds containing selenium metal. The result compounds were characterized by physical properties like melting point and retardation factor (R_f). Also they were characterized Proton Nuclear Magnetic Resonance (¹H-NMR), Carbon-13 Nuclear Magnetic Resonance (¹³C-NMR), Mass spectroscopy and elemental analysis (C, H, N).

Keywords: Potassium selenocyanate, Selenonitrile, Diorgano diselane, Schiff base

INTRODUCTION

The synthesis of Schiff base containing hetero atom compounds has been extensively studied [1], while the syntheses of selenonitrile and dislane analogues have not been widely studied. This is mainly for being decomposed easily such as in preparing aliphatic organoselenium compounds [2]. Organoselenium compounds have taken special interests due to their successful applications as building blocks in the synthesis of various natural and biologically active compounds [3]. Also Schiff base compounds are of marked interest because of their anti-tumor [4,5], antibacterial and other notable activities [6]. Many synthetic methods of organoselenium compounds derivatives have been extensively investigated [7,8]. In this research, potassium selenocyanate as inorganic reagent has used to prepare several new carbonyl compounds containing selenonitrile group and diselane group. The present work describes the condensation reaction between carbonyl group and amine group to synthesize a variety of several seleno-Schiff base compounds [9,10].

EXPERIMENTAL SECTION

Physical measurements

Fourier Transform Infra-Red (FTIR) spectra were measured by an instrument called Bruker and the range was between 375-4500 cm⁻¹. Proton Nuclear Magnetic Resonance (¹H-NMR) spectra were measured by an instrument called Bruker 300 MHz. The samples were recorded in Dimethyl Sulfoxide (DMSO) solutions containing Tetramethylsilane (TMS) as internal standard. Chemical shifts for all ¹H and ¹³C-NMR spectra were reported in δ units downfield from internal reference Me₄Si. Elemental analyses (C, H and N) were obtained and Mass spectra were measured.

Synthesis methods

All the carbonyl selenonitrile compounds were prepared from the reaction of the corresponding benzoyl chloride with potassium cyanide. Schiff base compounds were prepared from the condensation of carbonyl selenonitrile with amine compounds. All these compounds were prepared according to the literature method.

The general procedure of preparation organoselenonitrile

0.8 of KCN in absolute ethanol (50 ml) was a stirred and (1 g; 125 mol) of selenium was added. This reaction was in red color. The mixture was refluxed. After 3 h, (206 ml 0.025 mol) of substituted benzoyl chloride was added and refluxed for 2 h. The reaction was followed by Thin Layer Chromatography (TLC). The precipitated was filtered, washed, dried and recrystallized from absolute ethanol [11,12].

The general procedure of preparation diorganodiselenane

0.28 g; 1.02 mol of organoselenonitrile in 25 ml absolute ethanol was stirred and a solution of sodium hydroxide (0.16 g, 2.47 mol) in 15 ml absolute ethanol was added. The mixture was stirred for 50 min at 40°C. The solution was refluxed for 1 h. The result cooled to retention time and filtered. The filtrate was acidified with 10% HCl. A red solid compound was obtained, washed with a small amount of benzene and dried. Recrystallization from a mixture of methanol and dichloro methane (1:4), gave a red solid compounds [13].

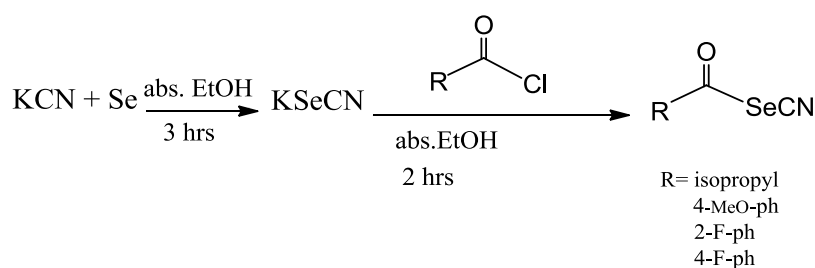
The general method to synthesize Schiff bases

0.028 mol of amine in absolute ethanol (160 ml) was stirred and (0.028 mol) of aldehyde was added with 3 drops of glacial acetic acid as a catalyst. The mixture was refluxed and the time of refluxed was different from compound to other depended on the type of substituent as shown in Table 1. The reaction was followed by TLC. The mixture was cooled and then the precipitated was filtered, washed, dried and recrystallized from absolute ethanol [14]. Schiff base structures and the physical properties are represented in Table 1.

