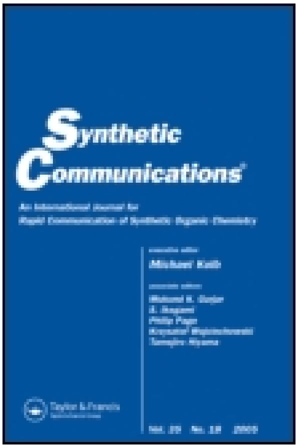

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Cerium Catalyzed Michael Addition of 1,3-Dicarbonyl Compounds Under Microwave Irradiation

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CERIUM CATALYZED MICHAEL ADDITION OF 1,3-DICARBONYL COMPOUNDS UNDER MICROWAVE IRRADIATION

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Abstract: Cerium chloride heptahydrate proves to be an efficient catalyst for Michael addition of 1,3-dicarbonyl compounds, through a simple solvent free reaction under microwave irradiations.

Development of efficient catalysis of carbon-carbon bond formations is the current subject of intensive investigations[1]. For Michael-type reactions of 1,3-dicarbonyl compounds, several catalysts including chiral ones have been developed[2]. It is usually carried out with a base as catalyst. But in the presence of strong bases, side reactions such as auto condensations, bis-additions, rearrangements and polymerisations are frequently encountered[1]. In the last few years various catalysts such as phase transfer catalysts[3], transition metal complexes[3], alumina[4], $SnCl_4$[3], $TiCl_4$[3], CsF[5], $Bu_2Sn(OTf)_2$[6] and $BF_3.Et_2O$[6] and lanthanides[7] were proposed. But a serious limitations of some of these

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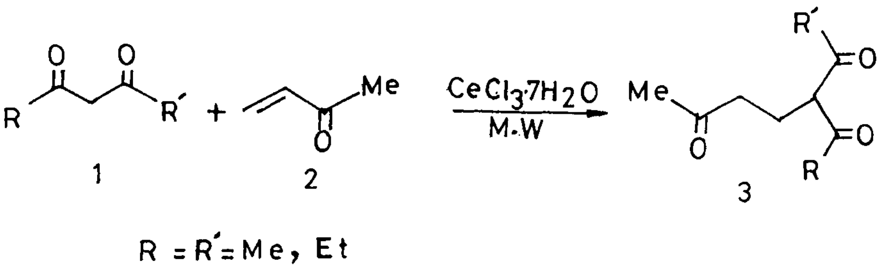
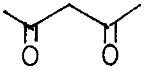
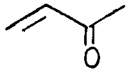
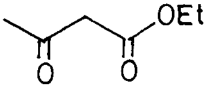
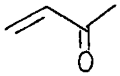
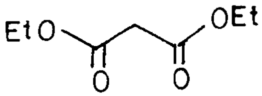
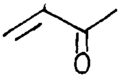
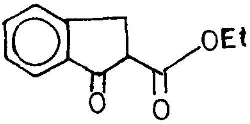
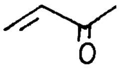
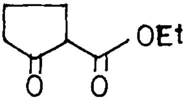
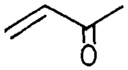
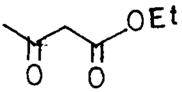
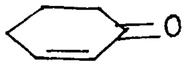
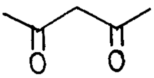
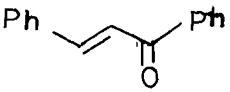
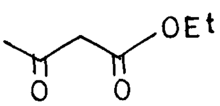
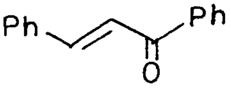
catalysts is toward the use of methyl vinyl ketone (MVK), the simplest enone due to its high tendency to polymerise[5,8]. All these promoted us to search for a new and efficient catalyst to circumvent the problem. Herein we wish to disclose the use of a new catalyst cerium chloride heptahydrate[9] for carbon-carbon bond formation under microwave irradiation. The reaction proceeds efficiently in excellent yields at ambient pressure within minutes time and in the absence of solvent.



In a typical case, acetyl acetone (10 mmol), MVK (10 mmol) and cerium chloride[10] (0.37g, 1 mmol) were mixed together without solvent in an Erlenmeyer flask and placed in a commercial microwave oven (operating at 2450 MHz frequency) and irradiated for 8 mins. The reaction mixture was allowed to reach room temperature and extracted with chloroform. Removal of solvent affords the Michael adduct (entry 1) in 92% yields without the formation of any side products. Results obtained using several Michael donors are listed in the Table. First we investigated the scope of the reaction by changing the structure of the Michael donor with MVK as the acceptor. Both cyclic and acyclic β-ketoesters were used in this reaction. In all cases, hydrolysis of the ester functionality was not observed. Furthermore yields are generally higher and reaction time is much less than the yields and times reported by earlier workers.

Table : $CeCl_3 . 7H_2O$ Catalysed Michael addition of 1,3-dicarbonyl compounds.

Entry	Michael donor	Michael acceptor	$CeCl_3$ time[b] (min.)	$CeCl_3$ Yield[a] (%)
1			8	92
2			9	86
3			10	85
4			10	78
5			12	75
6			11	86
7			12	78
8			15	76

[a] All the yields refer to isolated, chromatographically pure compounds. [b] All the assigned structures have been confirmed by spectroscopic data (IR, ^1H NMR, MS)

As regards the field of applicability of the above reaction, it has to be noted that β-substituted α,β-unsaturated ketones (for ex. cyclohex-2-en-1-one) undergo the usual addition with ethylacetoacetate with formation of the adducts, as 1:1 mixture of diastereoisomers. On the contrary, β,β-disubstituted ketones (for ex. 3-methyl-cyclopent-2-en-1-one) have proved to be non-reactive under above conditions. Interestingly, it was also observed that the presence of solvent slowered the reaction, (the above reaction takes about 20-25 hours for completion when carried out in refluxing dioxan) the reasons for the efficiency of the process on the solid phase are not yet clear. All the additions were carried out with 1:1 donor-acceptor proportions, and the corresponding Michael adducts were isolated in 75-92% yields (Table) and structure of these products were confirmed unambiguously by comparing with authentic samples.

In conclusion, this new method of C-C bond formation using cerium chloride without any solvent under microwave irradiation offers significant improvements over the existing procedures and thus help facile entry into a host of Michael adduct of potentially high synthetic utility. Also this simple and easily reproducible technique affords various adducts in minutes time, with excellent yields without involvement of toxic material and without the formation of any undesirable side products, than the classical homogeneous reaction in solvents

EXPERIMENTAL

General Procedure for the Michael Addition of 1,3-Dicarbonyl Compounds

Methyl vinyl kitone (0.7g, 10 mmol) and acetyl acetone (1g, 10 mmol) were mixed together without solvent in an Erlenmeyer flask and placed in a commercial microwave oven (operating at 2450 MHz frequency) and irradiated for 8 mins. The reaction mixture was allowed to reach room temperature and extracted with chloroform (3 x 30 ml). The combined organic extracts were washed with cold water (40 ml), dried over anhydrous sodium sulphate and evaporated under reduced pressure to furnish the Michael adduct in 92% yield (entry 1). This was further purified by thin layer chromatography using silica gel as adsorbent and chloroform as the eluent. The structure of the Michael adduct thus obtained was confirmed unambiguously by spectroscopic data and finally by comparison with an authentic sample. Similarly other substrates were reacted and the corresponding adducts were isolated in 75-92% yields (Table).

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