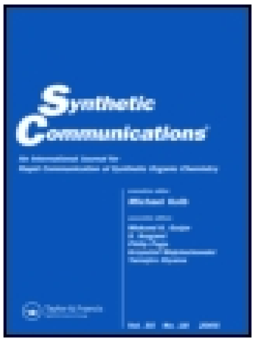

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N, N′-dimethyl formamide (DMF) mediated Vilsmeier–Haack adducts with 1,3,5-triazine compounds as efficient catalysts for the transesterification of β-ketoesters

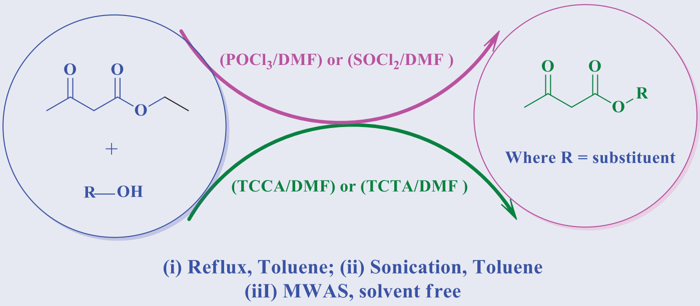
Govardhan Duguta[a,b], Chinna Rajanna Kamatala[a], Satish Kumar Mukka[a], Bhooshan Muddam[a,c], and Yadaiah Chityala[a]

[a]Department of Chemistry, Osmania University, Hyderabad, India; [b]P. G. College, Osmania University, Mirzapur (B), India; [c]Department of Chemistry, M.V.S.R. Engineering College, Hyderabad, India

ABSTRACT

N, N′-dimethyl formamide (DMF) mediated Vilsmeier–Haack (VH) adducts with 1,3,5-triazine compunds such as trichloroisocyanuric acid (TCCA) and trichlorotriazine (TCTA) were prepared by replacing classical oxy chlorides $POCl_3$, and $SOCl_2$, which were explored as efficient catalysts for the transesterification of β-ketoesters. The prepared (TCCA/DMF) and (TCTA/DMF) adducts improved greenery of the classical Vilsmeier–Haack reagents ($POCl_3$/DMF), and ($SOCl_2$/DMF), and demonstrated their better efficient catalytic ativity. Reaction times were in the range: 3.5 to 6.5 hr ($SOCl_2$/DMF); 2.8–5.2 hr ($POCl_3$/DMF); 2.5–5.2 hr (TCCA/DMF) and 2.5–5.0 hr (TCTA/DMF) catalytic systems. Ultrasonically (US) assisted protocols with these reagents further reduced the reaction times (two to three times), while microwave assisted (MW) protocols with these reagents were much more effective. The reactions could be completed in only few seconds (less than a minute) in MWassisted protocols as compared to US assited reactions, followed by good product yields.

GRAPHICAL ABSTRACT



Scheme: VH Reagents as catalysts for transesterification of beta keto esters

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KEYWORDS
β-Ketoesters; oxychloride/DMF adducts; rate enhancements; symmetric triazine/DMF adducts; transesterification

CONTACT Chinna Rajanna Kamatala kcrajannaou@yahoo.com Department of Chemistry, Osmania University, Hyderabad 500007, India.

Supplemental data for this article can be accessed on the publisher's website.

Introduction

Triazine compounds (1,3,5-triazine compounds) are special class of heterocyclic compounds which are known since two centuries which find their use in synthetic organic chemistry with a special emphasis in pharmaceutical, textile, plastic, and industrial applications. Besides, these compounds are also used as pesticides, dyestuffs, optical bleaches, explosives, and surface active agents.[1–6] Among several symmetric triazine derivatives, cyanuric chloride (2.4.6-trichloro 1,3,5-triazine or TCTA)), and trichloro isocyanuric acid (TCCA) received up surging attention in synthetic organic chemistry (Chart-I), because they are economically cheap, environmentally safe, easily available and easy to handle.[7–10]

The field of organic synthesis is a boon to human society, which provided several millions of useful compounds from lifesaving drugs to industrially important and day-to-day useful items. Transesterification is one of the most important chemical transformations, which converts one organic ester ($ROOR^1$) into another ester ($ROOR^2$) in the presence of alcohol (R2OH). In addition, β-ketoesters are multicoupling agents with nucleophilic carbon, and electrophilic carbonyl moiety, which makes them as valuable synthetic tools for the preparation of complex organic molecules. This methodology is useful to achieve medicinally important pharmaceuticals, and polyesters used in textile industry. But, transesterification of β-ketoesters is a highly sluggish reaction which demands large amounts of ketoester and high boiling alcohols for effective transestericaton. In view of this reaction required an efficient catalyst to accelerate transesterification. A survey of literature revealed that several Brønsted acids, Lewis acids, Lewis bases, enzymes, and metal ions used as efficient catalysts[11–20] to achieve transesterification. Recently, our research group also explored economically cheap Mn(II)salts, Cs(I) carbonate, and Prussian blue as catalysts for chemoselective transesterification of β-ketoesters.[20]

