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Solvent Free Reaction Under Microwave Irradiation: A New Procedure For Eu^{+3} - Catalyzed Michael Addition of 1,3-Dicarbonyl Compounds

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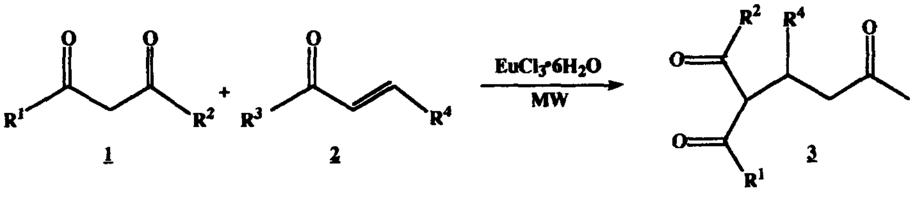
Abstract: C-C bond formation via Michael addition is achieved in high yields and short times by employing catalytic amounts of $EuCl_3$ in dry media under microwave irradiation.

The Michael addition of active methylene compounds to unsaturated carbonyl derivatives is a useful C-C bond forming reaction. In order to avoid the typical disadvantages of base-catalyzed processes (cyclization, self-condensation, retro-Michael, etc.), many procedures involving neutral conditions have been proposed in the last few years.[1,2] In particular, as regards 1,3-dicarbonyl compounds, the employment of transition metal and lanthanide catalysts has given very satisfactory results both in terms of efficiency and selectivity.[3-6]

The applications of microwave energy (MW) in organic chemistry are increasing very rapidly[7] since the pioneering papers of Giguere[8] and Gedye[9]. The time-saving ability together with the very short response times and the minimization of thermal decomposition products are the main advantages of microwave heating and further improvements will be allowed by the avaibility of a continous microwave reactor.[10]

Unfortunately, the exploitation of this technology for the conjugate addition of 1,3-dicarbonyl compounds was found to suffer from serious limitations because of the marked tendency of β-ketoesters to undergo alkoxydecarbonylation processes under microwave irradiation.[11]

Now we wish to report that this competitive process can be almost completely avoided by performing MW-mediated Michael addition of 1,3-dicarbonyl compounds in the presence of catalytic amounts of Eu^{3+} catalysts.



Michael adducts were usually obtained in satisfactory yields and very short reaction times and, on the basis of the results obtained for different donors 1 and acceptors 2 (Table), this procedure looks to be fairly general.

Table

Table - $EuCl_3$ -catalyzed Michael addition of 1,3-dicarbonyl compounds 1 under MW irradiation

Entry	R^1	R^2	R^3	R^4	% Cat.	Time Reac./Power	Yeld(%)a)
a	Me	Me	Me	H	2	10'/100 W	82
b	Me	OEt	Me	H	10	5'/150 W	68
c	Me	OEt	$-(CH_2)_3-$		5	10'/100 W	63b)
d	Ph	Me	Me	H	2	5'/100 W	88
e	Ph	Me	$-(CH_2)_3-$		10	3'/150 W	72b)
f	Ph	OEt	Me	H	10	5'/150 W	95
g	Ph	OEt	Me	H	10	5'/50 W	85c)
h	Ph	OEt	$-(CH_2)_3-$		10	3'/350 W	54b)

a) All the yields refer to isolated chromatographically pure compounds whose structures have been confirmed by IR, ^1H-NMR data.
b)Obtained as 1/1 diastereoisomeric mixtures.
c)In this case $Eu(fod)_3$ was used as catalyst

Furthermore, it has to be noted that in all entries involving the employment of β-ketoesters (entries b, c, f, g, h) no evidence of alkoxydecarbonylation, either of the starting materials or of Michael adducts, has been detected. Finally, the availability of Eu^{+3} catalysts soluble in the reaction mixture, like $Eu(fod)_3$, has allowed the reaction to be performed under milder conditions with a limited lowering of efficiency (entry g).

Experimental: A mixture of 1,3-dicarbonyl compound (2 mmol), Michael acceptor (2.4 mmol) and Eu^{+3}-catalyst is submitted to MW irradiation in a kitchen oven under the conditions reported in the Table. Then the crude mixture is directly poured onto the top of a silica gel chromatographic column and elution with petroleum ether/ethyl acetate mixtures affords pure adducts 3.

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