## Microwave-assisted Synthesis of Triazones and 4-Oxo-oxadiazinane in Dry Media†

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Three component condensation of N,N'-dimethylurea, paraformaldehyde and primary amines using montmorillonite K-10 in dry media under microwave irradiation leads to triazones **5a-f** in high yields.

Acceleration of organic reactions by microwave dielectric heating has been widely exploited. Microwave irradiation in solvent-free conditions has also shown its utility in organic synthesis.2 In this regard, montmorillonite clays which have received considerable attention as catalysts owing to their characteristic properties, are used for many organic reactions.<sup>3</sup> 1,3,5-tri-N-substituted hexahydro-2-oxo-1,3,5-triazines (triazones) have been known for many years in a variety of contexts. 4-6 Triazones are used as an amino protecting groups,<sup>7,8</sup> for the synthesis of polyamine,<sup>9</sup> polyfunctional amino acids and amino alcohols.<sup>7</sup> Many water-soluble triazones are used as fertilizers. 10 Triazones may be formed from a primary amine (a hydrochloric salt of a primary amine), an N, N'-substituted urea and aqueous formaldehyde in the presence of a co-solvent such as dioxane and toluene. 4-Oxo-oxadiazinane has been prepared by the condensation of a symmetrical disubstituted urea with aqueous formaldehyde in a 1:2 molar ratio in the presence of hydrochloric acid.4

We report here the synthesis of 4-oxo-oxadiazinane 3 and triazones 5a-f using montmorillonite K-10 under solvent free conditions and microwave irradiation.

Condensation of dimethyl urea and paraformaldehyde, supported on montmorillonite K-10 in dry media (without solvent and mineral acid) using microwave irradiation gave 4-oxo-oxadiazinane 3, and three component condensation of dimethyl urea, paraformaldehyde and primary amines supported on montmorillonite K-10 under microwave irradiation in dry media resulted in formation of triazones 5a-f.

Scheme 1

**Table 1**  $^{1}$ H NMR spectra ( $\delta$ ) and yields of 4-oxo-oxadiazinane and triazones **5a**-**f** 

Compound	Ring protons	Me <sub>2</sub> -3,5 protons	Substituent protons	Yield(%) <sup>a</sup>
3	4.80	2.95		67
5a	4.05	2.80		71
5b	4.10	2.85	2.75 (q, 2H, CH <sub>2</sub> )	76
			1.05 (t, 3H, CH <sub>3</sub> )	
5c	4.20	2.80	2.70 (t, 2H, CH <sub>2</sub> )	79
			1.50 (m, 2H, CH <sub>2</sub> )	
			1.00 (t, 3H, CH <sub>3</sub> )	
5d	4.10	2.80	2.70 (m, 1H, CH)	83
			1.00 (d, $J = 5.7 \mathrm{Hz}$ ,	
_	4.40	0.00	6H, 2CH <sub>3</sub> )	0.4
5e	4.10	2.90	2.80 (t, 2H, CH <sub>2</sub> )	84
			2.20 (m, 2H, CH <sub>2</sub> )	
			1.30 (m, 2H, CH <sub>2</sub> )	
E4	4.20	2.00	1.90 (t, 3H, CH <sub>3</sub> )	7.1
5f	4.20	2.90	2.80 (m, 1H, CH)	74
			1.50 (m, 2H, CH <sub>2</sub> ) 1.15 (d, 3H, CH <sub>3</sub> )	
			0.95 (t, 3H, CH <sub>2</sub> )	
			0.33 (t, 3H, CH <sub>2</sub> )	

<sup>a</sup>In all the experiments, the irradiation time used was 6 min.

Montmorillonite K-10 has Lewis acid character and it seems that in the presence of montmorillonite K-10, paraformaldehyde is slowly decomposed to formaldehyde which reacts with dimethyl urea and amines. Formation of 4-oxo-oxadiazinane 3 may occur by the attack of nucleophilic urea nitrogens on formaldehyde. After dehydration on the surface, 4-oxo-oxadiazinane 3 is formed. Formaldehyde may combine with a primary amine to give an imine-formaldehyde copolymer or oligomeric formaldehyde adducts which can be converted to triazones.7 In the <sup>1</sup>H NMR spectrum (Table 1) of oxadiazinane 3, methylene hydrogens resonate at  $\delta$  4.80 and in IR spectrum, the carbonyl group of the amide absorbs in 1650 cm<sup>-1</sup>.<sup>7-11</sup> The ring protons in triazones 5a-f resonate at  $\delta$  4.05-4.20 and in the IR spectra these compounds show a strong amide bond absorption in the region 1620–1640 cm<sup>-1</sup>.

In conclusion, the microwave irradiation of paraformaldehyde, dimethylurea and amines under solvent free (dry) conditions on montmorillonite K-10 provides triazones. High yields, low reaction times, mild reaction conditions, and easy set-up and work-up are advantages of this method compared to other methods.

## **Experimental**

IR spectra were recorded on a Shimadzu IR-408 spectrometer. <sup>1</sup>H NMR were measured on a Bruker AG 80 (80 MHz) and JEOL FX-90 (90 Hz) spectrometers in CDCl<sub>3</sub> and chemical shifts are expressed downfield from tetramethylsilane as internal reference. A domestic microwave (Moulinex FM 2735 A) at 2450 MHz (850 W) was used in all experiments.

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General Procedures for Preparation of Triazones 5a–f.—264 mg (3 mmol) N,N'-dimethylurea, 1 g paraformaldehyde, 3 mmol primary amine 4a–f and 2 g montmorillonite K-10 were irradiated by microwave in a Teflon vessel. The reaction mixture was filtered and washed with water. The organic phase was separated and dried with  $Na_2SO_4$  and concentrated by vacuum distillation.

Purification of the crude material by chromatography on a short column (silica gel, 70–230 mesh) and elution with dichloromethane, or vacuum distillation afforded triazones **5a–f**. The obtained yields were in the range of 67–84%.

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