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Solvent-Free Alkylation of 1,3-Dicarbonyl Compounds with Benzylic, Propargylic and Allylic Alcohols Catalyzed by $La(NO_3)_3 \cdot 6H_2O$

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An efficient and solvent free method for benzylation, propargylation and allylation of 1,3-dicarbonyl compounds with alcohols has been developed by using $La(NO_3)_3 \cdot 6H_2O$ as water tolerable catalyst. The reaction was shown to proceed smoothly for various 1,3-dicarbonyl compounds with benzylic, propargylic and allylic alcohols including 1^0 allylic alcohols, without any solvent, providing a clean access to the desired products in short reaction times with good to excellent yields and high selectivity.

Keywords: Solvent-free, Benzylic, Propargylic, Allylic alcohols, 1,3-Dicarbonyl, Alkylation, $La(NO_3)_3 \cdot 6H_2O$.

INTRODUCTION

The formation of carbon-carbon bonds is among the most important concerns in modern organic chemistry [1,2]. The benzylation of 1,3-dicarbonyl derivatives leads to the generation of many bioactive structural motifs such as warfarine (oral coagulant), reglitazar (diabetes drug) and tipranavir (HIV protease inhibitor) being representative examples [3,4]. Propargylation of 1,3-dicarbonyl derivatives provides access to valuable synthetic internmediates and heterocycles such as furans and pyrroles [5]. Similarly, allylic alkylations of 1,3-dicarbonyl compounds are an important type of carbon-carbon bond formation reaction that provide a convenient strategy for the construction of complex molecular structures from simple building blocks [6].

The standard protocol for the alkylation of 1,3-dicarbonyl compounds usually requires the usage of a stoichiometric amount of base and organic halide as alkylating agent which would generate undesirable by-products and decrease the atom economy [7,8]. Synthetic approach aiming at environmentally benign chemistry eliminates the formation of by-products, to afford high atom-efficient chemical process [9-11]. Although, the use of alcohols instead of halides and acetate compounds as electrophiles is an ideal method because it prevents waste salt formations, catalytic substitution of the hydroxyl group in alcohols is difficult to their poor leaving ability, which requires equimolar or greater amounts of reagents or promoter to enhance the leaving ability of the hydroxy group. Subsequently, transition metal based reagents such as palladium in the presence of an acid or a base and stoichiometric amount of cobalt salts have been reported for direct alkylation of 1,3-dicarbonyl with alcohols [12,13]. Recently, several acid catalysts such as $BF_3.OEt_2$, $FeCl_3$, $InCl_3$, $Bi(OTf)_3$, $Yb(OTf)_3$, PTSA, $HClO_4$ and H-montmorillonite have also been reported to catalyze these reactions [14-27].

However, many of these reported methods suffer from one or more disadvantages such as highly polar, volatile and hazardous solvents were used, most of them explained only the reactions of 2^0 alcohols with 1,3-dicarbonyl compounds, low selectivity, expensive reagents, long reaction time, difficulty in preparation of catalysts, strong acidic conditions, inert conditions. Therefore, we sought to develop a more efficient and convenient method for alkylation of 1,3-dicarbonyl compounds with alcohols, which avoids most of these drawbacks. Therefore, three types of alkylation reactions such as benzylation, propargylation and allylation including 1^0 allylic alcohols with 1,3-dicarbonyl compounds using mild and inexpensive catalyst and avoiding usage of toxic or volatile organic solvent in an environmentally benign process is highly desirable.

In recent years, solvent-free reactions have been paid more attention, often providing clean, efficient and high yielding

organic process in modern synthetic chemistry. On the other hand, organic reactions using a water tolerant catalyst also received more attention in recent years, as they can be handled conveniently and removed from the reaction mixture, making the experimental procedure simple and eco-friendly [28-31]. Furthermore, $La(NO_3)_3{\cdot}6H_2O$ is less expensive, commercially available catalyst. Recently, $La(NO_3)_3{\cdot}6H_2O$ as a mild and an efficient catalyst was explored in various organic transformations [32,33]. To our best of knowledge, there has been no protocol for the alkylation of 1,3-dicarbonyl compounds with benzylic, propargylic and allylic alcohols under solvent-free conditions using mild Lewis acid such as $La(NO_3)_3{\cdot}6H_2O$.

