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$BiCl_3$ or CdI_2 Catalyzed Michael Addition of 1,3-Dicarbonyl Compounds Under Microwave Irradiations

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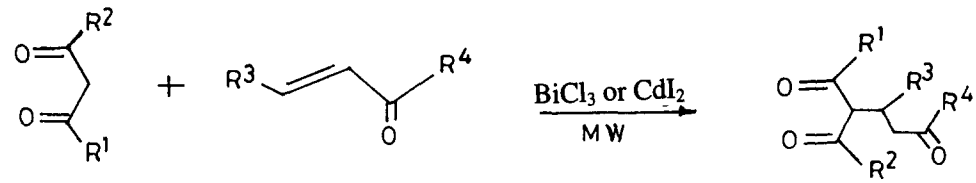
Abstract: CdI_2 proves to be an efficient catalyst for Michael addition of 1,3-dicarbonyl compounds under microwave irradiations, through a simple solvent free reaction.

The Michael reaction is one of the most efficient methods for effecting carbon-carbon bond formation[1] and has wide applications in organic synthesis[2] and biosynthesis[3]. 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, rearrangement and polymerisations are frequently encountered. In recent years various catalysts such as phase transfer catalysts[4], transition metal complexes[4], lanthanides[5], alumina[6], $SnCl_4$[4], $TiCl_4$[4], CsF[7], $Bu_2Sn(OTf)_2$[8] and $BF_3.Et_2O$[8] were proposed to circumvent this problem. But a serious limitation of some of these catalysts is toward the use of MVK, the simplest enone, as an acceptor due to its high tendency to polymerise, under certain reaction conditions[7,9]. Considering the great synthetic potentiality of the corresponding MVK adduct[10], herein we wish to report the use of a new catalyst $BiCl_3$ or CdI_2 for carbon-carbon bond formation under microwave irradiations. The reaction proceeds efficiently in excellent yields at ambient pressure within minutes time and in the absence of solvent.



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In a typical procedure, acetyl acetone (10 mmol), methyl vinyl ketone (10 mmol) and bismuth trichloride[11] (0.32g, 10% mol) were mixed together without solvent in an Erlenmeyer flask and placed in a commercial microwave oven (operating at 2450 MHz frequency) and irradiated for 15 mins. The reaction mixture was allowed to reach room temperature and extracted with chloroform. Removal of solvent and the residue on purification by passing through a short column of silica gel using chloroform as eluent, affords the Michael adduct (entry 1) in 90% yields without the formation of any side products. Similarly cadmium iodide (10% mol) was used in place of bismuth trichloride and the corresponding Michael adduct was isolated in 85% yields.

As shown in Table 1, several structurally varried donors including diethylmalonate, acetyl acetone and ethylacetoacetate underwent clean and remarkably fast Michael additions with methyl vinyl ketone and benzal

acetophenone under this procedure. Interestingly, it was observed that the presence of solvent slowered the reaction, (the above reaction takes about 16-20 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 adducts were isolated in 70-90% yields (Table 1).

In conclusion, this new method of carbon-carbon bond formation using $BiCl_3$ or CdI_2 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 shorter reaction time, with excellent yields without involvement of toxic and expensive material and without the formation of any undesirable side products, than the classical homogeneous reaction in solvents.

Table 1: $BiCl_3$ or CdI_2 catalysed Michael addition of 1,3-dicarbonyl compounds **2.**

Entry	R^1	R^2	R^3	R^4	$BiCl_3$		CdI_2	
					t,(min)	Yield[a](%)	t,(min)	Yield[b](%)
1	CH_3	CH_3	H	CH_3	15	90	20	85
2	CH_3	OC_2H_5	H	CH_3	12	82	16	83
3	OC_2H_5	OC_2H_5	H	CH_3	15	80	15	82
4	CH_3	CH_3	C_6H_5	C_6H_5	15	85	26	72
5	CH_3	OC_2H_5	C_6H_5	C_6H_5	16	80	30	70
6	OC_2H_5	OC_2H_5	C_6H_5	C_6H_5	15	85	25	72

[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).

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