# Montmorillonite K-10 Catalyzed Knoevenagel Condensation under Microwave Irradiation in Solventless System

Majid M. Heravi[a,]*, Mahmood Tajbakhsh[b], Bagher Mohajerani[c],
Mitra Ghassemzadeh[a]

[a] Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335–186,
Tehran, Iran
[b] Department of Chemistry, University of Mazandaran, Babolsar, Iran
[c] Institute of Petroleum Industry, Iran

Z. Naturforsch. **54b**, 541–543 (1999); received August 10, 1998

Knoevenagel Condensation, Solventless System, Microwave Irradiation

Montmorillonite K-10 catalyzed efficiently the Knoevenagel condensation of carbonyl compounds with malonitrile and ethylcyanoacetate in dry media under microwave irradiation.

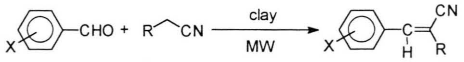
## Introduction

Knoevenagel condensation of carbonyl compounds on compounds containing an active methylene group is one of the most important preparation method of substituted alkenes. Reactions are generally catalyzed using bases or Lewis acids [1]. Recently use of inorganic solid supports as catalysts, resulting in higher selectivity, milder conditions and easier work up has rapidly increased and has been reported as a useful condition for Knoevenagel reaction. Thus Aluminium oxide [2], xonotlite [3], $AlPO_4$-$Al_2O_3$ [4], clays as KSF [5], K-10-$ZnCl_2$ [6], silica gel [7] or cadmium iodide [8], and modified Mg-Al [9] have been reported mainly for aldehydes and scarcely for ketones.

Microwave heating in organic synthesis is now widely used. Its application in the case of inorganic solid-supported reactions has been recently reviewed [5]. Solvent free organic reactions or dry media techniques under microwave irradiation are one of the main topics of research in our laboratory [10–13] and we reported recently an efficient promoted knoevenagel condensation using HZSM-5 zeolite as a reusable catalyst under non-aqueous conditions [14]. This method appeared to be very convenient but it took at least 5 h for completion. In this communication we wish to report a general and fast Knoevenagel condensation using montmorillonite K-10 under microwave irradiation in solventless system.

## Results and Discussion

It is well known that carbonyl condensation with active methylene compounds may be catalyzed both by base and by acid. However it has been claimed that the acid-catalyzed reaction leads to lower yields and does not appear efficient amongst conventional methods [15]. In continuation of our ongoing effort to develop newer environmentally benign methods for chemical transformations [10–13] we decided to investigate the effect of montmorillonite K-10 in the Knoevenagel condensation type. When benzaldehyde and malonitrile were adsorbed on montmorillonite K-10 and submitted to microwave irradiation for the appropriate time and power the desired olefin was obtained in excellent yields (eq. X=H, R=CN, entry 1).



Consequently a systematic study of this reaction to establish the generality of the method has been undertaken with various aldehydes and active methylene compounds utilizing montmorillonite K-10 under microwave irradiation in solventless system. Aliphatic aldehydes did not give any good results but aromatic aldehydes bearing a variety of functional group namely p-bromobenzaldehyde and p-nitrobenzaldehyde are reacted with methy-

---

* Reprint requests to Dr. M. M. Heravi.

lene compounds such as malonitrile and ethylcyanoacetate in the presence of montmorillonite K-10 under microwave irradiation in solvent free conditions. These reactions lead to completion in 2–10 min to produce olefinic products in 45–85% yield (Table). In the case of ketones, the condensation of cyclohexanone and 2-methyl-cyclohexanone readily occurred (entries 7 and 8), but the hindered 2,6-dimethylcyclohexanone failed to react. Reactions were more difficult with aromatic ketones. However we were able to isolate the products from the reaction of acetophenone and benzophenone with malonitrile in moderate yields (entries 9 and 10).

In order to evaluate the synergy between dry media and microwave irradiation in this reaction several experiments were tried. The irradiation of benzaldehyde and malonitrile without clay was unsuccessful and the aldehyde remained practically unchanged after irradiation. Similarly, when montmorillonite K-10 was used as catalyst in methylene chloride solution (10 h reflux), the corresponding alkene was not obtained. Although clay in dry media catalyzed the reaction at room temperature, yield was only 25% after 2 h of reaction, increase in temperature using classical heating (1 h, 120 °C) in the absence of solvent gave a moderate yield (40%) of the corresponding alkene. Only in the case of dry media completed with microwave irradiation, taking advantage of synergy between both methodologies, the Knoevenagel condensation proceeded efficiently.

In conclusion, this methodology, which associates dry heterogeneous media with microwave irradiation, appears easy, fast and clean to perform the Knoevenagel reaction. Furthermore, by development of a continuous microwave reaction for organic synthesis [16, 17] this work may have more industrial application where the absence of solvent and low cost of the method may lead to environmental and cost advantages.