On the other hand, since 1927, Vilsmeier–Haack (VH) reagents such as ($POCl_3$/DMF, $SOCl_2$/DMF, $POCl_3$/DMA, $SOCl_2$/DMA, $(COCl)_2$/DMF, etc.) have been widely used for a broad spectrum of reactions in organic synthesis.[21–35] These reactions include formylation,[26] acylation,[27,28] chloroformylation,[29] chloroacylation,[30] benzoylation,[31] bromination,[32] nitration,[33] nitrodecarboxylation,[34] and sulfonation,[35] under specific conditions. But the main difficulty for the preparation of classical VH adducts is the use of hazardous, toxic oxychlorides, which is also difficult to handling. To overcome environmental issues, Paul Anastas and John Warner suggested to adapt twelve (12) green chemistry principles which include prevention of hazardous materials, design of atom economy protocols comprising the use of less hazardous chemicals, catalysts, safer solvents, renewable feed stocks, and non-conventional energy sources to trigger the reactions.[30] Perusal of literature shows excellent papers, reviews, and books on the green chemistry aspects.[36] Encouraged by these aspects several research groups including our group tried to explore easily available, less hazardous and easy handling triazine compounds like cyanuric chloride (2.4.6-trichloro 1,3,5-triazine or TCTA)), and trichloro isocyanuric acid (TCCA) by replacing hazardous and fuming and suffocative oxychlorides for the preparation of VH reagents, which have been employed as efficient reagents/catalysts for formylation,[37] acetylation,[38] chlorodehydration,[39] and nitration[40–43] reactions. In the present study, we want to explore [TCTA/DMF] and

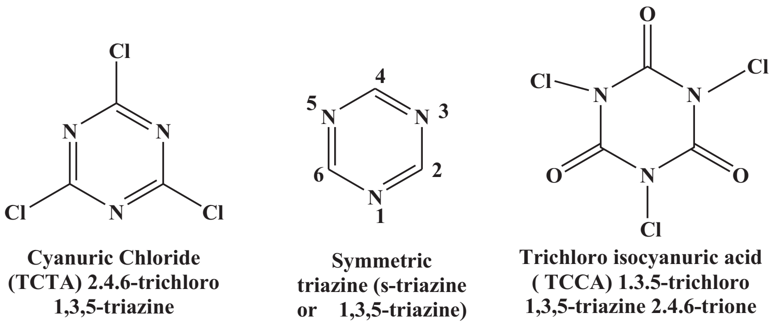


Chart-I. Symmetric triazine compunds.

Table 1. Transesterification of ethyl acetoacetate (β-ketoester) with $C_6H_5CH_2OH$ using different catalysts.

S.N.	Catalyst	R.T (hr)	Yield (%)	Reference
1	$SOCl_2$/DMF	4.5	85	Present work
2	$POCl_3$/DMF	4.0	80	
3	TCCA/DMF	3.5	80	
4	TCTA/DMF	3.0	78	
5	I_2	12.0	90	[44]
6	Zeolite H-FER	8.0	90	[14a]
7	Montmorillonite K-10	3.5	80	[17g]
8	Mn(III) salen complex	8.0	93	[45]
	Vanadyl acetate [V(IV)]	8.0	75	
9	Dealuminated H-β	10	80	[46]
10	Zn/I_2	5.0	66	[15a]
11	$MnSO_4$	18	72	[16a]
	$MnCO_3$	18	75	
12	Prussian blue	19	75	[16b]
13	Cs_2CO_3	18–20	75	[16c]

[TCCA/DMF] adducts for transesterification reactions, and also compare the obtained results with those obtained using classical VH reagents also as catalysts (Scheme-I).

