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Inorganic-Base-Catalysed Synthesis of α,β-Unsaturated Ketones and 3,5-Disubstituted Cyclohex-2-en-1-ones

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Abstract: Both acyclic and cyclic α, β-unsaturated ketones are important synthetic intermediates for many functional molecules. A simple and efficient strategy for providing either α, β-unsaturated methyl ketones or 3,5-disubstituted cyclohex-2-en-1-ones as the only product under appropriate reaction conditions was developed. When barium hydroxide was used as the catalyst, the reaction between aldehydes and ketones resulted in the formation of 3,5-disubstituted cyclohex-2-en-1-ones in high yield via a five-step domino reaction. On the other hand, potassium-carbonate-catalysed Claisen–Schmidt reactions between aldehydes and ketones furnished α, β-unsaturated ketone in high yields.

Keywords: aldehydes · aldol reaction · enones · ketones · Michael addition

Introduction

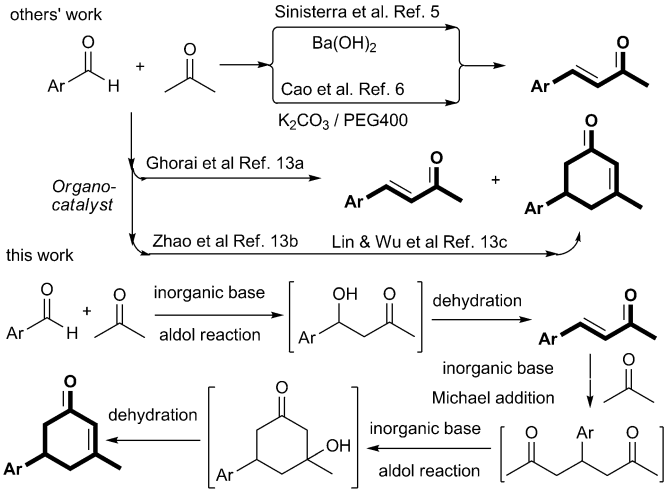
α,β-Unsaturated ketones are arguably one of the most versatile synthetic intermediates for the construction of structurally diverse bioactive compounds and other functional molecules.[1] Cyclohexenones are also well-known building blocks for a wide range of natural products and other useful compounds.[2] Compounds containing these skeletons can be involved in a large number of highly privileged organic transformations, which result in the formation of products of pronounced structural diversity.[3] The Claisen–Schmidt reaction of more readily available aldehydes and ketones as starting materials is one of the best routes towards the formation of α,β-unsaturated ketones. Many types of catalysts such as NaOH,[4] $Ba(OH)_2$,[5] K_2CO_3/PEG400,[6] metal complexes,[7] ionic liquids,[8] and organocatalysts[9] have been developed for the transformation. On the other hand, the intramolecular aldol cyclodehydration and Robinson annulation have been developed to construct cyclohexenone skeletons.[10] Although the Hajos–Parrish–Eder–Sauer–Wiechert reaction is well-established as a crucial method for the synthesis of enantioenriched cyclohexenone moieties,[11] the yields of 3,5-disubstituented cyclohexenone derivatives still remains an important issue.[12]

Very recently, Ghorai et al. published an organocatalytic transformation for the synthesis of both α,β-unsaturated ketone and cyclohexenone derivatives.[13] They used L-proline as catalyst and were able to achieve either (*E*)-α,β-unsaturated methyl ketones as the sole product or cyclohexenones as the major product in good yields under appropriate reaction conditions.

Continuing our research activities in aldol reactions of ketones,[14] we herein describe inorganic-base-catalysed reactions for the synthesis of either α,β-unsaturated ketones or 3,5-disubstituted cyclohex-2-en-1-ones as the only product from acetone and aldehydes (Scheme 1).

Results and Discussion

We initially attempted to use the reaction between benzaldehyde (**1a**) and acetone (**2a**) as a model reaction and use



Scheme 1. Synthesis of (*E*)-α,β-unsaturated ketone and cyclohexenone.

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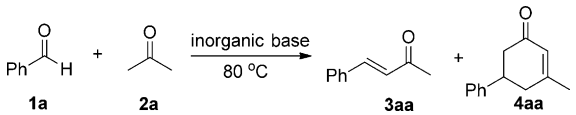
several common commercial available inorganic bases as catalysts. All the reactions were carried out under solvent-free conditions at 80 °C in sealed tubes (Table 1). When the reaction was catalysed by a strong base, such as NaOH or KOH, benzaldehyde reacted with acetone quite smoothly to form 4-phenylbut-3-en-2-one (**3aa**), which would continue to react with acetone to afford 3-methyl-5-phenylcyclohex-2-enone (**4aa**) in moderate yield (Table 1, entries 1–2). The use of LiOH or Cs_2CO_3 as the catalyst resulted in the formation of both **3aa** and **4aa** (Table 1, entries 3–4). To our delight, enone **3aa** was formed initially and then totally transformed into cyclohexenone **4aa** when $Ba(OH)_2$ was used as the catalyst. Up to 89% yield of **4aa** was obtained (Table 1, entry 5). Furthermore, the use of K_2CO_3 as catalyst led to the sole formation of enone **3aa** and no cyclohexenone was obtained (Table 1, entry 6). With a catalyst loading of 10 mol%, cyclohexenone **4aa** was obtained in 60% yield even after a long reaction time (Table 1, entry 7). With increasing the catalyst loading from 20 mol% to 30 mol% and 50 mol%, no higher yields of **4aa** were obtained (Table 1, entries 8–9). This might be because of the limited solubility of $Ba(OH)_2$ in the reaction mixture.

