Cerium(III) Chloride Catalyzed Michael Reaction of 1,3-Dicarbonyl Compounds and Enones in the Presence of Sodium Iodide Under Solvent-Free Conditions

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Cerium(III) chloride heptahydrate in the presence of sodium iodide catalyses the Michael addition of 1,3-dicarbonyl compounds to α,β-unsaturated ketones and α,β-unsaturated aldehydes with extraordinary efficiency. The very mild conditions allow high chemoselectivity as shown by the absence of the typical side reactions, which can be observed in the conventional base-catalyzed processes. More interestingly, when at least one of the starting materials is liquid at room temperature, the reaction can also be performed without solvents. The $CeCl_3 \cdot 7\ H_2O$/NaI catalyst system can be easily separated from the reaction mixture and it can be reused without an appreciable loss of activity. Advantages of the present procedure, which utilizes cheap and "friendly" reagents, over the previously reported ones, are discussed.

Introduction

The Michael reaction of 1,3-dicarbonyl compounds and enones provides one of the most efficient methods for effecting carbon−carbon bond formation and has wide applications in organic synthesis,[1] and biosynthesis.[2] The classical methodology is a high-yielding base-catalyzed process. However, in the presence of strong bases, side reactions such as self-condensation, ester solvolysis, bis-addition, rearrangements and polymerizations are frequently encountered. Therefore, in recent years various other kinds of catalysts able to work under neutral conditions have been proposed. In particular the employment of lanthanide(III) trifluoromethanesulfonates,[3] such as $Yb(OTf)_3$, as water-tolerant Lewis acids gave satisfactory results.[4] However, these methods suffer from the disadvantages of using expensive catalysts and involving long reaction times (typically five days). For this reason, major attention has been focused on the use of the cheaper cerium(III) chloride under microwave irradiation.[5] However, under these conditions[6] in the reaction of β-oxo esters as Michael donors alkoxydecarbonylation can occur.[7]

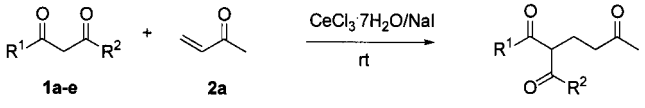
More recently, the ability of iron(III) chloride hexahydrate to catalyse the Michael reaction of β-dicarbonyl compounds and enones under mild and neutral conditions has been reported.[8] This methodology is very interesting since the reaction can proceed smoothly without solvent at room temperature. However, in some cases, the reaction requires temperatures over 50°C.[9] In addition, the adopted work-up procedure (filtration through a short column of silica gel to remove all iron-containing materials) does not allow the catalyst to be reused. All these reports prove the continuous effort of chemists to set up new simple, efficient and environmentally compatible procedures.[10]

In recent years, the use of $CeCl_3$ has been proposed in reactions which need the presence of a Lewis acid activator, since this compound is a very cheap, nontoxic and water-tolerant reagent.[11] During our studies on applications of cerium compounds in organic synthesis[12], we found that the $CeCl_3 \cdot 7\ H_2O$/NaI system acts as an efficient catalyst in the cleavage of carbon−oxygen[13] and silicon−oxygen[14] bond under neutral conditions.

We wish to report now that the $CeCl_3 \cdot 7\ H_2O$/NaI system is able to effectively catalyse the Michael addition of 1,3-dicarbonyl compounds like **1** to α,β-unsatured ketones and aldehydes allowing to set up a very simple and efficient procedure.

Results and Discussion

Preliminary experiments showed that the reaction between acetylacetone (**1a**) and methyl vinyl ketone (**2a**) is sluggish when carried out in acetonitrile and in the presence



1a: R^1=R^2=Me
1b: R^1=Ph, R^2=Me
1c: R^1=Me, R^2=OEt
1d: R^1=Ph, R^2=OEt
1e: R^1=Me, R^2=O^{t}Bu

Scheme 1. $CeCl_3 \cdot 7H_2O$/NaI system catalysed addition of 1,3-dicarbonyl compounds

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Table 1. Preparation of 3-acetyl-2,6-heptanedione (**3aa**) from Michael additions of acetylacetone (**1a**) to methyl vinyl ketone (**2a**) under different experimental conditions