Results and discussion

Initially we have studied transesterification of ethyl acetoacetate (β-ketoester) with $C_6H_5CH_2OH$ using classical VH reagents ($POCl_3$/DMF and $SOCl_2$/DMF), and also modified VH reagents with symmetric triazine (TCCA/DMF and TCTA/DMF) in order to optimize the reaction conditions. Reaction mixture containing ethyl acetoacetate (10 mmol), $C_6H_5CH_2OH$ (10 mmol) and one millimolar (1.0 mmol) catalyst ($POCl_3$/DMF, $SOCl_2$/DMF, TCCA/DMF and TCTA/DMF) in about 20 mL solvent (toluene) were taken in a clean round bottomed flask, and continuously stirred under reflux at about 60–70 °C temperature range. Thin layer chromatographic (TLC) method was used to monitor progress of the reaction till the completion of reaction. After ascertaining the completion of the reaction with periodic monitoring by TLC, products were isolated and compared with earlier reports.[39–41] Data presented in Table 1 clearly show that classical VH adducts and modified VH adducts with symmetric triazines exhibited better catalytic activity with comparable product yields and comparable with few important catalysts.

Table 2. Transesterification of β-ketoesters using various VH reagents as catalysts.

			Conventional conditions							
			$SOCl_2$/DMF		$POCl_3$/DMF		TCCA/DMF		TCTA/DMF	
Entry	Substrate	Product	Time (hrs	Yield (%)	Time (hr)	Yield (%)	Time (hr)	Yield (%)	Time (hr)	Yield (%)
1	Propane-1-ol	Propyl 3-oxobutanoate	3.5	82	3.5	85	3.0	80	2.5	82
2	Prop-2-en-1-ol	Allyl 3-oxobutanoate	3.5	80	3.2	85	3.0	80	3.0	81
3	Butan-1-ol	Butyl 3-oxobutanoate	3.5	80	2.8	80	2.5	75	2.5	78
4	Propan-2-ol	Isopropyl 3-oxobutanoate	3.5	75	3.2	78	3.5	75	3.0	85
5	2-Methylpropane-		3.6	76	3.5	82	2.5	75	2.5	79
	2-ol	Tert-butyl 3-oxobutanoate								
6	Cyclohexanol	Cyclohexyl 3-oxobutanoate	3.6	80	6.0	79	2.5	80	2.0	76
7	2-Methylpropane-1-ol	Isobutyl 3-oxobutanoate 2-Isopropyl-	4.0	8.0	5.0	85	4.5	80	4.0	78
8	2-Isopropyl-5-methylcyclohexanol	5-methyl Cyclohexyl 3-oxobutanoate	4.4	85	4.2	80	4.0	80	3.5	76
9	Phenyl methanol	Benzyl 3-oxoutanoate	4.5	85	4.0	80	3.5	80	3.0	78
10	*(E)*-3-Phenylprop-2-en-1-ol	Cinnamyl 3-oxobutanoate	4.5	78	4.5	81	4.0	82	4.0	83
11	p-Cresol	p-Tolyl 3-oxobutanoate								
12	Phenol		4.6	81	4.2	83	4.0	83	3.8	85
13	4-Cholrophenol	Phenyl 3-oxobutanoate	4.8	75	4.5	82	4.2	80	4.0	81
		4-Chlorophenyl 3-oxobutanoate	5.8	80	4.5	78	3.8	85	4.2	82
14	Furan-2-yl methanol	Furan-2-ylmethyl 3-oxobutanoate	5.5	87	5.5	75	4.5	80	3.9	79
15	Quinolin-8-ol	Quinolin -8-yl 3-oxobutanoate	5.2	75	5.2	80	5.0	75	5.0	82
16	7-Hydroxy-2H-chromen-2-one	2-Oxo-2H-chromen-7-yl 3-oxobutanoate	5.0	85	4.5	75	4.5	79	4.0	84
17	4-Hydroxy-2H-chromen-2-one	2-Oxo-2H-chromen-4-yl	5.0	80	5.0	80	4.2	78	4.0	81
18	Naphthalen-2-ol	3-oxobutanoate Naphthalen-2-yl 3-oxobutanoate	6.0	85	5.0	80	4.8	8.3	4.5	85
19	Naphthalen-1-ol	Naphthalen-1-yl 3-oxobutanoate	6.5	79	5.5	80	5.2	83	5.0	85

*Products are purified by column chromatography.

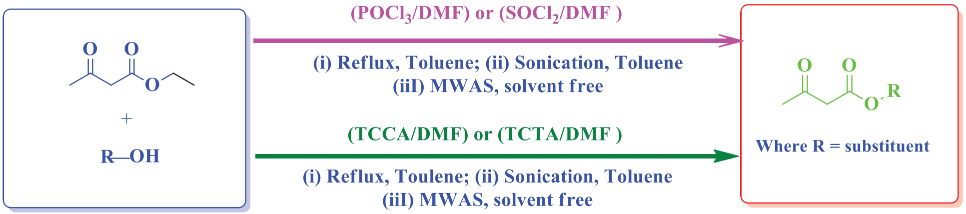
In view of this, we have taken up detailed study of transesterification of ethyl acetoacetate (β-ketoester) with different hydroxy compounds, which are presented in Table 2.