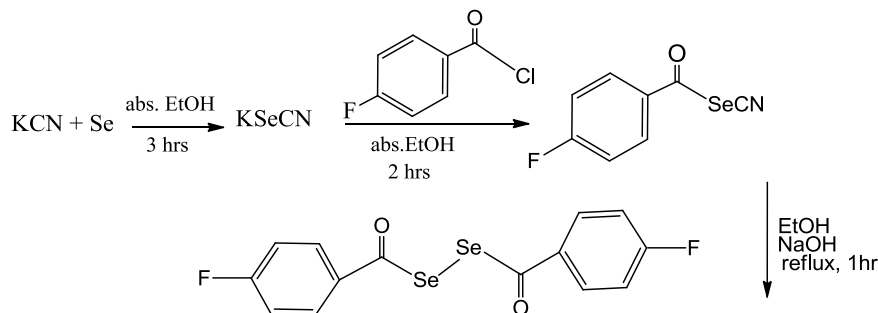
Table 1: Schiff bases structures and the physical properties

Symbols	Time of reflux (h)	Color	Yield%	Solution of TLC	Rf	Structures
S ₁	10	Brown	50	Carbon tetrachloride:Hexane 2.8:7.2	0.50	
S ₂	10	Yellow	63	Dichloromethane:Hexane 6.3:3.7	0.65	
S ₃	9	Yellow	75	Ethyl acetate:Chloroform 7.7:2.3	0.65	
S ₄	14	Yellow	76	Ethyl acetate:Hexane 4.8:5.2	0.54	
S ₅	6	Brown	69	Dichloromethane:Hexane	0.70	

The reaction of potassium selenonitrile with benzoylchloride gave carbonyl selenonitrile compounds as shown in Scheme 1:

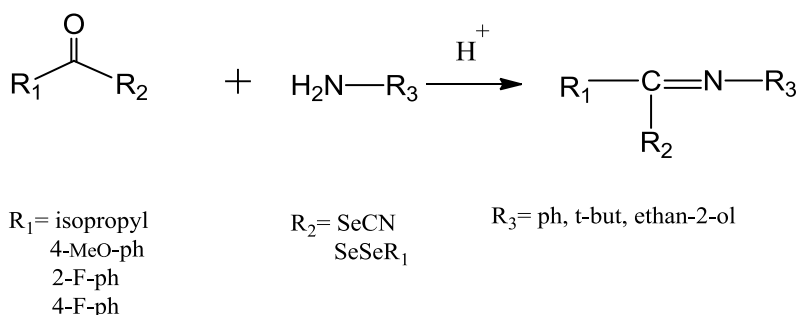
**Scheme 1: Reaction of potassium selenonitrile with benzoylchloride**

Diorganodiselenane can be prepared by the alkaline hydrolysis of carbonyl selenonitrile compounds, as shown in Scheme 2:

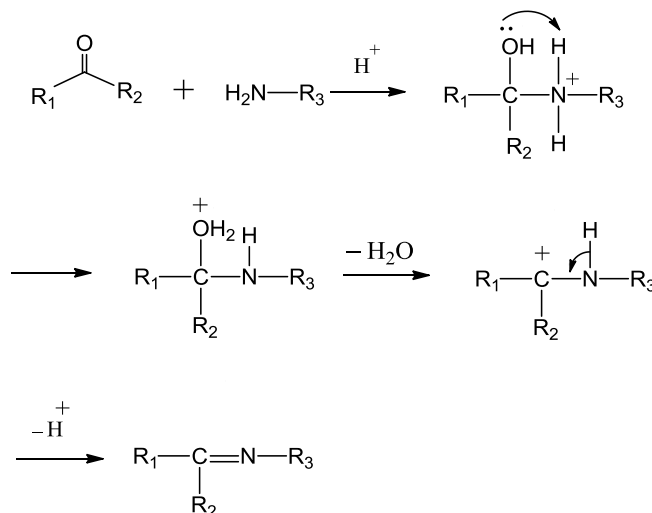


Scheme 2: Preparation of diorganodiselenane

Schiff base compounds can be synthesized by the condensation between carbonyl selenonitrile compounds and amine compound in good yield by the elimination of water, as shown in Scheme 3 and Scheme 4.



Scheme 3: Synthesis of Schiff base



Scheme 4: The mechanism of synthesis of Schiff base

RESULTS AND DISCUSSION

The resulting data were obtained for the synthesized compounds from analysis data as following:

2-((3-selenocyanatobutan-2-ylidene) amino) ethanol (S₁): Yield: 50%. m.p. 90-92°C. FTIR $\bar{\nu}/\text{cm}^{-1}$: 1605 (C=N), 1397 (C=C), 1330 (C-N), 583 (C-Se), 2100 (C \equiv N), 2998 (C-H aliph); ¹H-NMR [300 MHz, (DMSO), δ (ppm)]; m 1.75 (CH), m 3.1 (CH₃), m 1.6 (N-CH₂), m 3.9 (CH₂-O), 3.2 (OH); ¹³C-NMR [300 MHz, (DMSO), δ (ppm)]; 112 (C \equiv N), 159.6 (C=N), 72.6 (C-N), 60 (C-O), 23.8, 24.0 (CH₃), 33 (CH). For C₇H₁₁N₂OSe. (Found) 38.53% C, 5.04% H and 12.84% N. MS: m/z: 218 (M⁺).