## Experimental

Melting points were determined with a Reichert hot plate melting point apparatus. All compounds are known and exhibit satisfactory spectroscopic data. Yields refer to isolated products purified by column chromatography. Montmorillonite K-10 was dried and simultaneously activated in a microwave oven for 3 min at 780 W prior to use. Microwave irradiation was carried out in a National oven model 6755 at 900 W. For safety reasons all the experiments with microwave ovens should be performed in an efficient hood in order to avoid contact with vapors. If a tall beaker is used and the irradiation sequence is interrupted with a 60 sec cooling there is little vaporization and very high conversion can be observed.

### *Preparation of Alkenes by Knoevenagel Condensation*

*General Procedure:* Equimolar amounts (10 mmol) of carbonyl compounds and active methylene compound (malonitrile or ethylcyanoacetate) were dispersed on montmorillonite K-10 (5 g dried for 3 min in the microwave oven just before use) in a tall beaker. This mixture is then exposed to microwave irradiation for the appropriate time (Table). Then it was taken up into $CH_2Cl_2$ and the clay was separated by filtration and the solvent evaporated under reduced pressure. Pure products could be isolated by column chromatography using hexane-ethylacetate (9:1) as eluent.

Table. Montmorillonite K-10 assisted Knoevenagel condensation under microwave irradiation in solventless system.

| Entry | Carbonyl compound | R | Time [min] | Yield [%] | M.p., b.p. [°C] | Lit |
|---|---|---|---|---|---|---|
| 1 | Benzaldehyde | CN | 3 | 85 | 83 (m.p.) | [18] |
| 2 | | $CO_2Et$ | 5 | 74 | 51 (m.p.) | [18] |
| 3 | *p*-Bromobezaldehyde | CN | 5 | 68 | 164 (m.p.) | [19] |
| 4 | | $CO_2Et$ | 5 | 62 | 96 (m.p.) | [19] |
| 5 | *p*-Nitrobezaldehyde | CN | 8 | 68 | 159 (m.p.) | [18] |
| 6 | | $CO_2Et$ | 8 | 62 | 168 (m.p.) | [18] |
| 7 | Cyclohexanone | CN | 5 | 68 | 150 (b.p., 10 mmHg) | [18] |
| 8 | 2-Methylcyclohexanone | CN | 5 | 72 | 160 (b.p., 10 mmHg) | [20] |
| 9 | Acetophenone | CN | 10 | 45 | 92 (m.p.) | [21] |
| 10 | Benzophenone | CN | 10 | 42 | 138 (m.p.) | [22] |

[1] G. Jones, Organic Reactions, **15**, pp. 204 (1967).
[2] F. Texier-Boullet, A. Foucaud, Tetrahedron Lett. **23**, 4927 (1982).
[3] S. Chalais, P. Laszlo, A. Mathy, Tetrahedron Lett. **26**, 4453 (1985).
[4] J. A. Cabello, J. M. Campelo, A. Garcia, D. Luna, J. M. Marenas, J. Org. Chem. **49**, 5195 (1984).
[5] G. Bram, A. Loupy, D. Vellemin in Solid Supports and Catalysts in Organic Synthesis, Ed., K. Smith Ellis Harwood and Prentice Hall, Chichester, ch. 12 (19).
[6] D. Villemin, B. Martin, J. Chem. Res. **5**, 146 (1994).
[7] P. dela Cruz, E. Diez-Barra, A. Loupy, F. Langa, Tetrahedron Lett. **37**, 1113 (1996).
[8] D. Prajapati, J. S. Sanduh, J. Chem. Soc. Perkin Trans. I 739 (1993).
[9] K. M. Lakshmi, B. M. Choudary R. K. Kaleswara, F. Figueras, Chem. Commun. 1033 (1998).
[10] M. M. Heravi, K. Aghapoor, M. A. Nooshabadi, M. M. Mojtahedi, Monatsh. Chem. **128**, 1143 (1997).
[11] K. Aghapoor, M. M. Heravi, M. A. Nooshabadi, Ind. J. Chem. **37B**, 84 (1998).
[12] M. M. Heravi, R. Kiakojoori, K. Tabar-Hydar, J. Chem. Res. 656 (1998).
[13] M. M. Heravi, D. Ajami, M. Ghassemzadeh, Synth. Commun. (1998), in press.
[14] M. M. Heravi, M. Tajbakhsh, B. Mohajerani, Synth. Commun. (1998), in press.
[15] Z. Rappoport, S. Patai, J. Chem. Soc. 731 (1962).
[16] T. Cablewaski, A. F. Faux, R. Strauss, J. Org. Chem. **59**, 340 (1994).
[17] L. Bagnell, T. Cablewaski, C. R. Strauss, R. W. Trainor J. Org. Chem. **61**, 7355 (1996).
[18] J. A. Cabllo, J. M. Capelo, A. Garcia, D. Luna, J. M. Marinas, J. Org. Chem. **49**, 5195 (1984).
[19] J. Zabicky, J. Chem. Soc. 683 (1961).
[20] D. Kruger, A. E. Sopchik, C. A. Kingbury, J. Org. Chem. **79**, 778 (1984).
[21] F. Texier-Boullet, A. Foucaud, Tetrahedron Lett. **23**, 4927 (1982).
[22] D. M. W. Anderson, F. Bell, J. L. Duncan, J. Chem. Soc. 4705 (1961).