Entry	Solvent	Catalyst	Reaction time [h][a]	Yields (%)[b]
1	CH_3CN	$CeCl_3 \cdot 7\ H_2O$	96	30
2	CH_3CN	$CeCl_3 \cdot 7\ H_2O$ (1 equiv.)/NaI (0.1 equiv.)	10	90
3	CH_3CN	$CeCl_3 \cdot 7\ H_2O$ (0.2 equiv.)/NaI (0.1 equiv.)	12	96
4	no solvent	$CeCl_3 \cdot 7\ H_2O$ (0.2 equiv.)/NaI (0.1 equiv.)	6	97

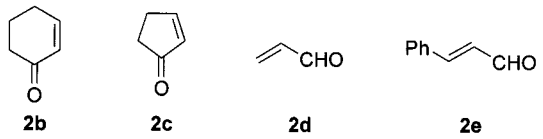
[a] All reactions were carried out at room temperature. – [b] Yields in pure isolated product.

of $CeCl_3 \cdot 7\ H_2O$ alone, even in stoichiometric amount, (30% yields after 4 d at room temperature, see Table 1, entry 1).

As previously reported[13,14] the addition of NaI dramatically increases the efficiency of cerium(III) chloride. In fact, in the presence of 10% of NaI the reaction goes to completion in about 10 h (Table 1, entry 2). Further experiments showed that also the amount of $CeCl_3 \cdot 7\ H_2O$ can be reduced without an appreciable loss of activity, the optimum conditions being 0.2 equiv. of $CeCl_3 \cdot 7\ H_2O$ and 0.1 equiv. of NaI (Table 1, entry 3).

The reaction can be carried out in shorter times without solvent (Table 1, entry 4). This allowed us to adopt a very simple work-up procedure for the recovery of the catalyst. The reaction mixture was treated with an organic solvent able to dissolve the organic material and not the catalyst (CH_2Cl_2) which could be easily removed by filtration and regenerated in an oven at 60°C for 2 h. We repeated this procedure three times for the reaction of **1a** with **2a** without noting any appreciable decrease in activity.

This simple methodology can be successfully applied to other Michael donors and acceptors. In fact, data reported in Table 2 show that the reactions of benzoylacetone (**1b**), ethyl acetoacetate (**1c**) and ethylbenzoyl acetate (**1d**) with methyl vinyl ketone (**2a**) give the corresponding Michael adducts in excellent yields. Moreover, these experimental results indicate that the reaction can be carried out without solvent, even if one of the two reagents is solid.



2b **2c** **2d** **2e**

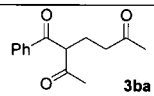
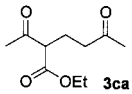
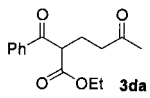
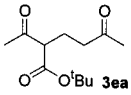
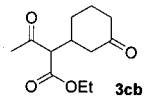
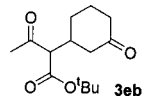
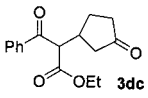
Figure 1. α,β-Unsaturated ketones and aldehydes used as Michael acceptores

The methodology is very efficient also when very bulky ester functions are present, as shown by the excellent results obtained in the reaction of *tert*-butyl acetoacetate (**1e**) with **2a**. Moreover, the adopted neutral conditions completely avoid the occurrence of ester solvolysis side processes.

The reaction proceeds smoothly with excellent yields under non-solvent conditions even in the case of sterically hindered and less reactive enones,[15] such as cyclohexenone (**2b**) and cyclopentenone (**2c**), although longer reaction times are required (Table 2, entries 5–7). The neutral and mild conditions allow the reaction to be applied to the addition of Michael acceptors having a high tendency to polymerize,[16] such as acrolein (**2d**) (see Table 3). Moreover, the observed high yields indicate that, in these cases, the 1,2-addition reaction occurs to a limited extent. This process becomes competitive only when a high steric hindrance is present both in the Michael donor and in the Michael acceptor. In fact, in the reaction of **1a** ($R^1 = R^2 = Me$) with cinnamaldehyde (**2e**) the conjugated addition accounts for the 90% of the yield, while in the reaction of sterically more hindered dicarbonyl compounds **1b** (R^1 = Ph, R^2 = Me) and **1d** (R^1 = Ph, R^2 = OEt) with the same aldehyde **2e**, 1,4-addition accounts only for 63% and 58% yield, respectively (Table 3, entries 5–7).

