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Synthesis of novel 2,5-disubstituted-1,3,4-selenadiazoles from fatty acid hydrazides

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Abstract A series of novel unsaturated hydroxy and non-hydroxy fatty acid residue substituted 1,3,4-selenadiazoles were described here. These derivatives were synthesized from the reaction of fatty acid hydrazide **1(a–d)** with acetyl chloride in the presence of anhydrous sodium carbonate in tetrahydrofuran and water at 0 °C, to form N'-acetyl undec-10-enoic hydrazide **2a**, N'-acetyl-(9Z)-octadec-9-enoic hydrazide **2b**, N'-acetyl-(9Z, 12R)-12-hydroxy-9-enoic hydrazide **2c**, and N'-acetyl-(9R, 12Z)-9-hydroxy-12-enoic hydrazide **2d**. Then these hydrazines (dicarbonyl compound) on reaction with Woollin's reagent (WR) in toluene led to the corresponding 2-(dec-9'-enyl)-5-methyl-1,3,4-selenadiazole **3a**, 2-[(8'Z)-heptadec-8'-enyl]-5-methyl-1,3,4-selenadiazole **3b**, 2-[(8'Z, 11'R)-11'-hydroxy-octadec-8'-enyl]-5-methyl-1,3,4-selenadiazole **3c**, and 2-[(8'R, 11'Z)-8'-hydroxy-octadec-11'-enyl]-5-methyl-1,3,4-selenadiazole **3d**, respectively. These synthesized compounds were characterized on the basis of IR, ¹H NMR, ¹³C NMR, mass spectra and elemental analysis results.

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1. Introduction

The first organo selenium compound diethyl selenide was synthesized in 1836 (Löwig, 1836). The selenoheterocyclic compounds are closely related to the sulfur compounds but their properties are quite different from the sulfur compounds. A number of hetero organo selenium compounds (Mlochowski

et al., 2007), such as isoselenazole, selenosulfide, selenadiazoles, and selenatriazoles, have been known from the literature.

Organo selenium compounds found its application in various fields such as organic synthesis (Patai and Rappoport, 1986; Back, 1994), ligand chemistry (Hope and Levason, 1993), material synthesis (Bochman, 1996), biochemistry (Burk, 1994), photography (Yamashita et al., 1994) and biologically relevant processes. In the organic synthesis, the organo selenium compounds can be used as an electrophile or as nucleophile for functional group manipulation in a variety of substrates under mild condition (Paulmier, 1986) and also utilized in modern asymmetric synthesis, which have generated a new trend in organo selenium chemistry (Wirth, 1999). In biochemistry field, the selenium atom is incorporated in the selenocystine residues in various enzymes such as tetraiodo thyronine-5'-deiodinase, formate dehydrogenase, glycine reductase, glutathione peroxidase, plasma protein P (Böck,

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1994) and hydrogenase, where it has been found to act as more reactive nucleophile than their sulfur counterparts. Sometimes organo selenium compounds are also used as selenoenzyme [mimics of glutathione peroxidase (GPx)], that protects the cell membrane from oxidative damage and helps in the reduction of various hydroperoxides (Mugesh and Singh, 2000).

In addition to these chemical properties, substituted organo selenium compounds also show a number of biological properties (Prabakaran et al., 2011), good electro optical properties (Velusamy et al., 2005), electroluminescent (Yang et al., 2005), and non linear optic potential candidates for two photon absorption and sensor application (Ostrowski et al., 2003). Substituted selenadiazole derivatives have been reported to possess cytotoxic (Jalilian et al., 2003), and antiproliferative activities as well. These compounds are found to be active against various types of cancer cells such as colon (HT-29), breast (MCF-7), lung (HTB-54) and leukemia (CCRF-CEM) (Plano et al., 2010) and also active against HIV-I replication in MT₄-cells (Zhan et al., 2009). Apart from the above mentioned biological properties selenadiazoles, have also been found to possess anticonvulsant, antitumor, antiinflammatory, analgesic, antibacterial, fungicidal (Shealy and Clayton, 1967; Padmavathi et al., 2009; Parveen et al., 2009; El Sadek et al., 2013) and pesticidal activities.