Reaction times were in the range: 3.5–6.5 hr ($SOCl_2$/DMF); 2.8–5.2 hr ($POCl_3$/DMF); 2.5–5.2 hr (TCCA/DMF) and 2.5–5.0 hr (TCTA/DMF) catalytic systems followed by very good product yields respectively. These trends further point out that VH reagents prepared from symmetric triazines and DMF (TCCA/DMF and TCTA/DMF) are promising catalysts, which not only improved greenery of the reactions (by avoiding the use of toxic and hazardous oxychlorides) in the preparation of VH reagents. In order to through light into the mechanism of reactions we need to consider the active species of catalyst. In large numbers of publications,[22–29] it has been earlier suggested that either "chloromethyleniminium cation $[(CH_3)_2N=C(R)Cl]^+$," and dipolar oxychloride active intermediate ($[(CH_3)_2N=C(R)Cl]^+[PO_2Cl_2]^-$ in case of ($DMF/POCl_3$) and ($[(CH_3)_2N=C(R)Cl]^+[SO_2Cl]^-$ in case of ($DMF/SOCl_2$) respectively) are active species, which are formed in situ during the course of reaction. Similar types of dipolar species ($[(CH_3)_2N=C(R)\ Cl]^+\ [TCCA]^-$or $[(CH_3)_2N=C(R)\ Cl]^+\ [TCTA]^-$) were considered by us when [TCTA–DMF] or [TCCA–DMF] were used as modified VH adducts.[37–40] These contentions were supported by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopic results obtained under different conditions. On the basis of the foregoing discussions, we feel that mechanism of transesterification proceeds through two steps.

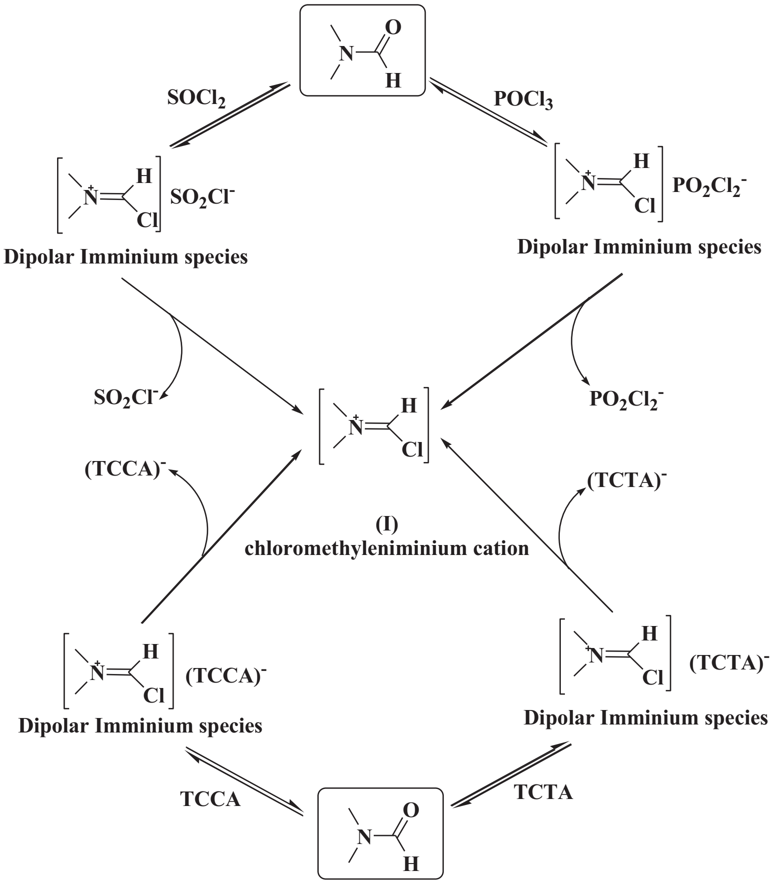
Scheme-II depicts the steps involved in the formation of "chloromethyleniminium cation" in ($DMF/POCl_3$), ($DMF/SOCl_2$), (TCTA/DMF) and (TCCA–DMF), while the Scheme-III elaborates "chloromethyleniminium cation" mediated transesterification of β-ketoester by alcohol (ROH). Chloromethyleniminium cation **($[(CH_3)_2N=C(H)Cl]^+$ or (I))** formed here in Scheme-II further interacts with alcohol (R–OH) in the first step to give transient species (TST-I), which in turn liberates HCl and also affords intermediate alkoxymethyleniminium cation species (II). In a further step, *in situ* liberated HCl most plausibly reacts with ethyl acetoacetate (β-ketoester) to give a transient dipolar species (III). Finally, a fast rearrangement step, the reaction between two intermediate species (II) and (III) afford end product (IV) as elaborated in Scheme-III.