Finally, compounds **3** from Michael additions to **2b**, **2c** and **2e** are isolated as a diastereomeric mixture, whose composition (about 1:1 ratio in all cases) reflects the relative

Table 2. Michael additions of 1,3-dicarbonyl compounds **1b–e** to enones **2a–c** at room temperature without solvent in the presence of $CeCl_3 \cdot 7\ H_2O$/NaI as catalyst

Entry	Michael donor	Enone	Product[a]	Reaction time [h]	Yields [%][b]
1	**1b**	**2a**	 **3ba**	6	98
2	**1c**	**2a**	 **3ca**	6	98
3	**1d**	**2a**	 **3da**	8	98
4	**1e**	**2a**	 **3ea**	10	95
5	**1c**	**2b**	 **3cb**	18	96[c]
6	**1e**	**2b**	 **3eb**	20	94[c]
7	**1d**	**2c**	 **3dc**	18	93[c]

[a] All products were identified by their IR, NMR, and GC/MS spectra. – [b] All yields refer to pure isolated compounds. – [c] As a mixture of two diastereomers in about 1:1 ratio in all cases.

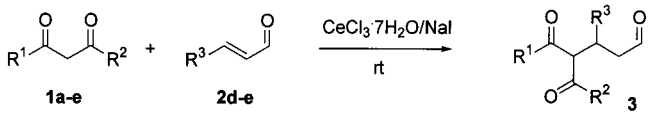


Table 3. Michael additions of 1,3-dicarbonylic compounds **1a−e** to aldehydes **2d−e** in the presence of $CeCl_3 \cdot 7\ H_2O$/NaI as catalyst

Entry	Michael donor	Aldehyde	R^1	R^2	R^3	Product[a]	Reaction time [h]	Yields (%)[b,c]
1	**1a**	**2d**	Me	Me	H	**3ad**	8	86
2	**1b**	**2d**	Ph	Me	H	**3bd**	14	88
3	**1c**	**2d**	Me	OEt	H	**3cd**	15	89
4	**1e**	**2d**	Me	O*t*Bu	H	**3ed**	16	85
5	**1a**	**2e**	Me	Me	Ph	**3ae**	16	90[d]
6	**1b**	**2e**	Ph	Me	Ph	**3be**	24	63[d,e]
7	**1d**	**2e**	Ph	OEt	Ph	**3de**	24	58[d,e]

[a] All products were identified by their IR, NMR, and GC/MS spectra. − [b] All yields refer to pure isolated compounds. − [c] Reaction carried out without solvent by adding **1** (1 mmol) and **2** (1 mmol) to a mixture of $CeCl_3 \cdot 7\ H_2O$ (0.2 mmol) and NaI (0.1 mmol), unless otherwise mentioned. − [d] As a mixture of two diastereomers in about 1:1 ratio in all cases. − [e] Besides 1,2-addition products as revealed by GC/MS analyses of the crude mixture of the reaction.

thermodynamic stability of the two diastereoisomers. In fact owing to the facile inversion of configuration at the asymmetric carbon atom in the α-position of a 1,3-dicarbonyl system via its enolic form, a rapid interconversion of each diastereomer into the other one occurs.

The success of the reaction in the case of α,β-unsatured aldehydes is very useful because it represents a new entry for the achievement of 5,6-disubstituted cyclohex-2-en-1-ones, important key intermediates in the synthesis of various natural products.[17]

In conclusion, present results show that the $CeCl_3 \cdot 7\ H_2O$/NaI system acts as an efficient catalyst for Michael additions of 1,3-dicarbonyl compounds to α,β-unsatured ketones and aldehydes. Our method shows the following advantages over the previous reported procedures: (a) No solvent needed when at least one of the two reagents is liquid. (b) It proceeds smoothly at room temperature and in neutral medium; under these very mild adopted conditions all side processes are completely depressed. (c) It adopts a very simple work-up procedure which allows for an easy recovery and regeneration of the catalyst which can be reused without any appreciable loss of activity. (d) Finally, it utilizes very "friendly" and cheap materials.

Experimental Section

General: ^{1}H-NMR data were recorded for solutions in $CDCl_3$ with TMS as internal standard at 25°C using a 200-MHz NMR spectrometer from Varian. − Mass spectra were determined with an HP5890 Series II capillary GC operating in split mode with helium as the carrier gas and fitted with a mass-selective detector (MSD). The column used was an HP5 capillary column 30 m × 0.25 mm with 0.25 μm film thickness of 5% phenylmethylsilicone gum. The temperature program used the initial temperature of 65°C for 3 min and then ramped at 15°C min^{-1} to 280°C. − Elemental analyses were performed using a C,H,N,S Analyzer Model 185 from Hewlett-Packard. − Column chromatography was carried out using 230−240 mesh silica gel; eluent hexane/ethyl acetate (7:3). − All starting materials were commercially available.

