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THE ROLE OF PENETRATION DEPTH OF CLAY IN MICROWAVE-INDUCED REACTIONS: SYNTHESIS OF PYRROLES

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Abstract: Clay-mediated microwave-mediated reactions for the preparation of pyrroles are conducted. The reaction between hexanedione with aromatic amines using different solid clays is studied. The penetration depth of the solids has influence on this reaction. Other acidic reagents are not necessary for the success of this reaction.

Key Words Clay, Synthesis, Penetration Depth, Microwave

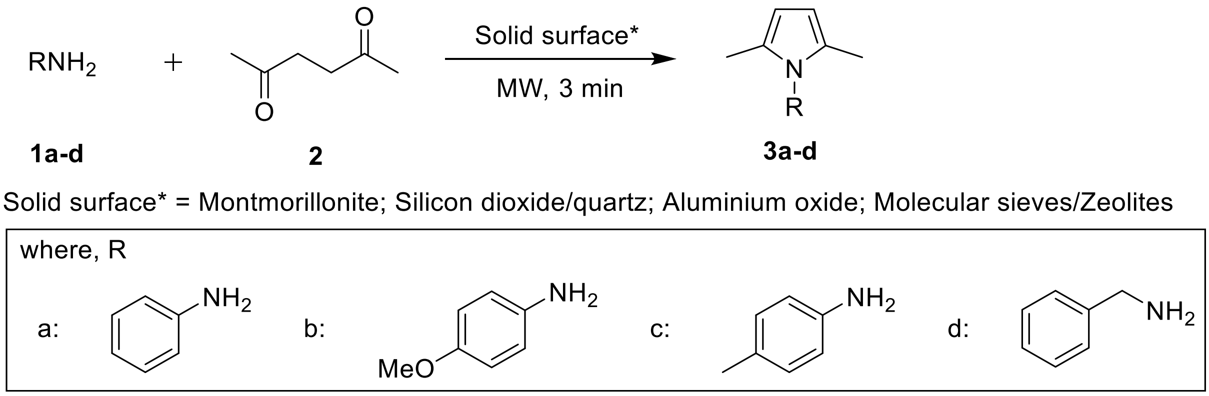
Introduction:
Different types of solid surfaces including clays are used in chemistry research [I-III]. Because of their acidic nature, these solids are able to accelerate certain organic reactions. The success of the clay-induced reactions partly depends on their internal bonding nature. These solid materials are able to bind reactants in their vacant portion of their structures and thus, suitable reactions can proceed due to the intimacy of the components. Moreover, the activation and reaction become stronger under microwave irradiation.
Microwave-induced reactions depend on a variety of factors. The penetration depth of the solids has a control in absorbing microwave energy [IV-V]. We disclose here the synthesis of *N*-substituted pyrrole derivatives by reacting 2, 5-dimethoxytetrahydrofuran and aromatic primary amines in the presence of different solid surfaces under microwave-induced reaction. The concept of penetration depth has not been used in organic synthesis before, apart from our own previous study.

Results and Discussions:
Clay has Brönsted and Lewis acid components. Bronsted sites are present in the interlayer part and the Lewis sites are present in the edge [VI]. Different types of solid supports have different percentage of metals bonded with oxygen. These metals are polar in nature and these can be activated in the presence of microwave. Unlike liquid, microwave radiation is not capable of heating all the solids equally when a solid substance is used. Electromagnetic

radiation penetrates into the surface of a solid substance. A portion of the radiation reflects from the outer surface and a part penetrates inside the surface. The radiation inside interacts with the molecules that are employed in a process. Importantly, the radiation can pass into the solid surface at specific depths and this depends on the nature of the substance. So, penetration depth is a crucial factor when solid substances are used in microwave.