An array of alcohols was chosen in this reaction. It is interesting to note that the nature and size of the alcohol involved in the reaction significantly affects the rate of transesterification. Simple aliphatic alcohols with high nucleophilicity generally facilitate transesterification faster than bulkier alcohols. Obtained products are characterized by physical data and spectroscopic results, which agree well with the data presented in our earlier publications, and elsewhere.

Data presented in Table 2 further show that transesterification also depend on the size and nature of alcohol as well as β-ketoester. Simple alcohols facilitate better transesterification with their higher nucleophilicity than bulkier alcohols. Reactions occurred smoothly with primary and sterically less hindered alcohols, while reactions with secondary and tertiary alcohols slowly with relatively longer reaction times and moderate product yields. In order to further improve the greenery of the reactions, we have taken up the transesterification under ultrasonication and microwave irradiation. Obtained results are compiled in Tables 3 and 4.



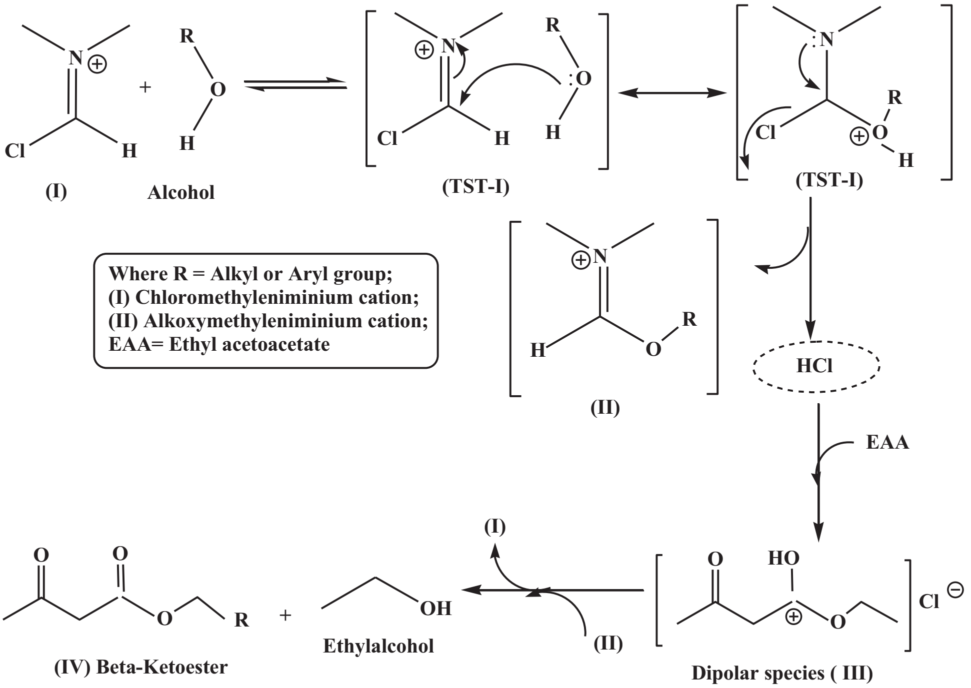
Scheme-I. VH Reagents as catalysts for transesterification of beta keto esters.



Scheme-II. Formation of chloromethyleniminum cation species.

Reaction times in ultrasonic assisted transesterification (USATEST), and microwave assisted transesterification (MWATEST) protocols (Tables 3 and 4) substantially reduced from the reaction times recorded in conventional method as shown below in table:

Among all the studied transesterification protocols, microwave assisted transesterification (MWATEST) protocols exhibited highly noticeable rate accelerations with the reaction times reduced from few hours (in conventional and USATEST) to few seconds, followed by very good yield of products. In ultrasonic assisted transesterification (USATEST), protocols also, the reaction times reduced two to three times as compared to conventional methods. Accelerating rates in ultrasonic assisted transesterification



Scheme-III. Transesterification of b-Ketoesters with R-OH using Iminium on species as catalyst.

reactions could be attributed to the larger fraction of molecules getting activated by absorbing the "cavitation energy" released due to the collapse of "cavitation bubbles". When ultrasound waves are propagated through the reaction mixture small cavitation bubbles are formed initially, which gradually increase in size and collapse when the size of the bubble unassumingly larger.[47–49] On the other hand, enormous microwave catalysis could be explained due to the bulk activation of molecules which is due to the rapid super heating of all reactant species, polar solvents and pressure effects.[50,51] We have done microwave assisted (MWA) transesterification experiments without using 500 mg of silica gel. We noticed about 4–5% decrease in the product yield. There is not much difference in the reaction time.

