J. Chem. Research (S), 1999, 392–393†

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

Saeed Balalaie,*[a] Mehri S. Hashtroudi[b] and Ali Sharifi[c]

[a] *Chemistry Department, K. N. Toosi University of Technology, P.O. Box 15875-4416, Tehran, Iran*

[b] *Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran*

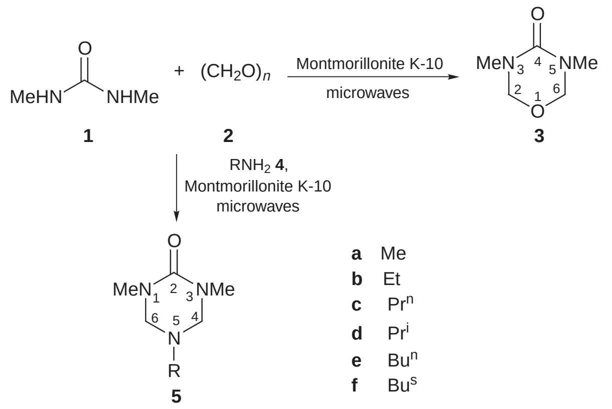
[c] *Chemistry and Chemical Engineering Research Center, P.O. Box 14355-186, Tehran, Iran*

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.[3] 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,[7,8] for the synthesis of polyamine,[9] polyfunctional amino acids and amino alcohols.[7] 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 (δ) and yields of 4-oxo-oxadiazinane and triazones **5a–f**

Compound	Ring protons	Me_2-3,5 protons	Substituent protons	Yield(%)[a]
3	4.80	2.95		67
5a	4.05	2.80		71
5b	4.10	2.85	2.75 (q, 2H, CH_2) 1.05 (t, 3H, CH_3)	76
5c	4.20	2.80	2.70 (t, 2H, CH_2) 1.50 (m, 2H, CH_2) 1.00 (t, 3H, CH_3)	79
5d	4.10	2.80	2.70 (m, 1H, CH) 1.00 (d, $J = 5.7$ Hz, 6H, $2CH_3$)	83
5e	4.10	2.90	2.80 (t, 2H, CH_2) 2.20 (m, 2H, CH_2) 1.30 (m, 2H, CH_2) 1.90 (t, 3H, CH_3)	84
5f	4.20	2.90	2.80 (m, 1H, CH) 1.50 (m, 2H, CH_2) 1.15 (d, 3H, CH_3) 0.95 (t, 3H, CH_2)	74

[a] 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 ^{1}H NMR spectrum (Table 1) of oxadiazinane **3**, methylene hydrogens resonate at δ 4.80 and in IR spectrum, the carbonyl group of the amide absorbs in 1650 cm^{-1}.[7–11] The ring protons in triazones **5a–f** resonate at δ 4.05–4.20 and in the IR spectra these compounds show a strong amide bond absorption in the region 1620–1640 cm^{-1}.

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. ^{1}H NMR were measured on a Bruker AG 80 (80 MHz) and JEOL FX-90 (90 Hz) spectrometers in $CDCl_3$ 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.

---

* To receive any correspondence (*e-mail*: Balalaie@sc.kntu.ac.ir).

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

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%.

We are grateful to the Research Council of K. N. Toosi, University of Technology for financial support.

Received, 9th February 1999; Accepted, 8th March 1999
Paper E/9/01114E

References

1 R. A. Abramovitch, *Org. Prep. Proc. Int*., 1991, **23**, 683; D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev*., 1991, **20**, 1; S. Caddick, *Tetrahedron*, 1995, **51**, 10403; C. R. Strauss and R. W. Trainer, *Aust. J. Chem*., 1995, **48**, 1665.

2 L. Deloude and P. Laszlo, *J. org. Chem*., 1996, **61**, 6360; R. S. Varma and R. Dahiya, *SynLett*, 1997, 857; R. S. Varma and H. M. Meshram, *Tetrahedron Lett*., 1997, **38**, 7973.

3 R. L. Augustine, *Heterogenous Catalysis for the Synthetic Chemist*, Marcell Decker Inc., New York, 1996, pp. 579–584; K. Smith, *Solid Supports and Catalysts in Organic Synthesis,* Ellis Harwood, Chichester, 1992; B. Perio, M. J. Dozias, P. Jacquault and J. Hamelin, *Tetrahedron Lett*., 1997, **38**, 7867; S. Jolivet-Fauchet, J. Hamelin, F. Texier-Boullet, L. Toupet and P. Jacquault, *Tetrahedron*, 1998, **54**, 4561; K. Toshima, Y. Ushilci, G. Matsuo and S. Matsumura, *Tetrahedron Lett*., 1997, **38**, 7375.

4 H. Peterson, *Synthesis*, 1973, 243.

5 D. E. Hardies and D. K. Krass, *US Pat*., 4150220, 1979 (*Chem. Abstr*., 1979, **91**, P57062e).

6 D. E. Hardies, *US Pat*., 4152516, 1979 (*Chem. Abstr*., 1979, **91**, P57063f).

7 S. Knapp, J. J. Hale, M. Bastos, A. Molina and K. Yu, *J. Org. Chem*., 1992, **57**, 6239.

8 S. Knapp, J. J. Hale, M. Bastos and F. S. Gibson, *Tetrahedron Lett*., 1990, **31**, 2109.

9 V. J. Jasys *et al., Tetrahedron Lett*., 1988, **29**, 6223; B. Carboni, M. Vaultier and R. Carrie, *Tetrahedron Lett*., 1988, **29**, 1279; R. J. Bergeron and J. S. McManis, *J. Org. Chem*., 1988, **53**, 3108; S. Knapp and A. T. Levorse, *Tetrahedron Lett*., 1987, **28**, 3213.

10 E. F. Hawkins, *US Pat*., 4778510, 1988.

11 B. R. Larsen, F. M. Nicolaisen and T. Nielsen, *J. Mol. Struct*., 1976, **32**, 247.