

Dry media reactions*

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Abstract: Dry media reaction under microwaves is an effort toward “green chemistry”. Effects of microwaves in dry media organic reactions have shown synthetic utility for the preparation of biodynamic heterocycles.

INTRODUCTION

Nowadays, the microwave dielectric heating effect uses the ability of some liquids and solids to transform electromagnetic energy into heat and thereby drive chemical reactions. This *in situ* mode of energy conversion has many attractions for chemists [1–2], because its magnitude depends on the properties of the molecules. This allows some control of the material’s properties and may lead to reaction selectivity. There are a variety of methods for carrying out microwave-assisted organic reactions using domestic or commercial ovens; this is basically known as microwave-induced organic reaction enhancement (MORE) chemistry [3]. Microwave heating has not been restricted to organic chemistry as various aspects of inorganic chemistry and polymer chemistry have also been investigated. However, usually the same chemistry (conventional heating) has been observed when the organic reactions involved were carried out. The difference lies in the choice of reaction conditions: The reactions were carried out in high boiling solvents (dimethylformamide, DMF). Heating is fast, but maximum temperatures were chosen below the boiling point of the solvent in order to avoid solvent evaporation. One could work this in open reaction vessels and could choose a small amount of solvent when targeting for solubility at the reaction temperature. Overall, Bose [3] claims that the method is more cost effective (only simple glassware needed) and environment friendly (less solvent needed).

To demonstrate the versatility of MORE chemistry, a variety of organic reactions have been done using domestic microwave oven or commercial ovens.

SOLID-STATE REACTIONS

Solid-state reactions are generally of three types [4].

- Reactions between neat reactants
- Reactions between supported reagents on solid mineral supports in “dry media” by impregnation of compounds on silica, alumina, or clays
- Phase-transfer catalysis (PTC) conditions in the absence of organic solvent, i.e., when a liquid reagent acts both as a reacting and an organic phase. This method is specific for anionic reactions as it involves “anionic activation”.

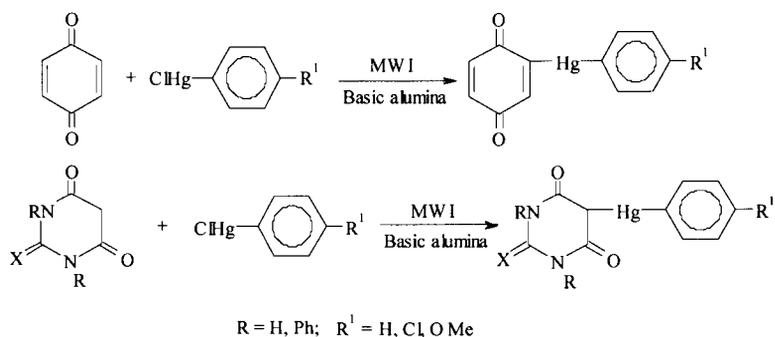
Avoiding organic solvents during the reactions in organic synthesis leads to a clean, efficient, and economical technology (green chemistry); safety is largely increased, work-up is considerably simplified, cost is reduced, increased amounts of reactants can be used in the some equipment, and the reactivities and sometimes selectivities are enhanced without dilution. Due to all these advantages there is

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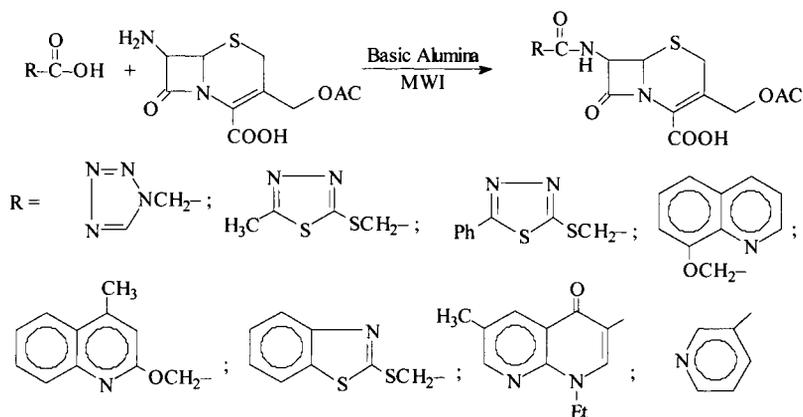
an increasing interest in the use of environmentally benign reagents and procedures. Or, in other words, the absence of solvents coupled with the high yields and short reaction times often associated with reactions of this type make these procedures very attractive for synthesis. In the present discussion, we describe the advantages of dry reaction techniques coupled with microwave activation and their applications to organic synthesis using solid supports.

