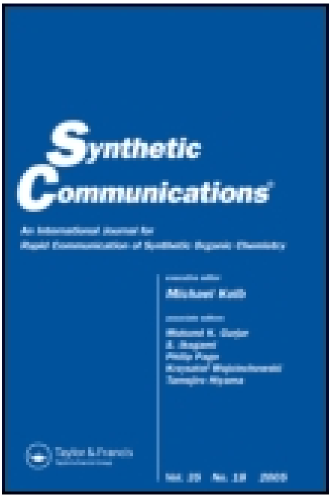

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Microwave Assisted Michael Addition of Cycloalkenones and Substituted Enones on the Surface of Alumina in Dry Media

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SYNTHETIC COMMUNICATIONS, 27(4), 621-626 (1997)

MICROWAVE ASSISTED MICHAEL ADDITION OF CYCLOALKENONES AND SUBSTITUTED ENONES ON THE SURFACE OF ALUMINA IN DRY MEDIA

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ABSTRACT : The Michael addition of ethyl acetoacetate, acetyl acetone and ethyl cyanoacetate to cycloalkenones and β-substituted enones and enal has been accomplished efficiently on the surface of alumina under microwave irradiation in dry media.

The Michael reaction is one of the most efficient methods for effecting carbon-carbon bond formation[1] and has wide synthetic applications.[2] A few years back we have introduced a simple and efficient method for Michael addition on the surface of alumina without any solvent.[3] Although this procedure works very well with unsubstituted α,β-unsaturated carbonyl compounds, the addition to substituted enones and cycloalkenones appeared difficult. We wish to report here that these difficulties are now overcome by carrying out the reaction under microwave irradiation.

In a typical procedure, a mixture of Michael donor and Michael acceptor, adsorbed on activated neutral alumina, was

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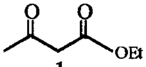
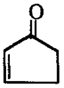
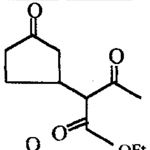
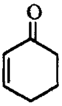
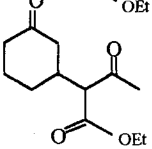
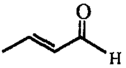
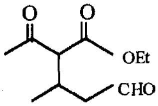
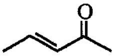
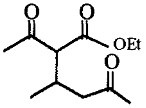
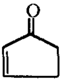
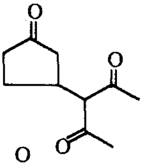
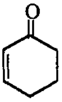
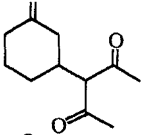
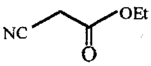
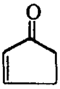
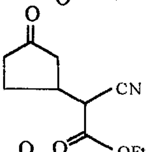
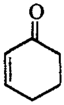
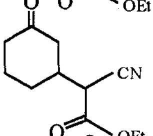
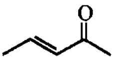
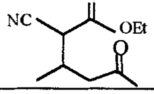
*To whom correspondence should be addressed irradiated with microwave in a domestic microwave oven for a certain period of time. The product was isolated by simple elution of the solid mass with methylene chloride and evaporation of solvent. Structurally varied donors such as ethyl acetoacetate, acetyl acetone and ethyl cyanoacetate underwent clean additions to acceptors like cyclopen-2-en-1-one, cyclohex-2-en-1-one, croton aldehyde and pent-3-en-2-one. The results are presented in Table 1. The reactions are very fast and the yields are also good.

