Environmentally Benign Synthesis of 1, 2, 4-Thiadiazoline by Microwave Irradiation

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Abstract

Novel 3-amino-5-aryl imino-1,2,4 thiadiazolines have been synthesized by oxidative cyclisation of aryl amidinothiocarbamides using iodine. The aryl amidinothiocarbamides are synthesized by microwave irradiation of Guanidine nitrate and aryl isothiocyanate. The structures of the compounds were confirmed by elemental analysis and spectral analysis. (H^1-NMR, IR spectra)

Keywords: Amidinothiocarbamide, 1,2,4 thiadiazolines, microwave irradiation.

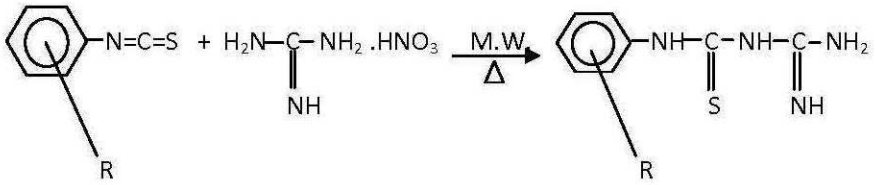
Introduction:

In recent years the chemical research has been focused on the eco friendly, environmentally, benign process to reduce the impact of environmental pollution. Green Chemistry [1-4] is placed in the frontier areas in this regard which involves the design, development and implementation of the performance criterion. So the 'greening' of conventional reactions is done to meet the ever increasing demands of selectivity in modern synthesis[5]. Microwave and sonochemical methods of synthesis use non classical forms of energy to modify the time duration and product yield by avoiding the undesired side products[6,7]. Microwave heating and sonochemical methods have emerged as a powerful energy and time saving techniques to promote a variety of chemical reactions[8-12]. These reaction methods, under solvent-free conditions are eco-friendly by reducing pollution and offer low cost, facile, safe and reproducible Experimental procedures[13]. Therefore Microwave Irradiation (MWI) [14-15] technique has gained popularity in past decade as a powerful tool for rapid, economic and efficient synthesis of variety of compounds because of selective absorption of Microwave energy by polar molecules[16].

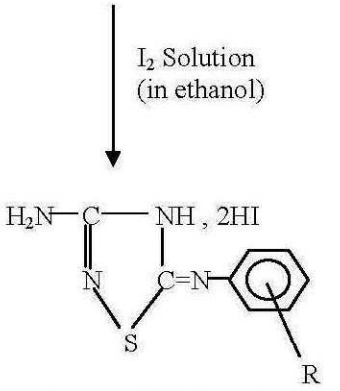
Application of microwave irradiation chemistry to enhance the efficiency and/or selectivity of organic reactions is one of the well-known challenges [17]. Microwave-assisted organic synthesis exploits a variety of factors such as milder and more efficient conditions, high yields and shorter reaction times, energy conservation, formation of purer products, waste minimization and easier manipulation. Microwave irradiation is well-known to promote the synthesis of a variety of compounds [18]. A literature survey reveals example of specific reactions, which do not occur under conventional conditional heating, but could be possible by microwave irradiation [19].

In view of our interest, we here reporting the synthesis of new, 3-amino 5-aryl imino-1, 2, 4 thiadiazolines by using microwave irradiation techniques.

(Scheme-1) The formation of product 3-amino-5-aryl imino-1, 2, 4 thiadiazolines is shown in Scheme-1

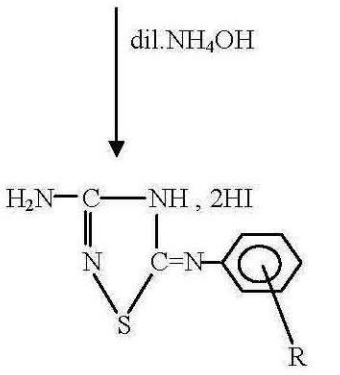


Aryl isothiocyanate (I) | Guanidine nitrate (II) | 1-aryl amidinothiocarbamide (III)



3 amino-5-aryl imino 1,2,4 thiadiazoline dihydroiodide

(IV)



3 amino-5-aryl imino 1,2,4 thiadiazoline

(V)

Where R=Va=H, R=Vb=2-methyl, R=Vc=3-methyl, R=Vd=4-methyl, R=Ve=4-Chloro.

Scheme-1

Experimental Part:

Methods for preparation of isothiocyanate[20]

The starting compound was synthesized according to reported literature.

Synthesis of 1-phenyl amidinothiocarbamide[20,21] **(IIIa):**

1-phenyl amidinothiocarbamide has been prepared by microwave heating of Guanidine nitrate and phenyl isothiocyanate in presence of NaOH for 30 seconds. On removal with water, a solid was obtained. It was crystallized from ethanol. M.P.134 ^{0}C.

The other 1-aryl amidinothiocarbamide were synthesized by extending the reaction of Guanidine nitrate to other aryl isothiocyanate and related products were isolated in good yield.