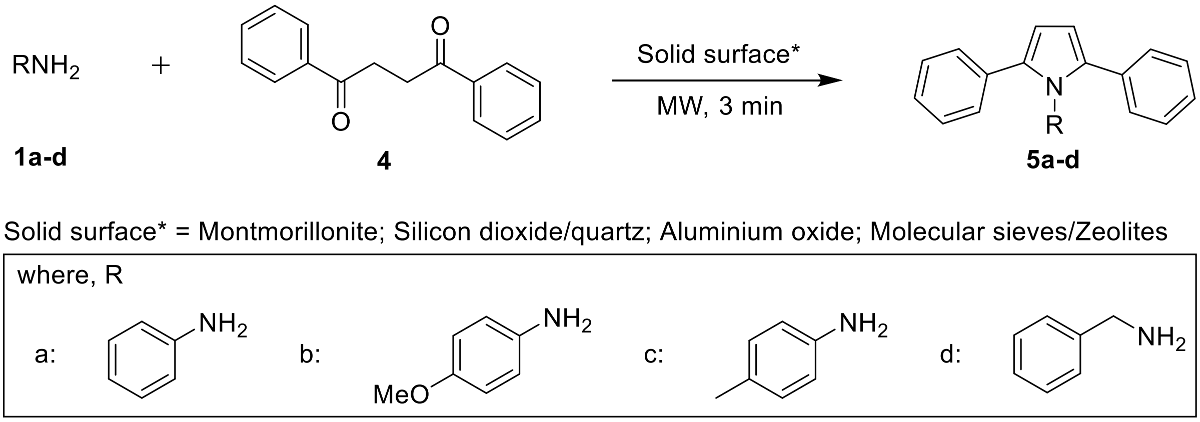
To identify the role of solid surfaces in the microwave-induced reactions, reaction of primary aromatic amines with hexane dione was investigated [VII-XXIV]. Four solids (silica gel, montmorillonite, alumina and molecular sieves) are used in this method. Aniline (**1a**), 4-methoxy aniline (**1b**), 4-methyl aniline (**1c**), and benzyl amine (**1d**) are employed in this investigation. A reaction using amine **1a-d** (1 mmol) and 2,5-dimethyl hexanedione **2** (1.1 mmol) with clay (2 gm) was irradiated in a domestic microwave for approximately 3 min using medium power. After the irradiation, methylene chloride (10 mL) was added to the reaction mixture, and it was shaken and then filtered. The solid mass was washed with dichloromethane (5mL), solvent was evaporated, and the crude pyrrole was isolated. The pyrroles formed were almost pure. Pure products **3a-d** were obtained by a simple filtration (**Scheme 1**) [XXV].

Scheme 1: Synthesis of N-aryl, 2, 5-dimethylpyrroles 3a-d



An identical method was followed with 2,5-diphenylhexanedione **4** and amines **1a-d.** After the irradiation, the product **5a-d** was obtained. It was crucial to note that pyrroles are formed in better yields with montmorillonite than the other solids (**Scheme 2**).

Scheme 2: Synthesis of N-aryl, 2, 5-diphenylpyrroles 5a-d



These reactions suggests that the lower penetration depth of solid support is the best helpful for the synthesis of pyrroles. Because of smaller penetration depth of montmorillonite compared to others solid surfaces, electromagnetic radiation can penetrate within this system more efficiently. So, an efficient heating is possible with montmorillonite. An effective heating by microwave irradiation produces the products in better yield. This suggest that silica (dioxide), alumina (trioxide), and molecular sieves are not efficient for this method, due to their high penetration depth values [14, 17–20]. Moreover, dielectric constant of these solid surfaces is also low compared to numerous polar liquids. But, a huge penetration depth value difference between montmorillonite and other solids is the cause for the success of this reaction.

Material	Penetration Depth (cm)	Dielectric constant
Montmorillonite	3-19	2-40
Silicon dioxide/quartz	1000-20000	3.5-5
Aluminium oxide	300-3000	8.5-9
Molecular sieves/Zeolites	>100	1-3

Table 1: Dielectric constant and penetration depths of the 2.45 GHz microwaves for solids

Experimental: A reaction using a mixture of amine (1 mmol), dimethyl hexanedione (1.1 mmol) and clay (2 gm) was conducted in a microwave oven for 3 min. A medium power level was used. After the reaction, dichloromethane (10 mL) was added and it was filtered. The solid was washed with dichloromethane (5 mL), solvent was removed and pyrrole was obtained.

An identical method was used for 2,5-diphenylhexanedione and the product was obtained after 4 min of irradiation.

Conclusions:

Montmorillonite is an excellent solid for the synthesis of pyrroles under microwave-induced reaction. The penetration depth of the solids in the microwave oven is a crucial data for this reaction.

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Conflict of Interest

The authors confirm that this result has no conflict of interest.

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