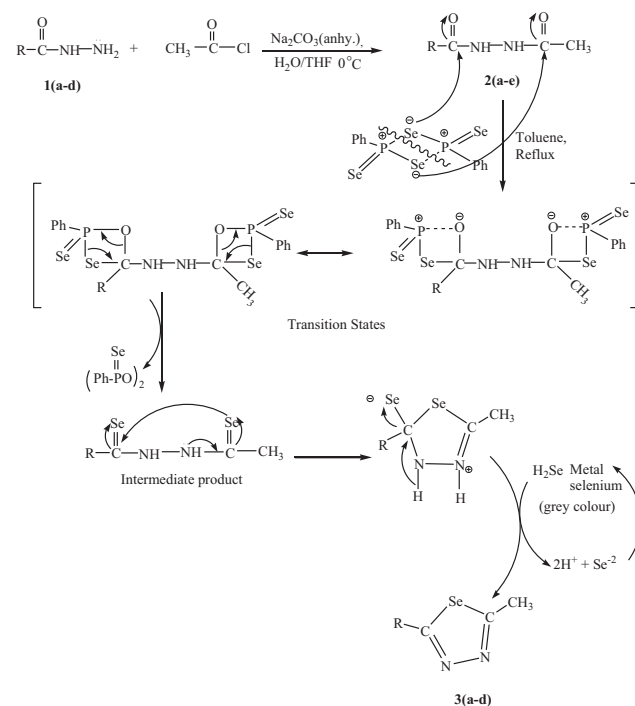
1,2,4-Aryl selenadiazoles can be obtained by the reaction of selenocarboxamides in the presence of iodine (Becker and Meyer, 1904; Cohen, 1978; Dotsenko et al., 2013) and substituted 1,3,4-selenadiazoles can be synthesized from the reaction of N,N'-diaryloxalodihydrazonoyldichlorides with potassium selenocyanate (Farag et al., 1994), but the selenocarboxamide gives better yield and less reaction time in the presence of palladium catalyst (Al-Rubaie et al., 2002). Substituted and Multi-arm/Multiple 1,2,3-selenadiazole rings have been prepared by the reaction of selenium dioxide with α -ketomethylene semicarbazones or hydrazones in the presence of acetic acid (Saravanan et al., 2007; Al-Smadi and Ratrou, 2005; Al-Smadi and Al-Momani, 2008). The synthesis of 1,2,3-selenadiazoles under ultrasonic and microwave irradiation has also been reported in the literature (Shinde et al., 2010). 3,5-Diaryl-1,2,4-selenadiazoles have been synthesized from selenoamides (Rong and Sen, 2002), these selenoamides are not only useful for the synthesis of selenium-nitrogen heterocycles but also for the reaction with various organic and inorganic reagents because of the high reactivity of their carbon selenium double bond. The selenadiazoles are utilized in the synthesis of cadmium selenide (Khanna et al., 2004), which is an important semi conductor that can act as optoelectronic material. Here, we are generally focusing on the synthesis of 2,5-disubstituted-1,3,4-selenadiazoles. A number of methods have been reported for their syntheses, all these methods are limited due to some consequences. But 2,4-diphenyl-1,3-diselenadiphosphetane-2,4-diselenide (Hua et al., 2009) [PhP(Se)(μ -Se)]₂, is found to be the more appropriate reagent in every aspect for the synthesis of 2,5-disubstituted-1,3,4-selenadiazoles, although WR is very useful in the synthesis of a wide variety of cyclic and acyclic selenium containing compounds (Hua et al., 2013).

The fatty acid organo selenium compounds were synthesized earlier (Agarwal et al., 1990; Saeed et al., 1991) from our laboratory. In this paper, we report the synthesis of fatty acid residue substituted 1,3,4-selenadiazoles with Woollin's

reagent (WR) through the corresponding 1,2-dicarbonyl compound selenation.

2. Results and discussion

We report the synthesis of 2-alkenyl/hydroxy alkenyl-5-alkyl-substituted-1,3,4-selenadiazole **3(a-d)**, from the corresponding intermediate N'-acetyl fatty acid hydrazide **2(a-d)**, on reaction with Woollin's reagent in dry toluene. These substituted hydrazides **2(a-d)**, were synthesized by the reaction of fatty acid hydrazide **1(a-d)**, with acetyl chloride in THF/H₂O solvent in the presence of anhydrous Na₂CO₃ at 0 °C. The synthetic pathway for the synthesis of substituted fatty acid hydrazides **2(a-d)** and 2,5-disubstituted 1,3,4-selenadiazoles **3(a-d)**, is presented in Scheme 1 and proposed mechanism of the reaction was also described. All the synthesized compounds were purified by column chromatography and characterized by IR, ¹H NMR, ¹³C NMR elemental analyses and mass spectra. The detailed spectral description of compound **2(a)** is given below.



The IR spectrum of the compound showed characteristic peaks at 3314, 3219 cm⁻¹ (N=H stretching), 1628 cm⁻¹ (C=O stretch) and at 1265 cm⁻¹ (N-N stretch). The ¹H NMR spectra of the compound showed some diagnostic peaks. Two singlets were observed at δ 9.07, 8.82 for two N-H stretching. The methine proton of C₁₀ showed a signal at δ 5.79. The methylene protons designated as H_b and H_a, displayed two distinct δ values when coupled with adjacent C₁₀ methine protons. Thus, spectra showed two doublets at δ 4.98, 4.92 and a sharp singlet at δ 2.17 for methyl protons. The ¹³C NMR spectra showed peaks at δ 174.2, 172.1 for carbonyl carbon and at 18.5 for methyl carbon adjacent to

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