Synthesis of 3 amino-5-phenyl imino 1,2,4 thiadiazoline (Va)

It is prepared by simple classical methods 1-phenyl amidinothiocarbamide is suspended in a china dish with small amount of ethanol to prepare a paste. Then I_2 solution in ethanol is added in it with constant stirring. Initially, the colour of iodine disappeared. On further addition of I_2 solution in ethanol, the colour of iodine persisted. After some time, dry crystalline solid i.e. dihydroiodide was obtained. The M.P. of dihydrioiodide is found to be 114 ^{0}C. Then it was basified with dil. Ammonium hydroxide solution. The compound Va is obtained. M.P. 120 ^{0}C.

Synthesis of 3 amino-5-tolyl imino 1,2,4 thiadiazoline (Vc)

It is prepared by simple classical methods 1-p-tolyl amidinothiocarbamide is suspended in a china dish with small amount of ethanol to prepare a paste. Then I_2 solution in ethanol is added in it with constant stirring. Initially, the colour of iodine disappeared. On further addition of I_2 solution in ethanol, the colour of iodine persisted. After some time, dry crystalline solid i.e. dihydroiodide was obtained. The M.P. of dihydrioiodide is found to be 164 ^{0}C. Then it was basified with dil. Ammonium hydroxide solution. The compound Vc is obtained. M.P. 218 ^{0}C.

Spectral data for compounds

1-p-chlorophenyl amidinocarbamide(IIIa)

IR[22,23,24] : 3431.4(N-H Str), 1544.0(C-S Str), 1304.4(C-N Str), 1246.5(C=S Str)

3 amino-5-p-tolyl imino 1,2,4 thiadiazoline (Vc)

IR[22,23,24]**:** 3147.3(N-H Str), 1550.0(C=C Str) 1507.7(C=N Str) 1310.7(C-N Str) 811.2(C-S Str), 496.5(S-S Str)

H^1 NMR[22,24]**:** δ 9.2743(H,N-H), δ 7.3100(H,Ar-H), δ 2.2894(3H,Ar-CH_3) δ 7.1731(2H,NH_2),

3 amino-5-p-chlorophenyl imino 1,2,4 thiadiazoline (Ve)

IR[22,23,24]: 3183.4(N-H Str), 1543.5(C=C Str), 1488.0(C=N Str), 1306.8(C-N Str), 823.7(C-S Str), 500.9(S-S Str)

H^1 NMR[22,24]: δ 8.0139(H,N-H), δ 7.5093(2H,NH_2), δ 7.2857(H,Ar-H)

Table: Formation of 3 amino-5-aryl imino 1,2,4 thiadiazoline

Reactant: 1-aryl amidinothiocarbamide and iodine solution

Sr. No.	1-aryl amidinothiocarbamide (III)	3 amino-5-aryl imino 1,2,4 thiadiazoline (V)	Yield %	M.P (^{0}C)	Calculated % (Found)			
					C=, (C)	H=, (H)	N=, (N)	S=, (S)
1.	1-phenyl amidinothiocarbamide (IIIa)	3 amino-5-phenyl imino 1,2,4 thiadiazoline (Va)	41	120	50 (49.5)	4.16 (3.66)	29.16 (28.66)	16.66 (16.16)
2.	1-o-tolyl amidinothiocarbamide (IIIb)	3 amino-5-o-tolyl imino 1,2,4 thiadiazoline (Vb)	47	140	52.42 (51.92)	4.85 (4.35)	27.184 (26.68)	15.53 (15.03)
3.	1-p-tolyl amidinothiocarbamide (IIIc)	3 amino-5-p-tolyl imino 1,2,4 thiadiazoline (Vc)	51	218	52.42 (51.89)	4.85 (4.34)	27.18 (26.65)	15.53 (15.05)
4.	1-m-tolyl amidinothiocarbamide (IIId)	3 amino-5-m-tolyl imino 1,2,4 thiadiazoline (Vd)	39	98	52.42 (51.94)	4.85 (4.36)	27.18 (26.59)	15.53 (14.98)
5.	1-p-chlorophenyl amidinothiocarbamide (IIIe)	3 amino-5-p-chlorophenyl imino 1,2,4 thiadiazoline (Ve)	44	190	42.38 (41.88)	3.09 (2.59)	24.72 (24.22)	14.12 (13.62)

Result and Discussion:

The compound aryl amidinothiocarbamide have been prepared by microwave induced method, i.e. Guanidine nitrate and aryl isothiocyanate were heated in 1:1 ratio in presence of NaOH for 30 seconds in microwave. The aryl amidinothiocarbamide was treated with I_2 solution. The amidinothiocarbamide was oxidatively cyclised. It was crystallized from ethanol.

Conclusion:

In conclusion, we describe an efficient and extremely fast procedures for oxidative cyclisation of aryl amidinothiocarbamide to 3 amino-5-aryl imino 1,2,4 thiadiazoline by microwave irradiation under solvent free conditions. Shorter reaction time, simple reaction conditions and higher yield render this method superior.

Acknowledgement:

Author is thankful to Dr.V.G.Thakare, Principal, Shri Shivaji Science College, Amravati, for providing necessary facilities during the process of carrying out this work. The author is also thankful to Punjab University, Chandigarh for providing the H^1 NMR, IR Spectra and elemental analysis.

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