As part of our continuous interest in developing novel routes for C-C and C-hetero bond formations [4,34-37], here in we demonstrate a clean and convenient alkylation reaction of 1,3-dicarbonyl compound with benzylic, propargylic and allylic alcohols catalyzed by $La(NO_3)_3{\cdot}6H_2O$ without any solvent. The reaction proceeded expediently for wide variety of starting materials to afford excellent yields.

EXPERIMENTAL

All commercial reagents were used without purification and all solvents were reagent grade. IR spectra were recorded on a Perkin-Elmer FT/IR-240 C spectrophotometer with KBr optics. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer 300 MHz. IR spectra were recorded on Nicolet Fourier Transform spectrometer. Mass spectra were obtained on a 7070H or VG Autospec Mass spectrometer. Thin-layer chromatography (TLC) was performed on GF-25U (Anal. Tech) plates and silica gel glass-backed plates. Routine column chromatography was conducted using silica gel 100-200 mesh.

A mixture of 1,3-dicarbonyl compound **1** (0.75 mmol), alcohol **2** (0.50 mmol) and $La(NO_3)_3{\cdot}6H_2O$ (5 mg) was allowed to heat at 90 °C for the indicated time (Table-2). After completion of the reaction as noticed by TLC, the reaction mixture was cooled to room temperature and diluted with water (5 mL) and extracted into ethyl acetate (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get crude product, which was purified on silica gel column chromatography using hexane and ethyl acetate as eluent to give the pure product **3**.

Spectral data for selected compounds

3-(1-Phenylethyl)pentane-2,4-dione (3a): m.p.: 38-40 °C; IR (KBr, ν_{max}, cm^{-1}): 3063, 2968, 2877, 1721, 1702, 1494, 1453, 1421, 1358, 1267, 1188, 1157, 1083, 952, 863, 762, 702, 680; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.17 (5H, m), 4.04 (1H, d, *J* = 11.3 Hz), 3.64-3.51 (1H, m), 2.24 (3H, s), 1.80 (3H, s), 1.20 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.4, 203.3, 142.9, 128.7, 127.2, 126.9, 76.6, 40.3, 29.7, 29.6, 20.8; MS (ESI-) *m/z*: 227 [M + Na]$^+$; HRMS (ESI) *m/z* calcd for $C_{13}H_{16}O_2Na$: 227.1043, found: 227.1048.

1,3-Diphenyl-2-(1-phenylethyl)propane-1,3-dione (3b): m.p.: 129-131 °C; IR (KBr, ν_{max}, cm^{-1}): 3052, 3021, 2956, 1702, 1586, 1453, 1294, 1267, 1210, 1187, 993, 750, 702, 685; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* = 7.2 Hz), 7.72 (2H, d, *J* = 7.5 Hz), 7.55-6.99 (11H, m), 5.56 (1H, d, *J* = 10.1 Hz), 4.12-3.99 (1H, m), 1.33 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6, 194.3, 143.7, 137.1, 133.5, 132.9, 128.7, 128.4, 128.3, 127.6, 126.5, 64.8, 41.1, 20.1; MS (ESI-) *m/z*: 351 [M + Na]$^+$.