Conclusion

In this part of the study we have synthesized modified VH adducts with symmetric triazine (1,3,5-triazine) compounds such as trichloroisocyanuric acid (TCCA) and trichlorotriazine (TCTA) along with DMF (TCCA/DMF, and TCTA/DMF), which are used as green catalysts for efficient transesterification of β-ketoesters with different alcohols. The developed green Vilsmeier–Haack adducts such as (TCCA/DMF), and (TCTA/DMF)] are found superior over classical VH reagents ($POCl_3$/DMF), and ($SOCl_2$/DMF) in terms of easy handling and environmentally safety. Observed reaction times were in the range: 3.5–6.5 hr ($SOCl_2$/DMF);2.8–5.2 hr ($POCl_3$/DMF); 2.5–5.2 hr (TCCA/DMF) and 2.5–5.0 hr (TCTA/DMF) catalytic systems. These reaction times were further reduced by two to three times under ultrasonication, while microwave assisted protocols

Table 3. Ultrasonic Assisted Transesterification (USTEST) of *β*-ketoesters using VH reagents as catalysts.

			Ultrasonic Assisted Transesterification							
			$SOCl_2$/DMF		$POCl_3$/DMF		TCCA/DMF		TCTA/DMF	
Entry	Substrate	Product	Time (hr)	Yield (%)	Time (hr)	Yield (%)	Time (hr)	Yield (%)	Time (hr)	Yield (%)
1	Propane-1-ol	Propyl 3-oxobutanoate	1.2	79	1.0	81	1.0	82	0.9	84
2	Prop-2-en-1-ol	Allyl 3-oxobutanoate	1.5	80	1.0	82	1.0	83	1.0	85
3	Butan-1-ol	Butyl 3-oxobutanoate	1.8	78	1.5	80	1.5	82	1.2	82
4	Propan-2-ol	Isopropyl 3-oxobutanoate	1.5	75	1.0	78	1.0	79	0.8	86
5	2-Methylpropane-2-ol	Tert-butyl 3-oxobutanoate	1.8	78	1.5	82	1.5	84	1.2	85
6	Cyclohexanol	Cyclohexyl 3-oxobutanoate	2.0	80	1.5	82	1.2	82	1.0	85
7	2-methylpropane-1-ol	Isobutyl 3-oxobutanoate	1.8	78	1.6	80	1.5	80	1.2	81
8	2-Isopropyl-5-methylcyclohexanol	2-Isopropyl-5-methylcyclohexyl-3-oxobutanoate	2.2	79	2.0	80	2.0	82	1.5	83
9	Phenyl methanol	Benzyl 3-oxoutanoate	1.5	80	2.0	80	1.0	82	1.0	86
10	*(E)*-3-Phenylprop-2-en-1-ol	Cinnamyl 3-oxobutanoate	2.5	80	2.0	82	2.0	85	1.5	87
11	p-Cresol	p-tolyl 3-oxobutanoate	1.6	81	1.5	82	1.5	85	1.0	86
12	Phenol	Phenyl 3-oxobutanoate	1.5	78	1.5	80	1.0	82	1.0	84
13	4-Cholrophenol	4-Chlorophenyl 3-oxobutanoate	2.0	80	1.5	82	1.5	82	1.3	85
14	Furan-2-yl methanol	Furan-2-ylmethyl 3-oxobutanoate	2.0	81	1.8	84	1.5	85	1.2	87
15	Quinolin-8-ol	Quinolin -8-yl 3-oxobutanoate	2.2	79	2.0	80	1.5	82	1.3	83
16	7-Hydroxy-2H-chromen-2-one	2-Oxo-2H-chromen-7-yl 3-oxobutanoate	2.4	81	2.2	83	2.0	85	1.8	85
17	4-Hydroxy-2H-chromen-2-one	2-Oxo-2H-chromen-4-yl 3-oxobutanoate	2.5	81	2.2	82	2.0	84	1.3	84
18	Naphthalen-2-ol	Naphthalen-2-yl 3-oxobutanoate	2.0	82	1.8	82	1.5	83	1.5	85
19	Naphthalen-1-ol	Naphthalen-1-yl 3-oxobutanoate	2.2	78	2.0	80	1.8	81	1.6	84

*Products are purified by column chromatography.

dramatically reduced the reaction times from few hours to only few seconds (less than a minute) followed by very good product yields. The developed methods allowed rapid access to diverse esters (–OR) without using large excess of the corresponding alcohol (often as a solvent). The compounds TCCA, TCTA and DMF used for catalysts are inexpensive, operationally simple laboratory desktop chemicals.

