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Microwave assisted Synthesis of 3,4-dihydropyrimidin-2(1H)-thione derivatives of thiadiazole.

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Abstract: *Various substituted 3,4 -dihydropyrimidin-2(1H)-thiones have been synthesized by conventional heating method. 2—amino thiadizole was condensed with substituted derivatives of 3,4 -dihydropyrimidin-2(1H)-thiones to get the final product. Synthesized compounds were characterized by IR, NMR and mass spectral data.*

Keywords: *3,4 -dihydropyrimidin-2(1H)-thiones,1,3,4-thiadizole, Microwave irradiations.*

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I. Introduction

Dihydropyrimidin-2-ones and thiones[1a,b] have attracted attention of scientific community due to their biological activity such as anti-inflammatory, antibacterial[2], antihypertensive[3], α-1a-antogonished calcium channel[4] Thiadiazole derivatives show the wide range of therapeutic activities like antimicrobial[5] , atifungal[6], antipsychotic[7], anti-inflammatory[8]. It also show interesting antitumour activity.[9]

Schiff bases are the class of organic compound with pharmacologically active azomethine group. Schiff bases are synthesized by condensation reaction of amino compound with carbonyl compound in presence of acid catalyst[10]. Schiff bases are common legand in co-ordination compounds. The nitrogen atom of imines is basic in nature and show pi-acceptors properties. Conjugated shiff bases show interesting opto electronic property. They are used in solar cells[11].

Microwave irradiation has become a powerful tool for rapid and efficient synthesis of a variety of compound because of selective absorption of microwave energy by polar molecules[12]. Microwaves have been used to speed up chemical reaction in the laboratories[13] which led scientists to investigate the mechanism of microwave dielectric heating and to identify the advantages of the technique for chemical synthesis[14.] Microwave has been extensively used for carrying out chemical reactions and have become a useful non-conventional energy source for performing organic synthesis[15].

II. Materials And Methods

Melting point of all synthesized compounds was taken in open capillaries and is uncorrected. IR spectra (KBr) were recorded on Shimadzu IR spectrometer and ^{1}H-NMR were recorded on 300 MHz spectrometer using TMS as internal standard. Purity of the synthesis compound was checked by TLC using Silica gel Plate using hexane-ethyl acetate as solvent.

III. Experimental

3.1. Synthesis of 5-(5-amino-1,3,4-thiadiazol-2-yl)-4-(4-hydroxy-3-methoxyphenyl)-6-methyl-3,4-dihydropyrimidine-2(1*H*)-thione (Compound 3)

Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(Compound 1) was prepared according to the reported procedure.[16]Compound 1(17 gm,0.0586 mole) was refluxed with Thiosemicarbazide(5.34 gm,0.0586 mole) in presence of ethanol for (8-10 hr) and cooled and poured into ice-cold water. The solution was filtered and washed with ice cold water and dried. Compound 2was formed and concentrated $H_2SO_4$was added with continuous stirring at room temperature and left overnight. It was then poured into crushed ice. The resulting solution was basified with ammonia solution, solid obtained was filtered and dried and purified by crystallization.

3.2. Preparation of 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-5-(5-{[(1*E*)-phenylmethylene] amino}-1,3,4-thiadiazol-2-yl)-3,4-dihydropyrimidine-2(1*H*)-thione (Compound 4a-j)

a. Conventional heating method:

In a round bottom flask, substituted aldehyde (1 mol) and Compound 3(1 mol) weretaken in ethanol and few drops of glacial acetic acid were added. The reaction mixture was reflux for about 8 hrs till the completion of the reaction. Progress of the reaction was checked with TLC (Hexane: Ethyl acetate – 8:2) Then it was cooled with ice cold water. It was filtered and washed with cold water and dried and recrystallized from ethanol.