The present investigation thus provides a very simple, efficient and general methodology for Michael addition to cycloalkenones and substituted enones. The notable advantages of this methodology are : (a) use of environmentally safe and inexpensive reagents; (b) fast reaction; (c) high yields and (d) operational simplicity. This also shows high potential of microwave technology in organic synthesis.[4]

EXPERIMENTAL

General Procedure for Michael Addition - A mixture of Michael donor (1 mmol) and Michael acceptor (1 mmol) was added to alumina (neutral, Brockmann activity; grade 1 for column chromatography, SRL, India; 1 g, activated at 180°C for 4 h at 0.05 mm of Hg) in a small pyrex round bottom flask and shaken well. The flask was then placed in a porcelain basin containing alumina and irradiated with microwave at 200 W in a domestic microwave oven (BPL, model BMO-700T) for a certain period of time as required for completion (Table 1). After

Table 1: Al_2O_3- mediated Michael addition under microwave irradiation

Entry	Donor	Acceptor	Time	Product	Yield(%)^a
1	 1		5		88
2	1		5		90
3	1		4		65
4	1		4		70
5	 2		7		76
6	2		7		78
7	 3		5		72
8	3		6		75
9	3		6		74

^{a}Yields refer to isolated products

being allowed to cool, the solid mass was then taken in a column with a short plug of silica gel and eluted with methylene chloride. Evaporation of solvent furnished the practically pure product which was further purified by column chromatography over silica gel.

The products are mostly known compounds and are in good agreement with their spectral data which are recorded below in order of their entries in the Table. (IR spectra were recorded on thin film and ^{1}H NMR spectra were run at 60 MHz in CCl_4 solution with tetramethysilane as an internal standard).

1 IR : 1715, 1750 cm^{-1}; ^{1}H NMR δ : 1.3 (t, J = 7.5 Hz, 3H), 1.5-2.5 (m, 7H), 2.2 (s, 3H), 3.1 (d, J = 9 Hz, 1H), 4.19 (q, J = 7.5 Hz, 2H).

2 IR : 1715, 1740 cm^{-1}; ^{1}H NMR δ : 1.3 (t, J = 8 Hz, 3H), 1.67-2.5 (m, 9H), 2.2 (s, 3H), 3.3 (d, J = 8 Hz, 1H), 4.20 (t, J = 8 Hz, 2H).

3 IR : 1710-1740 cm^{-1}; ^{1}H NMR δ : 1.0 (d, J = 6.5 Hz, 3H), 1.29 (t, J = 7 Hz, 3H), 2.16 (s, 3H), 2.26-2.6 (m, 3H), 3.35 (dd, J_1 = 7 Hz, J_2 = 2 Hz, 1H), 4.17 (t, J = 7 Hz, 2H), 9.7 (t, J = 2 Hz, 1H).

4 IR : 1715, 1740 cm^{-1}; ^{1}H NMR δ: 0.96 (d, J = 6 Hz, 3H), 1.3 (t, J = 8 Hz, 3H), 2.1 (s, 3H), 2.16 (s, 3H), 2.1-2.7 (m, 3H), 3.3 (d, J = 7 Hz, 1H), 4.16 (q, J = 8 Hz, 2H).

5 IR : 1700, 1745 cm^{-1}; ^{1}H NMR δ : 1.4-2.4 (m, 7H), 2.16 (s, 3H), 2.19 (s, 3H), 3.6 (d, J = 9.5 Hz, 1H).

6 IR : 1710 cm^{-1}; ^{1}H NMR δ : 1.4-2.6 (m, 9H), 2.15 (s, 6H), 3.56 (d, J = 9.5 Hz, 1H).

7 IR : 1735-1755, 2230 cm^{-1}; ^{1}H NMR δ : 1.36 (t, J = 7 Hz, 3H), 1.66-3.0 (m, 7H), 3.66 (d, J = 5 Hz, 1H), 4.3 (t, J = 7 Hz, 2H).

8 IR : 1710, 1740, 2230 cm^{-1}; ^{1}H NMR δ : 1.34 (t, J = 7 Hz, 3H), 1.53-2.66 (m, 9H), 3.5 (d, J = 5 Hz, 1H), 4.3 (q, J = 7 Hz, 2H).

9 IR : 1720, 1745, 2230 cm^{-1}; ^{1}H NMR δ : 1.05 (d, J = 6 Hz, 3H), 1.37 (t, J = 8 Hz, 3H), 2.15 (s, 3H), 2.43-2.66 (m, 3H), 3.63 (dd, J_1 = 16 Hz, J_2 = 4 Hz, 1H), 4.23 (t, J = 8 Hz, 2H).

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