New fungicidal organomercurials of benzoquinone, barbituric acid, and thiobarbituric acid with substituted aryl mercuric chloride have been synthesized (Scheme 1) by adsorbing on basic alumina using microwave irradiation (MWI) in a few minutes with improved yields [5].



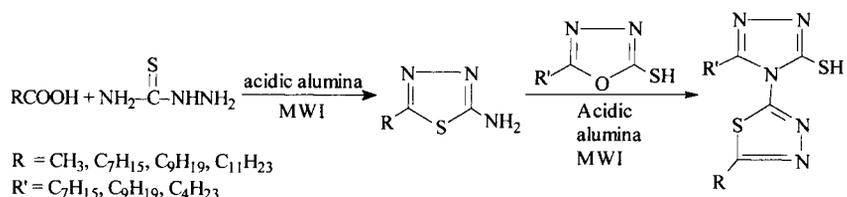
Scheme 1

Reaction of 7-ACA with carboxylic acids by adsorption on basic alumina under MWI for 90–120 s (Scheme 2) afforded the 7-substituted cephalosporanic acid derivatives with amidic bond [6].



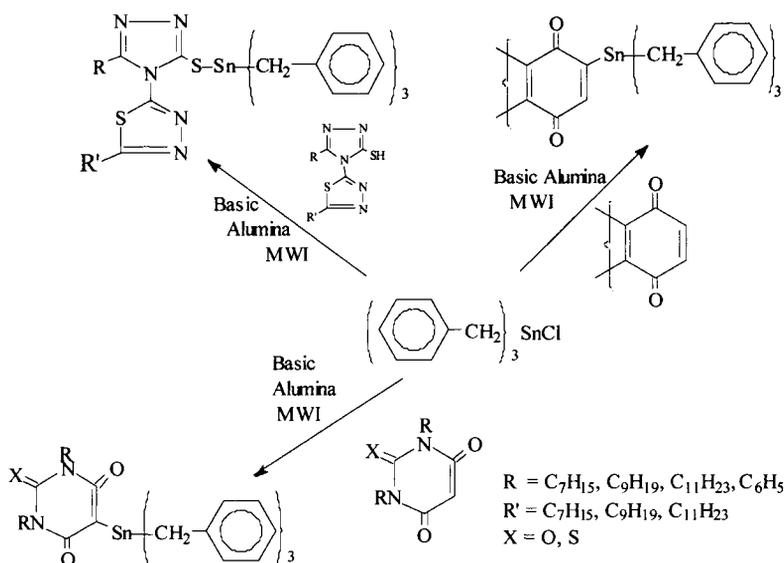
Scheme 2

5-Substituted-2-amino-1,3,4-thiadiazoles were synthesized within 40–80 s with improved yield using acidic alumina, which undergo insertion reaction with 5-alkyl-2-mercapto-1,3,4-oxadiazoles yielding the thiadiazolyl-substituted triazoles within 40–80 s (Scheme 3). A drastic reduction in reaction time and improved yield was observed due to the rapid heating capability of solid support under microwaves [7].