N-(tert-butyl)-4-fluorobenzimidic diselenoperoxyanhydride (S₂): Yield: 63%. m.p. 77-75°C. FTIR $\bar{\nu}/\text{cm}^{-1}$: 1601 (C=N), 1388 (C=C), 1329 (C-N), 2109, (C \equiv N), 587 (C-Se), 2990 (C-H aliph), 3100 (C-H arom.) 1540 (C-F); ¹H-NMR [300 MHz, (DMSO), δ (ppm)]; m 1.1 (CH₃), m 7.2 (ph). ¹³C-NMR [300 MHz, (DMSO), δ (ppm)]; 160.4, 160.6 (C = N), 30.3, 30.5, 31.3, 31.5, 32.3, 32.7 (CH₃), 158.7, 158.9, 121.2, 121.4, 122.1, 122.3, 122.9, 123.5, 123.9, 129.5, 129.9, 130.4 (ph), 61.4, 61.9 (C-N). For C₂₂H₂₆N₂F₂Se₂. (Found) 51.36% C, 5.05% H and 5.44% N. MS: m/z: 514 (M⁺).

Cyanic-N-(2-hydroxyethyl)-4-methoxybenzimidic selenoanhydride (S₃): Yield: 75%. m.p. 95-97°C. FTIR $\bar{\nu}/\text{cm}^{-1}$: 1604 (C=N), 1390 (C=C), 1335 (C-N), 589 (C-Se), 2109 (C \equiv N), 2991 (C-H aliph), 3099 (C-H arom.); ¹H-NMR [300 MHz, (DMSO), δ (ppm)]; 3.7 (CH₃), 7.06 (2H-ph), 7.7 (2H-ph), 1.5 (N-CH₂), 4.1 (CH₂-O), 3.9(OH); ¹³C-NMR [300 MHz, (DMSO), δ (ppm)]; 111 (C \equiv N), 50.8 (CH₃), 124.9, 127.7, 128.3, 129.8, 130.5, 132.4 (ph), 161.4 (C = N), 69.5 (C-N), 62.1 (C-O). For C₁₁H₁₂N₂OSe. (Found) 46.64% C, 4.24% H and 9.89% N. MS: m/z: 283 (M⁺).

Cyanic-4-methoxy-N-phenylbenzimidic selenoanhydride (S₄): Yield: 76%. m.p. 80-81°C. FTIR $\bar{\nu}/\text{cm}^{-1}$: 1606 (C=N), 1395 (C=C), 1330 (C-N), 587 (C-Se), 2110 (C \equiv N), 2998(C-H aliph), 3101 (C-H arom.); ¹H-NMR [300 MHz, (DMSO), δ (ppm)]; 6.9 (2H-ph), 7.4 (2H-ph), m 7.7 (5H-ph), 3.8 (CH₃); ¹³C-NMR [300 MHz, (DMSO), δ (ppm)]; 51.1 (CH₃), 125.4, 128.6, 129.0, 131.5, 133.6, 139.0 (ph-N), 133.5, 133.7, 133.9, 134.2, 134.5, 160.4 (ph-O), 164 (C=N), 110 (C \equiv N). For C₁₅H₁₂N₂OSe. (Found) 57.14% C, 3.80% H and 8.88% N. MS: m/z: 315 (M⁺).

Cyanic-2-fluoro-N-phenylbenzimidic selenoanhydride (S₅): Yield: 69%. m.p. 94-96°C. FTIR $\bar{\nu}/\text{cm}^{-1}$: 1600 (C=N), 1398 (C=C), 1300 (C-N), 583 (C-Se), 2109 (C \equiv N), 2996(C-H aliph), 3111 (C-H arom.) 1550 (C-F); ¹H-NMR [300 MHz, (DMSO), δ (ppm)]; 7.9 (3H-ph), 7.6 (2H-ph), 7.3 (5H-ph); ¹³C-NMR [300 MHz, (DMSO), δ (ppm)]; 124.6, 124.9, 126.1, 128.1, 128.9, 137.0 (ph-N), 120.3, 120.9, 121.5, 122.4, 123.6, 162.3 (ph-O), 165 (C=N), 115 (C \equiv N). For C₁₄H₉N₂FSe. (Found) 55.44% C, 2.97% H and 9.24% N. MS: m/z: 303 (M⁺).

The relevant IR spectral bands that can provide from disappear of band (C=O) of carbonyl compounds in the range (1660-1670 cm⁻¹) and band (NH₂) of amine compounds in the range (3000-3100 cm⁻¹) stretching and (1600-1610 cm⁻¹) bending. The appearance of bands (C=N) in the range (1600-1606 cm⁻¹) that verify the synthesis of Schiff bases [15,16]. In ¹H-NMR spectra disappear bands in the range (3-5 ppm) which belongs to (NH₂) of amine compounds. Mass spectroscopy gives the molecular ion and other fragments which indicated the structure of synthesized Schiff base. The elemental analysis found resemble to theoretical values. The yield of products depends on the type of substituted groups. Therefore, the selenoaromatic products are more yield than selenoaliphatic products because they are more stable [17,18]. The presence of electron donating groups in carbonyl selenonitrile increases the yield of products more than the drawing group.

CONCLUSION

Five new Schiff base compounds were obtained from the condensation between carbonyl group and amine group. Carbonyl selenonitrile compounds were prepared from the reaction of potassium cyanide with benzoyl chloride in different substituents. This method was easier than other methods to produce organoselenium compounds. The chemical structures of new Schiff base compounds were characterized by identification methods.

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