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RAPID, CONVENIENT MICROWAVE ASSISTED ENVIRONMENTALLY BENIGN SYNTHESIS OF NOVEL 1, 2, 4, 5 DITHIADIAZINES DERIVATIVES UNDER SOLVENT FREE CONDITIONS

S. V. TAMBAKHE*

Sipna's College of Engineering & Technology, AMRAVATI - 444605 (M.S.) INDIA

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ABSTRACT

We report efficient and extremely fast procedures for the synthesis of novel 3-aryl imino-6-amino-1,2,4,5 dithiadiazines by oxidative cyclisation of 1-aryl bis thioureas using iodine. The bis thioureas are synthesized by microwave irradiation of thiosemicarbazide and aryl isothiocyanate in microwave under solvent free conditions. The structure of the compounds were confirmed by elemental analysis and spectral analysis. (H^1-NMR, IR spectra)

Key words: Bis-thiourea, 1,2,4,5 dithiadiazines, Microwave method.

INTRODUCTION

Environmentally benign synthesis is a part of Green Chemistry. It focuses on a process that reduces the use and generation of hazardous substances or byproducts. The chemists all over the globe are motivated not only for the environmentally benign synthesis of new products but also to develop green synthesis for existing chemicals. This has been possible by the replacement of the organic solvents, which are hazardous by water or eliminate the use of solvent altogether. With the advancements of knowledge and new developments, it is now possible to carry out large number of reactions in microwave technologies.

Recently, Microwave heating has emerged as a powerful technique to promote a variety of chemical reactions[1]. Microwave reactions under solvent free conditions are attractive in offering reduced pollution, low cost and offer high yields together with simplicity in processing and handling[2]. The application of microwave irradiation to organic synthesis has been the focus of considerable attention in recent years and is becoming an increasingly popular technology[3]. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in chemical yields[4,5], further more preparative scales. In view of our interest and under the work of Green Chemistry, we have developed an environmentally benign method for synthesizing 3 aryl imino 6-amino 1,2,4,5 dithiadiazines by microwave irradiation under solvent free condition. (Scheme 1).

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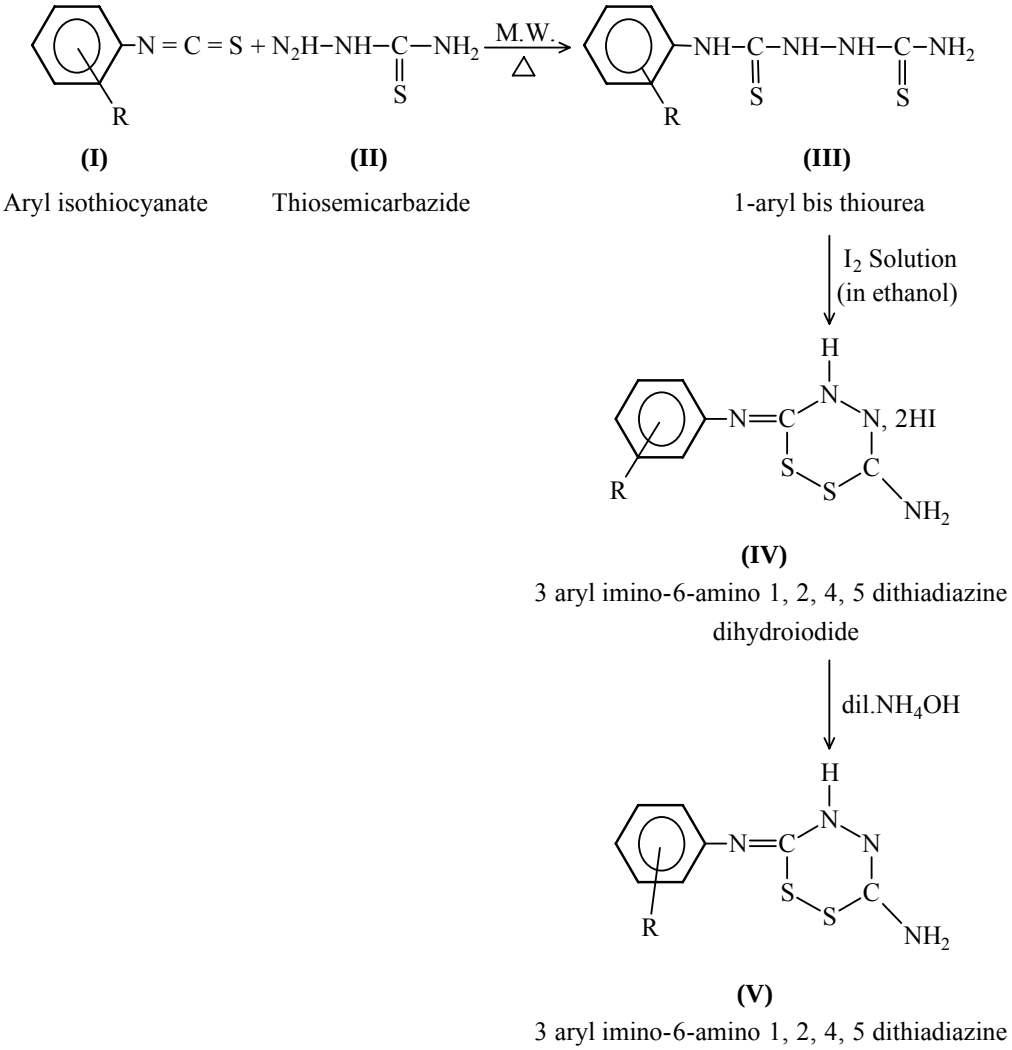
*Author for correspondence; E-mail: nnshirbhate@rediffmail.com

The formation of product 1,2,4,5 dithiazines is shown in Scheme 1



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

Scheme 1

EXPERIMENTAL

Methods for preparation of isothiocyanate[6]

The starting compound was synthesized according to reported literature.