1,3-Diphenyl-2-(1-phenylpropyl)propane-1,3-dione (3d): mp 154-156 °C; IR (KBr, ν_{max}, cm^{-1}): 3061, 2959, 2870, 1684, 1593, 1447, 1270, 1190, 1021, 962, 840, 760, 684, 598; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08-8.02 (m, 2H), 7.74-7.67 (m, 2H), 7.57-7.06 (m, 11H), 5.49 (d, 1H, *J* = 10.5 Hz), 3.85-3.76 (m, 1H), 1.83-1.55 (m, 2H), 0.71 (t, 3H, *J* = 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.9, 27.0, 29.7, 48.7, 64.6, 126.6, 128.2, 128.3, 128.4, 128.6, 128.8, 132.8, 133.5, 137.0, 137.4, 141.2, 194.3, 195.1; MS (ESI) *m/z*: 365 (M+Na).

Ethyl-2-diphenylmethyl-3-oxobutanoate (3e): m.p.: 88-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.15 (m, 8H), 7.14-7.12 (m, 2H), 4.74 (d, *J* = 12.4 Hz, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 3.96 (q, *J* = 14, 7.2 Hz, 2H), 2.10 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.6, 167.5, 141.5, 141.2, 128.9, 128.7, 127.8, 127.7, 126.8, 126.7, 65.1, 61.4, 50.7, 29.9, 13.6; MS (ESI-) *m/z*: 319 [M + Na]$^+$.

3-(Diphenylmethyl)pentane-2,4-dione (3f): m.p.: 93-95 °C; IR (KBr, ν_{max}, cm^{-1}): 1693; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.28 (m, 10H), 4.81 (d, *J* = 12 Hz, 1H), 4.76 (d, *J* = 12 H, 1H), 1.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.5, 141.0, 128.7, 127.6, 126.8, 74.1, 50.9, 29.5; MS (ESI-) *m/z*: 289 [M + Na]$^+$.

2-[1-(4-Methoxy phenyl)ethyl]-1,3-diphenylpropane-1,3-dione (3g): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.40-7.45 (m, 1H), 7.28-7.35 (m, 3H), 7.15-7.19 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 5.51 (d, *J* = 10 Hz,1H), 3.98-3.93 (m, 1H), 3.57 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 194.7, 158.2, 137.2, 136.9, 135.8, 133.5, 133.0, 128.84, 128.80, 128.7, 128.5, 128.4, 113.8, 65.1, 55.1, 40.5, 20.4; MS (ESI-) *m/z*: 358 [M + Na]$^+$.

2-[1-(4-Chlorophenyl)ethyl]-1,3-diphenylpropane-1,3-dione (3h): m.p.: 107-109 °C; IR (KBr, ν_{max}, cm^{-1}): 3063, 2930, 2876, 1694, 1664, 1593, 1491, 1448, 1276, 1188, 1097, 984, 830, 761, 691; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* = 7.5 Hz), 7.74 (2H, d, *J* = 7.5 Hz), 7.58-7.08 (10H, m), 5.41 (1H, d, *J* = 9.8 Hz), 4.11-3.99 (1H, m), 1.30 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6, 194.3, 142.3, 136.9, 136.6, 133.6, 133.2, 132.2, 129.0, 128.8, 128.7, 128.5, 128.4, 64.7, 40.5, 20.2; MS (ESI-) *m/z*: 385 [M + Na]$^+$.

3-[1-(4-Chlorophenyl)ethyl]pentane-2,4-dione (3i): m.p.: 77-79 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (d, *J* = 6 Hz, 2H), 7.14 (dd, *J* = 6.4, 2 Hz, 2H), 3.99 (d, *J* = 11.6 Hz, 1H), 3.63-3.55 (m, 1H), 2.27 (s, 3H), 1.88 (s, 3H); 1.20 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.7, 202.6, 141.5, 132.5, 128.7, 128.5, 76.4, 39.6, 29.6, 29.4, 20.5; MS (ESI-) *m/z*: 261 [M + Na]$^+$.