Experimental

Chemicals used in this study are obtained from laboratory desk, which are supplied by SD, Loba, and Finar Chemicals (India). Sonicator bath with a frequency of 33 kHz and 100 W electric power rating (Optics Technology, Shakurpur, Delhi) for ultrasonically assisted reactions, and “Bench mate” model Micro-wave oven (CEM-908010, 300 W) for microwave assisted reactions were used in this study. Classical Vilsmeier Haack reagents

Table 4. Microwave Assisted Transesterification (MWTEST) of β-ketoesters using VH reagents as catalysts.

			Microwave Assisted Transesterification							
			$SOCl_2$/DMF		$POCl_3$/DMF		TCCA/DMF		TCTA/DMF	
Entry	Substrate	Product*	Time (sec)	Yield (%)	Time (sec)	Yield (%)	Time (sec)	Yield (%)	Time (sec)	Yield (%)
1	Propane-1-ol	Propyl 3-oxobutanoate	45	79	40	80	36	82	30	83
2	Prop-2-en-1-ol	Allyl 3-oxobutanoate	48	81	40	83	38	85	35	87
3	Butan-1-ol	Butyl 3-oxobutanoate	45	78	40	81	35	81	32	82
4	Propan-2-ol	Isopropyl 3-oxobutanoate	55	77	50	79	45	80	42	83
5	2-Methylpropane-2-ol	Tert-butyl 3-oxobutanoate	46	80	42	82	40	83	35	85
6	Cyclohexanol	Cyclohexyl 3-oxobutanoate	55	81	52	83	50	84	45	87
7	2-methylpropane-1-ol	Isobutyl 3-oxobutanoate	48	79	45	80	45	81	40	82
8	2-Isopropyl-5-methylcyclohexanol	2-Isopropyl-5-methylcyclohexyl-3-oxobutanoate	46	79	45	79	42	83	40	84
9	Phenyl methanol	Benzyl 3-oxoutanoate	50	80	50	80	45	82	45	82
10	*(E)*-3-Phenylprop-2-en-1-ol	Cinnamyl 3-oxobutanoate	55	81	55	82	50	86	45	87
11	p-Cresol	p-tolyl 3-oxobutanoate	50	78	50	80	45	82	42	82
12	Phenol	Phenyl 3-oxobutanoate	55	79	50	82	50	83	40	85
13	4-cholrophenol	4-Chlorophenyl 3-oxobutanoate	58	80	55	81	50	82	45	84
14	Furan-2-yl methanol	Furan-2-ylmethyl 3-oxobutanoate	45	80	45	82	40	83	40	86
15	Quinolin-8-ol	Quinolin-8-yl 3-oxobutanoate	55	78	55	79	50	84	45	88
16	7-Hydroxy-2H-chromen-2-one	2-Oxo-2H-chromen-7-yl 3-oxobutanoate	50	81	50	82	45	85	40	86
17	4-Hydroxy-2H-chromen-2-one	2-Oxo-2H-chromen-4-yl 3-oxobutanoate	50	83	50	85	45	85	40	89
18	Naphthalen-2-ol	Naphthalen-2-yl 3-oxobutanoate	50	78	50	80	45	84	40	86
19	Naphthalen-1-ol	Naphthalen-1-yl 3-oxobutanoate	50	79	50	82	48	86	40	89

*Products are purified by column chromatography.

(DMF/$POCl_3$, and DMF/$SOCl_2$) were prepared as detailed in earlier publications,[21–29] while modified Vilsmeier Haack reagents (DMF/TCCA, and DMF/TCTA) were synthesized according to the suggested methods given in our recent publications.[35–40]

General procedure for transesterification under conventional method

Ethyl acetoacetate (10 mmol), $C_6H_5CH_2OH$ (10 mmol) and one millimolar (1.0 mmol) catalyst ($POCl_3$/DMF, $SOCl_2$/DMF, TCCA/DMF and TCTA/DMF) were suspended in a round bottomed flask containing 20 mL solvent (toluene), and stirred continuously at room temperature till the completion of reaction. Progress and completion of the reaction was monitored by thin layer chromatographic (TLC) method. After completion, reaction mixture was treated with sodium bicarbonate solution followed by ethylacetate or ether. Organic layer was then separated, dried over sodium sulfate (Na_2SO_4) and purified with column on silica gel (ethyl acetate: petroleum ether) to afford the ester as a viscous liquid in very good yields.