General Procedure: A flask was charged in succession with 1,3-dicarbonyl compounds **1** (1 mmol), Michael acceptors [methyl vinyl ketone (**2a**), enones **2b−c** or aldehydes **2d−e**] (1.1 mmol), cerium(III) chloride heptahydrate (0.2 mmol) and sodium iodide (0.1 mmol). The mixture was then stirred at room temp. until all the 1,3-dicarbonyl compound was consumed (6 to 24 h). The reaction was treated under stirring with CH_2Cl_2 (20 mL) and the catalyst mixture was removed by filtration and rinsed with CH_2Cl_2. The filtered extracts were concentrated under reduced pressure, and then the crude product was purified by silica gel chromatography to give the corresponding Michael adduct. Yields are reported in Tables 1 and 2; physical data of new compounds follow.

***tert*-Butyl 2-Acetyl-5-oxohexanoate (3ea):** Pale yellow oil, 95% yield. − IR (film): $\tilde{\nu}$ = 3061 cm^{-1}, 1735, 1705, 1685, 1612. − ^{1}H NMR: δ = 1.50 [s, 9 H, $C(CH_3)_3$], 2.12 (s, 3 H, 6-CH_3), 2.15−2.30 (m, 2 H, 3-CH_2), 2.52−2.67 (m, 2 H, 4-CH_2), 4.87 (t, *J* = 6.7 Hz, 1 H, 2-CH), 7.40−7.48 (m, 3 H, arom.), 7.56−8.01 (m, 2 H, arom.). − MS (70 eV); *m*/*z* (%): 290 [M$^+$], 247, 189, 105 (100), 77, 65, 57, 43. − $C_{17}H_{22}O_4$ (290.36): calcd. C 70.32, H 7.63; found C 70.29, H 7.60.

***tert*-Butyl 3-Oxo-2-(3-oxocyclohexyl)butanoate (3eb):** Colorless oil consisted of two diastereomers[18] (**A/B** = 55:45 by ^{1}H NMR), which were equilibrating and, thus, could not separated, 92% yield. − IR (film): $\tilde{\nu}$ = 1730 cm^{-1}, 1705. − ^{1}H NMR: δ = 1.32−1.46 (m, 2H), 1.47 [s, 9 H, $C(CH_3)_3$], 1.49 [s, 9 H, $C(CH_3)_3$], 1.51−1.83 (m, 2 H), 1.95−2.14 (m, 8 H), 2.15 (s, 3 H, 1′-CH_3), 2.17 (s, 3 H, 1′-CH_3), 2.27 (dd, *J* = 11.2 and 4.7 Hz, 4 H, 2 2-CH_2), 2.65−2.74 (m, 2 H, 2 3-CH), 3.87 (d, *J* = 7.1 Hz, 1 H, CHCO), 3.95 (d, *J* = 7.0 Hz, 1 H, CHCO). − MS (70 eV); *m*/*z* (%): 254 [M$^+$], 211, 138, 81, 68, 57, 55, 43 (100). − $C_{14}H_{22}O_4$ (254.32): calcd. C 66.11, H 8.72; found C 66.09, H 8.70.

Ethyl 3-Oxo-2-(3-oxocyclopentyl)-3-phenylpropionate (3dc): Colorless oil consisted of two diastereomers (**A/B** = 55:45 by ^{1}H NMR), which were equilibrating and, thus, could not be separated, 94% yield. − IR (film): $\tilde{\nu}$ = 3063 cm^{-1}, 1732, 1685, 1596. − ^{1}H NMR: δ = 1.12 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.16 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.31−1.82 (m, 2 H), 1.90−2.35 (m, 6H), 2.40 (dd, *J* = 11.4 and 4.5 Hz, 4 H, 2 2-CH_2), 2.70−2.88 (m, 2 H, 2 3-CH), 4.10 (q, *J* = 7.0 Hz, 2 H, OCH_2), 4.13 (q, *J* = 7.3 Hz, 2 H, OCH_2), 4.24 (d, *J* = 6.7 Hz, 1 H, CHCO), 4.28 (d, *J* = 5.2 Hz, 1 H, CHCO), 7.39−7.48 (m, 4 H, arom.), 7.51−7.56 (m, 2 H, arom.), 7.91−7.99 (m, 4 H, arom.). − MS (70 eV); *m*/*z* (%): 274 [M$^+$], 229, 201, 178, 123, 105 (100), 77, 65, 51. − $C_{16}H_{18}O_4$ (274.31): calcd. C 70.05, H 6.61; found C 70.01, H 6.59.