Ethyl 3-oxo-2-(1-phenylethyl)butanoate, diastereomer mixture (3j): IR (Neat, ν_{max}, cm^{-1}): 1717, 1745; ^{1}H NMR (300 MHz, $CDCl_3$): δ Diasteromixture (1:1 approx.) 7.31-7.26 (m, 4H), 7.23-7.18 (m, 6H), 4.22 (q, *J* = 7 Hz, 2H), 3.87 (q, *J* = 7 Hz, 2H), 3.79 (d, *J* = 11 Hz, 2H), 3.74 (d, *J* = 11 Hz, 2H), 3.58-3.50 (m, 2H), 2.29 (s, 3H), 1.92 (s, 3H), 1.29 (d, *J* = 7 Hz, 3H), 1.28 (t, *J* = 7 Hz, 3H), 1.24 (d, *J* = 7 Hz, 3H), 0.95 (t,

J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ Diasteromixture (1:1 approx.) 202.31, 168.45, 168.06, 143.17, 143.01, 128.62, 128.35, 127.36, 127.29, 126.83, 126.74, 67.45, 66.91, 61.40, 61.05, 39.97, 39.71, 29.83, 29.46, 20.49, 20.28, 14.05, 13.65; MS (ESI-) *m/z*: 234 $[M + Na]^+$.

Methyl 2-acetyl-3,5-diphenyl-4-pentynoate (3o): IR (KBr, ν_{max}, cm^{-1}): 3028, 2921, 2851, 1739, 1598, 1490, 1439, 1354, 1280, 1249, 1149, 755. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.25 (m, 10H), 4.60 (d, 1H, *J* = 10.1 Hz), 3.97 (d, 1H, *J* = 10.1 Hz), 3.81 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.0, 35.1, 75.5, 84.8, 85.4, 126.6, 127.7, 128.2, 128.3, 128.6, 128.8, 131.6, 138.1, 201.5; MS (ESI-) *m/z*: (M+Na) 329.

3-(1,3-Diphenyl-2-propenyl)pentane-2,4-dione (3p): IR (Neat, ν_{max}, cm^{-1}): 1724 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.20 (m, 10H), 6.43 (d, *J* = 15.8 hz, 1H), 6.20 (ddd, *J* = 15.8, 5.6, 2.8 Hz, 1H), 4.34 (d, *J* = 2.7 Hz, 1H), 4.32 (d, *J* = 5.6 Hz, 1H), 2.25 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.8, 202.7, 140.0, 136.5, 131.6, 129.21, 129.01, 128.50, 127.90, 127.70, 127.24, 126.33, 74.51, 49.13, 30.01, 29.72; MS (ESI-) *m/z*: 315 $[M + Na]^+$.

RESULTS AND DISCUSSION

Initial studies were conducted using acetyl acetone and 1-phenylethanol as a proto type reaction, various reaction conditions of this transformation were extensively investigated with the results summarized in Table-1.

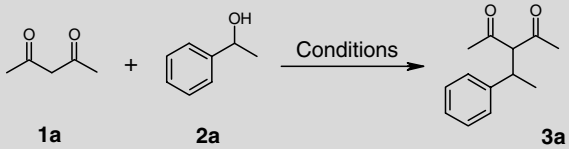
The reaction was examined by using various solvents to facilitate this transformation. When the reaction was performed in toluene, benzene, acetonitrile and tetrahydrofuran afforded the product only in moderate yield (Table-1, entries 1-4). However, the corresponding product was obtained in high yield, when nitromethane, dichloromethane, dichloroethane was used as a solvent (Table-1, entries 5-7). The $La(NO_3)_3 \cdot 6H_2O$ catalyzed solvent-free reaction at 28 °C only afforded the trace product (Table-1, entry 8), elevating the reaction temperature increased the yields obviously (Table-1, entry 9-11). The best result was achieved, when the $La(NO_3)_3 \cdot 6H_2O$ catalyzed reaction was performed under neat condition at 90 °C, it proceeded rapidly and afforded the desired product in excellent yield (94 %) within 0.5 h (Table-1, entry 11), however no product was observed in the absence of $La(NO_3)_3 \cdot 6H_2O$ even after 12 h of long reaction time and conducted in different solvent mediums such as PEG-400, DCE and [TPA][L-Pro] IL (tetrapropyl ammonium L-prolinate ionic liquid) (Table-1, entry 12-14).