For instance, 2-hydroxyphenyl-3-oxobutanoate is obtained from the transesterification ethylacetoacetate(1.4 ml, 11 mmol), by 2-hydroxyphenol (1.2 g, 11 mmol), VHR [TCCA (0.23 g, 1 mmol), TCTA (0.18 g, 1 mmol), $SOCl_2$ (0.7 ml, 10 mmol), $POCl_3$ (0.9 ml, 10 mmol), DMF (0.39 ml, 5 mmol). Yield: Given in Tables 1–3. 1H NMR ($CDCl_{3,}$ 400 MHz) δ 7.32–7.30 (d, $J = 8.0$ Hz, 2H, Ar-H), 6.59 (s, 1H, -Ar-H), 6.01 (s, 1H, -Ar-H), 3.93 (s, 2H, -CH_2), 3.35 (s, 3H, –$COCH_3$). 13 C NMR ($CDCl_{3,}$ 101.6 MHz) (δ ppm) 165.8, 162.7, 160.4, 151.4, 144.7, 127.0, 126.8, 125.9, 41.6, 34.0. LCMS: *m/z* calcd for $C_{10}H_{10}O_4$ (M^++1): 195.15. Anal calcd for $C_{10}H_{10}O_4$ (in %): C-61.9; H-5.2. Found: C-61.7; H-5.0.

In another case, p-tolyl-3-oxobutanoate is obtained as the product from the transesterification of ethyl acetoacetate (1.4 ml, 11 mmol), p-Cresol (1.2 g, 11 mmol), VHR [TCCA (0.23 g, 1 mmol), TCTA (0.18 g, 1 mmol), $SOCl_2$ (0.7 ml, 10 mmol), $POCl_3$ (0.9 ml, 10 mmol), DMF (0.39 ml, 5 mmol). Yield: Given in Tables 1–3. 1H NMR ($CDCl_{3,}$ 400 MHz) δ 7.74–7.72 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.44–7.42 (d, $J = 8.0$ Hz, 2H, Ar-H), 4.02 (s, 2H, -CH_2), 3.44 (s, 3H, Ar-CH_3), 3.02 (s, 3H, –$COCH_3$). 13 C NMR ($CDCl_{3,}$ 101.6 MHz) (δ ppm) 166.4, 161.8, 150.7, 144.5, 129.2, 128.1, 41.5, 34.0, 28.5. LCMS: *m/z* calcd for $C_{11}H_{12}O_3$ (M^+ +1): 193.00. Anal calcd for $C_{11}H_{12}O_3$ (in %): C-68.7; H-6.3. Found: C-68.6; H-6.2.

General procedure for ultrasonically assisted transesterification

In ultrasonically assisted transesterification (USATEST), a flask containing mixture of β-ketoesters (0.1 mol), alcohol (0.1 mol) and catalysts (0.01 mol) in toluene (20 mL) was placed in a Sonicator bath with a frequency of 33 kHz and 100 W electric power rating (Optics Technology, Shakurpur, Delhi) and stirred at room temperature and the progress of the reaction was monitored by thin layer chromatography (TLC) till completion of the reaction. After a similar workup procedure to obtain final product as discussed above.

General procedure for microwave assisted (MWA) transesterification (MWATEST) under solvent free conditions

Reaction mixture containing β-ketoesters (0.1 mol), alcohol (0.1 mol), catalyst (0.01 mol) along with 500 mg of silica gel were mixed thoroughly in a microwave reaction vial and placed in a beaker containing silica gel powder. The beaker was then placed in a laboratory microwave oven (CEM-908010, benchmate model 300 W laboratory microwave reactor) till the reaction is completed as ascertained by TLC. The reaction mixture (contents of the test tube) was treated with sequentially with aqueous sodium bicarbonate and ethyl acetate. SiO_2 gets precipitated in aqueous layer, while the end product is extracted in organic layer. After a regular work-up final product could be obtained.

Elemental analysis, and spectroscopic (^{1}H NMR, ^{13}C NMR, and mass) data of certain isolated products for this article can be accessed on the publisher's website..

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Disclosure statement

Authors declare that they do not have any conflict of interest.

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