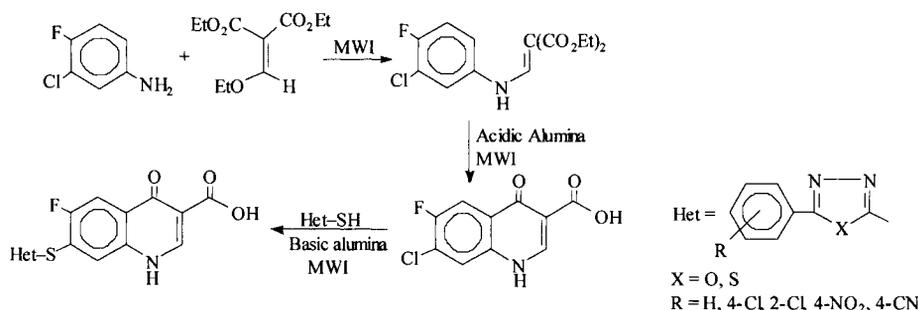
Scheme 3

A series of novel bioactive organotin compounds have been synthesized on basic alumina in an open vessel under MWI (Scheme 4). The reaction time has been brought down from hours to seconds as compared to the conventional heating [8].



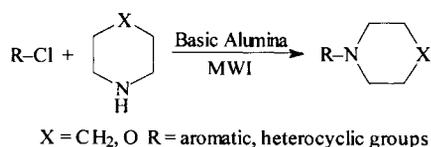
Scheme 4

Microwave-activated solid support synthesis of new antibacterial quinolones (Scheme 5) was reported [9].



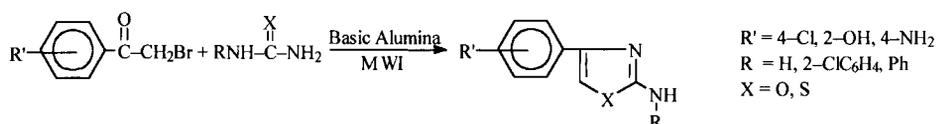
Scheme 5

A nonconventional synthetic procedure for nucleophilic aromatic substitution of cyclic amines using microwaves avoiding catalysts, has been developed (Scheme 6). Results obtained show the drastic reduction in reaction time and improved yield in solid-phase reaction compared to other methods.

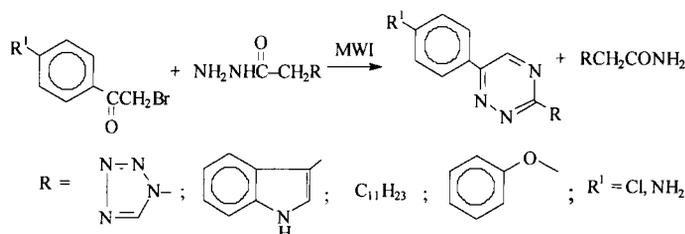


Scheme 6

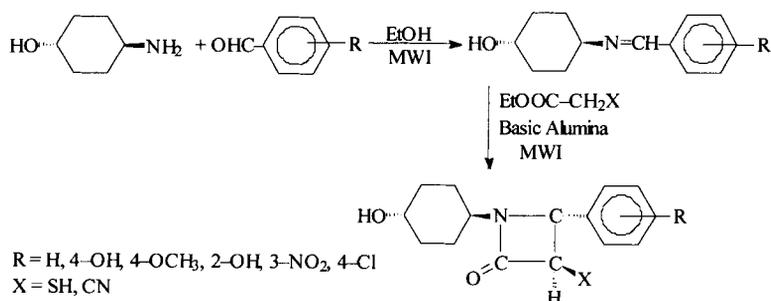
2-Aminothiazoles and oxazoles have been synthesized (Scheme 7) using solvent-free microwave technique; the reaction time has been drastically reduced with improved yield as compared to conventional method [11].

**Scheme 7**

An environmentally benign, solventless synthesis of 1,2,4-triazines using microwaves is reported (Scheme 8). Results showed that neutral alumina is the best support in terms of yield and time for the synthesis of 1,2,4-triazines [12].

**Scheme 8**

N-(4-hydroxycyclohexyl)-3-mercapto/cyano-4-arylazetidone were synthesized from *N*-(4-hydroxycyclohexyl)-aryaldimine by reacting with ethyl α -mercapto/ α -cyanoacetate on basic alumina under microwaves (Scheme 9), with reduction in reaction time and improved yield [13].

**Scheme 9**

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