To define the scope of the reactions catalyzed by $La(NO_3)_3 \cdot 6H_2O$ under solvent-free conditions, we applied this process to various alcohols and 1,3-dicarbinyl compounds. As shown in the Table-2, benzylic alcohols such as 1-phenyl-ethanol, 1-phenylpropanol, diphenylmethanol were reacted efficiently with 1,3-dicarbonyl compounds and afforded the corresponding products in excellent yields within short reaction time (Table-2, entries 1-6). Notably this included the alkylation of less acidic β-ketoester which gave the products in good yield (Table-2, entries 5, 10 and 15), benzylic alcohol with electron donating group in *para* position (Table-2, entry 7) afforded slightly higher yield compared to electron withdrawing group in *para* position (Table-2, entries 8 and 9).

To explore the generality of the reaction condition, we also examined the reactions of 1,3-dicarbonyl compounds with various propargyl alcohols such as 1,3-diphenyl-2-propyn-1-ol, 1-phenyl-2-heptyn-1-ol, reactions were proceeded well and gave the respective products in excellent yield (Table-2, entries 11-15).

Allylation of 1,3-dicarbonyl compounds with various allylic alcohols also afforded the products in excellent yields. Reaction of cinnamyl alcohol with dibenzoylmethane furnishes the corresponding product (Table-2, entry 17) in 88 % yield, exclusively as a single regio-isomer with *trans* stereo chemistry.

TABLE-1
OPTIMIZATION OF REACTION CONDITIONS. ALKYLATION REACTION OF 1-PHENYLETHANOL WITH ACETYL ACETONE UNDER VARIOUS CONDITIONS[a]

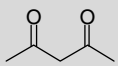
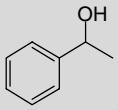
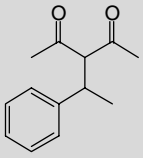
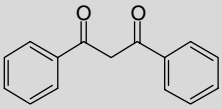
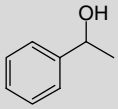
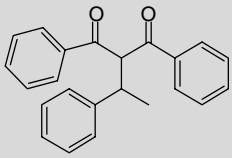
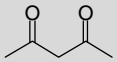
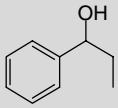
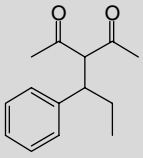
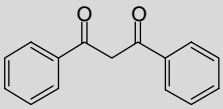
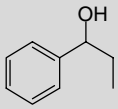
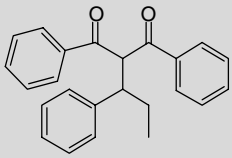
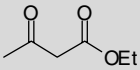
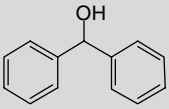
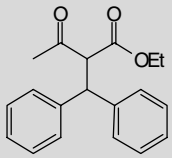
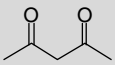
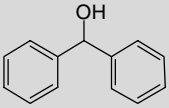
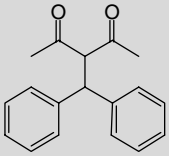
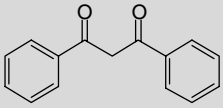
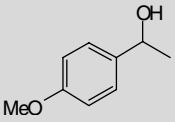
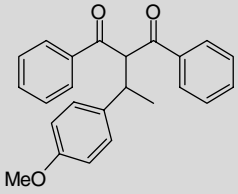
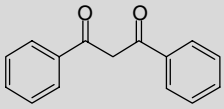
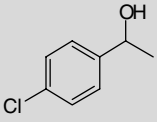
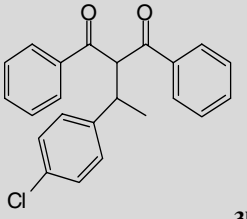
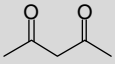
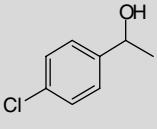
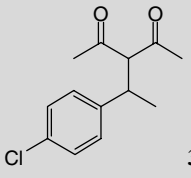
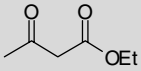
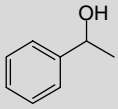
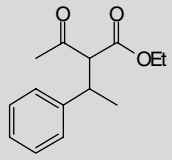