Synthesis of 1-phenyl bisthiourea[6,7] (IIIa)

1-phenyl bisthiourea has been prepared by microwave heating of thiosemicarbazide and phenyl isothiocyanate in 1 : 1 proportion in presence of few drops of ethanol for 30 seconds. On removal with water, a solid was obtained. It was crystallized from ethanol. M.P. 178^{o}C.

The other 1-aryl bis thiourea were synthesized by extending the reaction thiosemicarbazide to other and aryl isothiocyanate and related product were isolated in good yield.

Synthesis of 3-phenylimino-6 amino 1,2,4,5 dithiadiazine (va)

It is prepared by simple classical methods 1-phenyl bisthiourea 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. hydroiodide was obtained. The M.P. of hydrioiodide is found to be 168^{o}C. then it was basified with dil. Ammonium hydroxide solution. The compound IVa is obtained. M.P. 142^{o}C.

Table 1: Formation of 3-aryl imino-6-amino 1,2,4,5 dithiadiazines

Reactant: 1-aryl bisthiourea and iodine solution

S. No.	1-aryl bisthiourea (III)	3-aryl imino-6-amino 1,2,4,5 dithiadiazines (V)	Yield %	M.P (^{0}C)	Calculated % (Found)			
					C=, (C)	H=, (H)	N=, (N)	S=, (S)
1	1-phenyl bisthiourea (IIIa)	3-phenyl imino 6 amino 1,2,4,5 dithiadiazine (Va)	52	142	42.80 (42.3)	3.57 (3.07)	25.00 (24.50)	28.57 (28.07)
2	1-o-tolyl bisthiourea (IIIb)	3-o-tolyl imino 6 amino 1,2,4,5 dithiadiazine (Vb)	58	210	42.47 (41.98)	4.42 (3.92)	24.77 (24.27)	28.31 (27.81)
3	1-p-tolyl bisthiourea (IIIc)	3-p-tolyl imino 6 amino 1,2,4,5 dithiadiazine (Vc)	63	162	42.47 (41.90)	4.42 (3.89)	24.77 (24.30)	28.31 (27.85)
4	1-m-tolyl bisthiourea (IIId)	3-m-tolyl imino 6 amino 1,2,4,5 dithiadiazine (Vd)	48	128	42.47 (41.87)	4.42 (3.90)	24.77 (24.21)	28.31 (27.78)
5	1-p-chlorophenyl bisthiourea (IIIe)	3-p-chlorophenyl imino 6 amino 1,2,4,5 dithiadiazine (Ve)	74	148	36.85 (36.35)	3.45 (2.95)	21.49 (20.99)	12.28 (11.78)

Spectral data for compounds

1-phenyl bis thiourea(iiia)

IR[8,9,10]: 3363.5 (N-H Str), 1526.2 (C=C Str), 1312.5 (C-N Str), 1249.1 (C = S Str)

3-phenyl imino-6-amino-1,2,4,5 dithiadiazine(va)

IR[8,9,10]: 3365.1 (N-H Str), 1539.7 (C-C Str), 1493.0 (C = N Str), 1312.0 (C-N Str), 799.8 (C-S Str), 1252.1 (C = S Str), 499.5 (S-S Str)

H^1 NMR[8,10]: δ 7.6961 (H, N-H), δ 7.4441 (2H, NH_2), δ 7.1586 (H, Ar-H)

3-p-tolyl imino-6-amino 1,2,4,5 dithiadiazine(vc)

IR[8,9,10]: 3422.7 (N-H Str), 1550.7 (C = C Str), 1490.6 (C = N Str) 1311.6 (C-N Str), 809.8 (C-S Str), 497.4 (S-S Str)

H^1 NMR[8,10]: δ 7.5997 (H, N-H), δ 7.2636 (H, Ar-H), δ 2.2972 (3H, Ar-CH_3)

RESULTS AND DISCUSSION

The compound 1-aryl bis thiourea have been prepared by microwave induced method, i.e. thiosemicarbazide and aryl isothiocyanate were heated in 1 : 1 ratio in presence of few drops of ethanol for 30 seconds in microwave. The 1-aryl bis thiourea was teated with I_2 solution. The bis thiourea was oxidatively cyclised. It was crystallized from ethanol.

CONCLUSION

In conclusion, we describe an efficient and extremely fast procedure for oxidative cyclisation of 1-aryl bisthiourea to 3-aryl imino-6-amino 1,2,4,5 dithiadiazines by microwave irradiation under solvent free conditions. Shorter reaction time, simple reaction conditions and higher yield render this method superior.

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