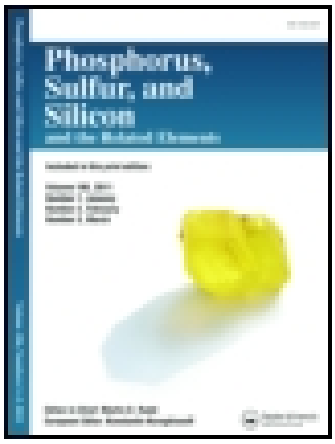

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New Synthesis of [1,3,4] Thiadiazolo [2,3-C][1,2,4] Triazinone; Transfer of Active Electron by Microwaves

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NEW SYNTHESIS OF [1,3,4] THIADIAZOLO [2,3-C][1,2,4] TRIAZINONE; TRANSFER OF ACTIVE ELECTRON BY MICROWAVES

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Reaction of various aromatic aldehydes with 4-amino-6-methyl-1,2,4-triazin-5-one supported on to montmorillonite-K10 in the presence of nitrobenzene under microwaves irradiation, afforded the corresponding [1,3,4] thiadiazole [2,3-c][1,2,4]-triazinones.

Keywords: Aromatic aldehydes; electron transfer; microwave irradiation; thiadiazolotriazine

INTRODUCTION

[1,3,4] Thiadiazolo [2,3-c][1,2,4] triazines constitute a class of compounds that is interesting from the view point of chemical reactivity and biological activity.[1–5] Reaction of 4-amino-6-methyl-1,2,4-triazin-5-one **1** (R^1 = Me) with a variety of carboxylic acids in phosphorus oxychloride has afforded 2-substituted, [1,3,4] thiadiazolo [2,3-c][1,2,4] triazine-4-one **3**.[6,7] **1** also has been reacted with a variety of carboxylic acids in the presence of sulfuric acid to give **3** in good to high yields.[8,9]

Microwave irradiation in organic synthesis presently is used widely. Its application in the case of inorganic solid supported reactions recently has been reported.[10] Solvent free organic reactions or dry media techniques under microwave irradiation are one of main topics of research in our laboratory.[11–13] The use of microwave iradiation in the formation of radical-cation in oxidation of benzothiazolines to benzothiazole has been recently reported.[14]

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Armed with these experiences in this communication we report a new route to thiadiazolo [2,3-c][1,2,4] triazinones starting from aromatic aldehydes.

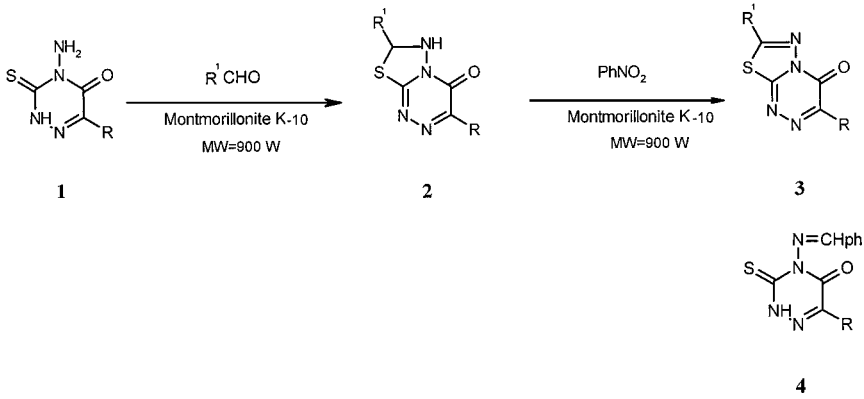
RESULTS AND DISCUSSION

As mentioned above the synthetic route to [1,3,4] thiadiazolo [2,3-c][1,2,4] triazinone has been achieved through condensation and ring closure of 3-thio-4-amino-1,2,4-trazin-5-one **1**[15] and a variety of carboxylic acids. Phosphours oxychloride and sulfuric acid have been used as dehydrating agents.[6–9] In contrast to this procedure, we attempted to use aldehyde and an oxidizing agent in an one pot reaction to obtain 1,3,4-thiadiazolo[2,3-c][1,2,4] triazinone.

Treatment of **1** (R = Me) with benzaldehyde in the presence of nitrobenzene did not give either the cyclized product **2** or the cyclized and aromatized product **3**. The isolated product was only the imine **4** (Scheme 1).

However, when a mixture of **1**, benzaldehyde and nitrobenzene were irradiated by microwave in the presence of montmorillonite K-10 the corresponding thiadiazolo [2,3-c][1,2,4] triazinone **3** (R = Me, R^1 = ph) was obtained in 58% yield (Scheme 1). When montmorillonite K-10 was exchanged with silica gel, in the same condition, the yield of the reaction decreased to 23%.

To establish the generality of the method, a variety of aromatic aldehydes were used to obtain different substituted **3** (Table I). It is noteworthy to mention that this reaction is not successful with aliphatic aldehydes and thus it can be considered to be limited to aromatic aldehyde.

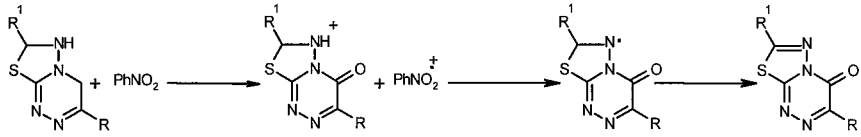


SCHEME 1

TABLE I Physical Properties and Yields of the Prepared **3**

R	R^1	MP(°C)	MP(C lit)[7]	Yield(%)
CH_3	Ph	268	265	56
CH_3	p-$CH_3C_6H_4$	214	215	58
CH_3	p-$CH_3OC_6H_4$	224	227	62
CH_3	p-ClC_6H_4	231	230	51
CH_3	p-$NO_2C_6H_4$	268	270	50

Most probably the above reaction proceeds through formation of radical cations. Microwave irradiation has caused the electron transfer. Montmorillonite K-10 probably facilitates the transfer of electrons by generating an electric field [16] and water molecules prevent the reverse of electron transfer[17] (Scheme 2).



SCHEME 2

In conclusion we have introduced a simple one-pot synthesis of [1,3,4] thiadiazolo [2,3-c][1,2,4] triazinone starting from aromatic aldehydes. The reaction conditions are mild and relatively eco-friendly. The yields of reactions are good to high. Solvent free condition and using microwave irradiation has apparently facilitated the electron transfer and water molecules have prevented the reverse of electron transfer processes.

EXPERIMENTAL

All products are known compounds and were identified by comparison of their physical data with those of authentic samples.

SYNTHESIS OF THIADIAZOLO [2,3-C][1,2,4] TRIAZIN-4-ONES, TYPICAL PROCEDURE

6-Methyl-3-thio-4-amino-1,2,4-triazin-5-one (10 mmol), benzaldehyde (20 mmol) and nitrobenzene (10 ml) were mixed with montmorillonite K-10 (1 g) to make an intimate mixture in a flask. The flask was placed in a house hold microwave oven and irradiated for 15 min 3 times with an interval of 5 min. The reaction mixture was filtered, washed with chloroform, and from the filtrate the solvent distilled off to dryness. The residue was triturated with dilute sodium hydroxide solution to remove unreacted product. The solid residue was crystallized from acetic acid to afford the corresponding [1,3,4] thiadiazolo [1,2,4] triazine (Table I).

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