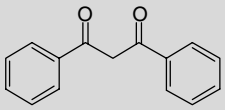
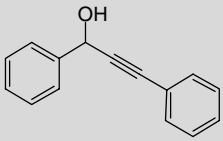
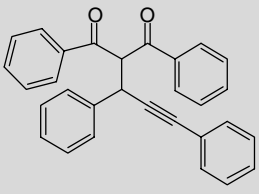
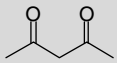
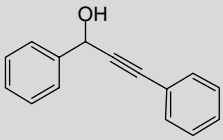
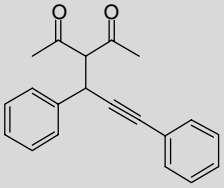
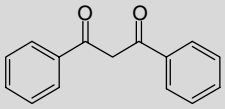
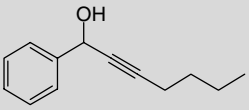
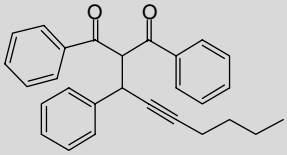
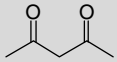
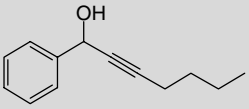
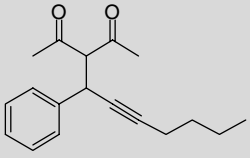
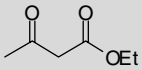
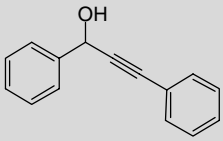
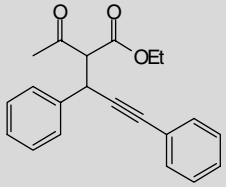
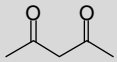
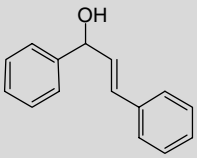
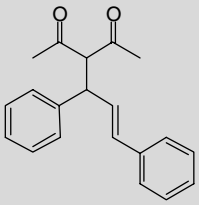
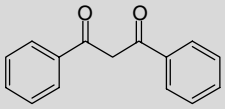
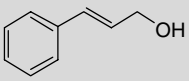
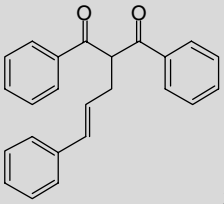
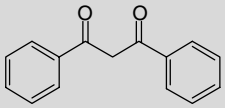
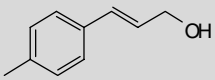
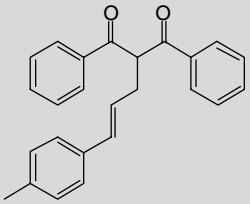
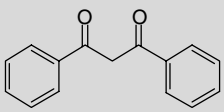
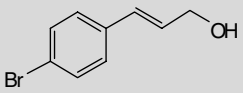
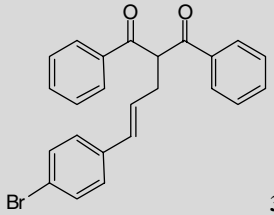
1a 2a 3a