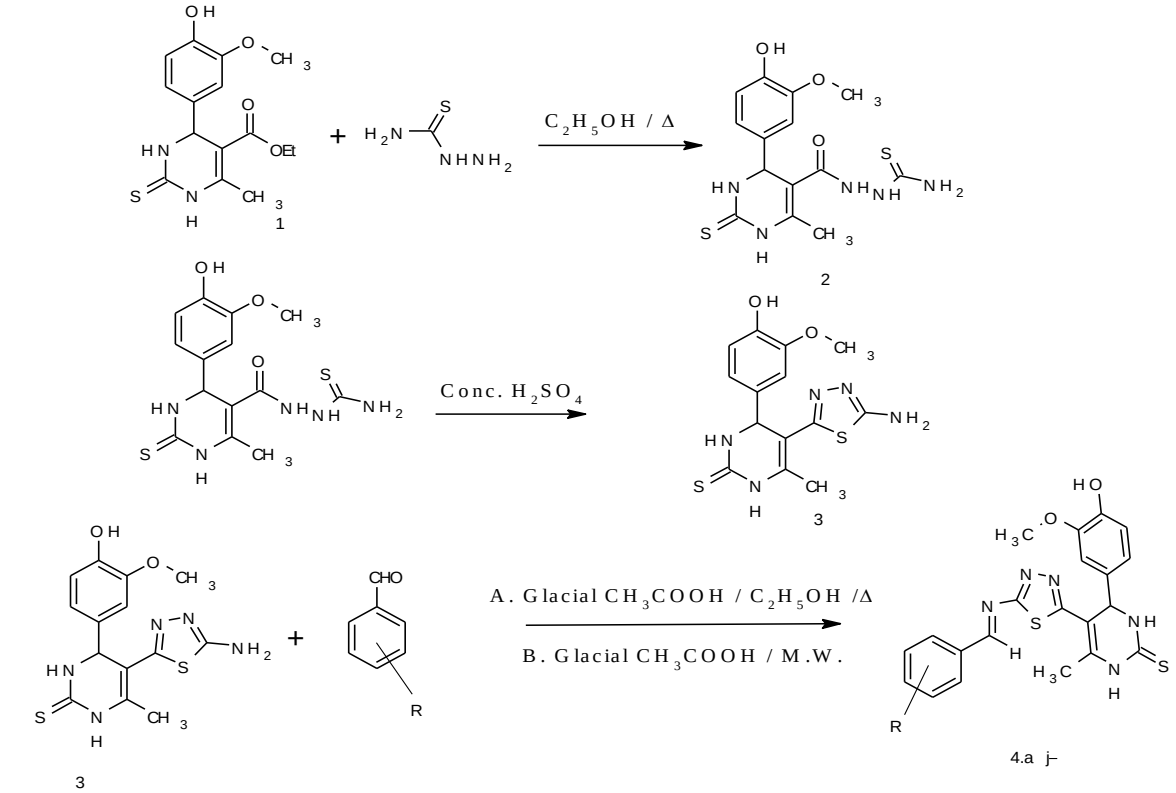
b. Microwave irradiation method:

A mixture of substituted aldehyde (1 mol), Compound 3 (1 mol)and few drops of Glacial Acetic Acidwere added in a hard glass tube and irradiated in microwave oven at appropriate power and time Completion of the reaction was monitored by TLC, mixture was cooled and poured with ice cold water. And the resulting Solid filtered dried and recrystallized from ethanol.

IR,(KBr) cm^{-1}: 3417 (-NH);2947 (CH); 1620(Ar-C=C), 748,(Ar-CH), ^{1}H-NMR (DMSO d^6) δ: 10.2 (1H,s,NH),9.5(1H,s, NH),), 7.0-6.7(8H,m,Ar-H), 9.0(1H,s,CH=N),5.1(1H,d,CH),3.7(3H,s,OCH_3), 2.25(3H,s,CH_3-C=C), MS:- m/z = 437 (m+)

Figures and tables:

Figure 1 : Schematic Representation of Titled Compounds:



Where R=H, -Cl. CH_3, -Cl, -NO_2, -OC_2H_5 etc.

Table 1: Comparative table Conventional methods and Microwave Irradiation Methods.

Entry	R	Conventional heating		Microwave heating			mp. ^{0}C
		Time in Hours	% Yields*	Microwave power in Watt	Time in min.	% yield*	
4a	H	8	54	300	4	91	191^{0}C
4b	Furfuryl	8	48	300	5	88	199^{0}C
4c	1-Naphthyl	8	53	300	5	85	185^{0}C
4d	4-N,N-di-CH_3	8	64	300	3	93	184^{0}C
4e	4-OH, 3-OCH_3	8	58	300	3	90	210^{0}C
4f	3-NO_2	8	46	300	5	75	203^{0}C
4g	4-NO_2	8	68	300	5	94	246^{0}C
4h	4-OCH_3	8	55	300	3.5	88	292^{0}C
4i	4-OH	8	56	300	3	89	272^{0}C
4j	2-OH	8	59	300	3	87	271^{0}C

*Yield refer to purified compounds

IV. Results

As per table 1 different substituted aldehydes were reacted with 5-(5-amino-1,3,4-thiadiazol-2-yl)-4-(4-hydroxy-3-methoxyphenyl)-6-methyl-3,4-dihydropyrimidine-2(1*H*)-thione in conventional as well as microwave irridation method.Microwave irridation method show high percentage of yields as compared to conventional heating method. Formation of CH=N bond was confirmed from NMR value of CH proton showing sharp deshielded singlet at 9 ppm. The structure of synthesized compounds was confirmed by IR, ^{1}H NMR, and GC-MS analysis.

V. Conclusion

Reaction was carried out in conventional heating as well as microwave irridation method. Microwave assisted reaction required shorter reaction time as compared to conventional yields comparatively high and workup procedure was easy.Microwave assisted organic synthesis in an eco-friendly, fast, efficient, safe making this techniqueclean and green.

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