4-Benzoyl-5-oxohexanal (3bd): Colorless oil, 88% yield. − IR (film): $\tilde{\nu}$ = 3062 cm^{-1}, 2850, 1721, 1710, 1673, 1596. − ^1H NMR: δ = 2.15 (s, 3 H, 6-CH_3), 2.24−2.39 (m, 2 H, 4-CH_2), 2.53−2.62 (m, 2 H, 5-CH_2), 4.56 (t, *J* = 6.9 Hz, 1 H, 3-CH), 7.46−7.66 (m, 3 H, arom.), 8.01−8.03 (m, 2 H, arom.), 9.76 (s, 1 H, CHO). − MS (70 eV); *m*/*z* (%): 218 [M^+], 189, 158, 120, 105 (100), 96, 77, 65, 51, 43. − $C_{13}H_{14}O_3$ (218.25): calcd. C 71.54, H 6.46; found C 71.52, H 6.43.

***tert*-Butyl 2-Acetyl-5-oxopentanoate (3ed):** Colorless oil, 85% yield. − IR (film): $\tilde{\nu}$ = 2845 cm^{-1}, 1728, 1712. − ^1H NMR: δ = 1.48 [s, 9 H, C(CH_3)$_3$], 1.99−2.08 (m, 2 H, 3-CH_2), 2.13 (s, 3 H, 1′-CH_3), 2.55−2.64 (m, 2 H, 4-CH_2), 3.72 (t, *J* = 7.0 Hz, 1 H, 2-CH), 9.76 (s, 1 H, CHO). − MS (70 eV); *m*/*z* (%): 214 [M^+], 185, 141, 129, 73, 57, 43 (100). − $C_{11}H_{18}O_4$ (214.26): calcd. C 61.66, H 8.46; found C 61.65, H 8.43.

4-Acetyl-5-oxo-3-phenylhexanal (3ae): Colorless oil consisted of two diastereomers (**A/B** = 55:45 by ^1H NMR), which were equilibrating and, thus, could not be separated, 90% yield. − IR (film): $\tilde{\nu}$ = 3038 cm^{-1}, 2818, 1725, 1708, 1604. − ^1H NMR: δ = 1.94 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 2.76−2.79 (m, 2 H, 2-CH_2), 2.86−2.88 (m, 2 H, 2-CH_2), 3.54 (d, *J* = 7.0 Hz, 1 H, 4-CH), 3.59 (d, *J* = 7.1 Hz, 1 H, 4-CH), 4.00−4.08 (m, 2 H, 2 3-CH), 7.15−7.28 (m, 10 H, arom.), 9.65 (s, 1 H, CHO), 9.71 (s, 1 H, CHO). − MS (70 eV); *m*/*z* (%): 232 [M^+], 189, 175, 147, 103, 77, 65, 51, 43 (100), 29. − $C_{14}H_{16}O_3$ (232.28): calcd. C 72.39, H 6.94; found C 72.38, H 6.94.

4-Benzoyl-5-oxo-3-phenylhexanal (3be): Colorless oil consisted of two diastereomers (**A/B** = 53:47 by ^1H NMR), which were equilibrating and, thus, could not be separated, 63% yield. − IR (film): $\tilde{\nu}$ = 3061 cm^{-1}, 2817, 1725, 1690, 1598. − ^1H NMR: δ = 2.00 (s, 3 H, 6-CH_3), 2.03 (s, 3 H, 6-CH_3), 2.79−2.82 (m, 2 H, 2-CH_2), 2.92−2.95 (m, 2 H, 2-CH_2), 3.75 (d, *J* = 7.0 Hz, 1 H, 4-CH), 3.81 (d, *J* = 7.2 Hz, 1 H, 4-CH), 4.15−4.20 (m, 2 H, 2 3-CH), 7.11−7.14 (m, 8 H, arom.), 7.26−7.35 (m, 12 H, arom.), 9.73 (s, 1 H, CHO), 9.81 (s, 1 H, CHO). − MS (70 eV); *m*/*z* (%): 294 [M^+], 251, 239, 197, 191, 105 (100), 103, 77, 51, 43. − $C_{19}H_{18}O_3$: calcd. C 77.53, H 6.16; found C 77.50, H 6.15.

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