Entry	Solvent	Catalyst	Temperature (°C)	Time (h)	Yield (%)[b]
1	Toluene	$La(NO_3)_3 \cdot 6H_2O$	90	4.0	59
2	Benzene	$La(NO_3)_3 \cdot 6H_2O$	Reflux	4.0	56
3	CH_3CN	$La(NO_3)_3 \cdot 6H_2O$	Reflux	3.0	64
4	THF	$La(NO_3)_3 \cdot 6H_2O$	Reflux	4.0	48
5	CH_3NO_2	$La(NO_3)_3 \cdot 6H_2O$	90	1.0	87
6	DCM	$La(NO_3)_3 \cdot 6H_2O$	Reflux	1.5	82
7	DCE	$La(NO_3)_3 \cdot 6H_2O$	Reflux	1.0	90
8	Neat	$La(NO_3)_3 \cdot 6H_2O$	28	4.0	Trace
9	Neat	$La(NO_3)_3 \cdot 6H_2O$	50	2.5	65
10	Neat	$La(NO_3)_3 \cdot 6H_2O$	70	1.0	86
11	Neat	$La(NO_3)_3 \cdot 6H_2O$	90	0.5	94
12	PEG-400	None	90	12.0	NR[c]
13	DCE	None	Reflux	12.0	NR[c]
14	[TPA][L-Pro]	None	90	12.0	NR[c]

[a]Reactions were performed with 0.5 mmol of 1-phenylethanol, 0.75 mmol acetyl acetone and 5 mg of $La(NO_3)_3 \cdot 6H_2O$ in neat or the presence of indicated solvent and temperature. [b]Isolated yield. ; [c]No reaction based on TLC analysis.

TABLE-2
AKYLATION OF 1,3-DICARBONYL COMPOUNDS WITH BENZYLIC, PROPARGYLIC AND ALLYLIC ALCOHOLS CATALYZED BY $La(NO_3)_3 \cdot 6H_2O$ UNDER SOLVENT-FREE CONDITIONS

Entry	Substrate **1**	Substrate **2**	Product[a] **3**	Time (h)	Yield[b] (%)
1			 **3a**	0.5	94
2			 **3b**	0.5	93
3			 **3c**	0.5	93 [Ref. 27]
4			 **3d**	0.75	92
5			 **3e**	1	85
6			 **3f**	0.5	96
7			 **3g**	0.5	93
8			 **3h**	0.75	88
9			 **3i**	0.5	85
10[c]			 **3j**	0.75	88

11			 **3k**	0.5	92 [Ref. 27]
12			 **3l**	0.75	90 [Ref. 27]
13			 **3m**	1	87 [Ref. 27]
14			 **3n**	1	89 [Ref. 27]
15 [c]			 **3o**	1	84
16			 **3p**	0.75	85
17			 **3q**	0.5	88 [Ref. 27]
18			 **3r**	0.5	85
19			 **3s**	0.75	78

[a]Products characterized by ^{1}H NMR, ^{13}C NMR, IR and Mass spectrometry; [b]Isolated yield after silica gel column chromatography; [c]1:1 Mixture of diastereomers.

It shows that the present method is more regio-selective compared to previous methods for this reaction. Furthermore, it was found that, less reactive 1^0 allylic alcohols reacted efficiently with 1,3-dicarbonyl compounds to afford the respective products (Table-2, entries 17, 18 and 19), allylic alcohols bearing electron withdrawing and donating groups proceeded in good to excellent yield (Table-2, entries 18 and 19).

Conclusion

In conclusion, we have described an efficient and a solvent-free protocol for the direct alkylation of 1,3-dicarbonyl compounds with benzylic, propargylic and allylic alcohols catalyzed by $La(NO_3)_3 \cdot 6H_2O$. The reactions proceeded in excellent yields with high selectivity and is applicable to various alcohols and 1,3-dicarbonyl compounds which could be performed in air. Moreover, short reaction time, simplicity, practicability and avoided the usage of toxic or volatile organic solvent in an environmentally benign process, which makes the current protocol more attractive and important addition to the existing methods.

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