Table 1. Initial investigation of base-catalysed reaction between **1a** and **2a**.



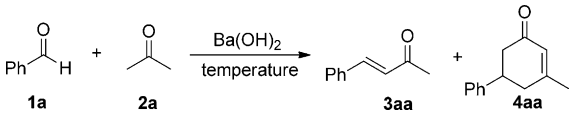
1a **2a** **3aa** **4aa**

Entry[a]	Catalyst	t [h]	Yield of **3aa** [%][b]	Yield of **4aa** [%][b]
1	NaOH	6[c]	0	66
2	KOH	6[c]	0	58
3	LiOH	72	61	34
4	Cs_2CO_3	144	78	20
5	$Ba(OH)_2$	60[c]	0	89
6	K_2CO_3	120	95	0
7	$Ba(OH)_2$[d]	72[c]	0	60
8	$Ba(OH)_2$[e]	60[c]	0	89
9	$Ba(OH)_2$[f]	60[c]	0	85

[a] Unless noted, all the reactions were performed as follows: the mixture of benzaldehyde (**1a**, 0.2 mmol), acetone (**2a**, 1.0 mL), and catalyst (20 mol%) was stirred in a sealed tube at 80 °C for the time given in the table. [b] Isolated yield. [c] At this moment, enone **3aa** was fully consumed and the reaction mixture was then worked up. [d] $Ba(OH)_2$ (10 mol%) was used. [e] $Ba(OH)_2$ (30 mol%) was used. [f] $Ba(OH)_2$ (50 mol%) was used.

Having identified the best catalyst for the synthesis of cyclohexenone **4**, optimisation of reaction conditions was carried out. The reaction temperature was first investigated (Table 2). When the reaction was carried out at room temperature, benzaldehyde reacted with acetone smoothly to form linear enone **3aa**, which would further react with acetone and totally transformed into cyclohexenone **4aa** in 87% yield after 120 h (Table 2, entry 1). Increasing the reaction temperature clearly accelerated the conversion of **3aa** into **4aa** without compromising the yield of the reaction (Table 2, entries 2–5). When the reaction temperature was raised to 80 °C, the reaction between benzaldehyde and acetone furnished cyclic enone **4aa** in 89% yield in 60 h (Table 2, entry 6). Further increasing reaction temperature led to a shorter reaction time, but the yield of cyclic enone **4aa** dropped sharply to 52% (Table 2, entry 7).

Table 2. Screening of the reaction temperature.



1a **2a** **3aa** **4aa**

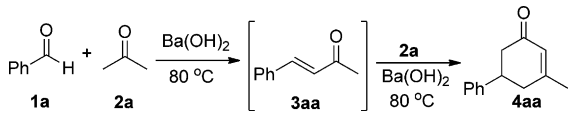
Entry[a]	T [°C]	t [h][b]	Yield of **3aa** [%][c]	Yield of **4aa** [%][c]
1	RT	120	0	87
2	40	109	0	89
3	50	96	0	88
4	60	86	0	89
5	70	72	0	89
6	80	60	0	89
7	100	36	0	52

[a] The reactions were performed as follows: the mixture of benzaldehyde (**1a**, 0.2 mmol), acetone (**2a**, 1.0 mL), and $Ba(OH)_2$ (20 mol%) was stirred in a sealed tube at indicated temperature for the time given in the table. [b] At this moment, enone **3aa** was fully consumed and the reaction mixture was then worked up. [c] Isolated yield.

In the reaction between aldehydes and acetone for the synthesis of cyclohexenones **4**, the reactant acetone was thought to also serve as the solvent. Therefore, the effect of the amount of acetone on the reaction was then investigated, and representative results are displayed in Table 3. When the reaction was scaled up to 0.6 mmol of benzaldehyde, 3.0 mL of acetone was used accordingly to afford cyclic enone **4aa** in 88% yield in 72 h (Table 3, entry 1). Generally, decreasing the amount of solvent led to increasing of reaction rate and resulted in higher yield within shorter time. When the reaction was carried out in 2.0 mL acetone, linear enone **3aa** was transformed into cyclohexenone **4aa** with 62% total yield in 64 h (Table 3, entry 2). Without any exception, linear **3aa** was transformed into cyclic enone **4aa** more quickly when less acetone was used. However, the yield of the expected products **4aa** decreased accordingly, which might be caused by a high concentration of catalyst leading to more side reaction.

Abstract in Chinese:
分别开发了简单、高效合成链状烯酮和 3，5-二取代环己烯酮的方法。在碳酸钾的催化下，醛与酮发生羟醛缩合反应得到单一产物链状甲基烯酮。使用氢氧化钡做催化剂，醛与酮发生串联的五步反应，最后得到单一产物 3，5-二取代的环己烯酮。该合成策略可以分别高收率地制备链状烯酮和 3，5-二取代的环己烯酮。

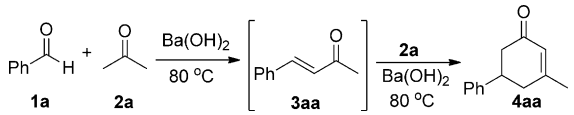
Table 3. Screening of the amount of acetone.



Entry[a]	Acetone [mL] (mmol)	t [h][b]	Yield of **4aa** [%][c]
1	3.0 (40.8)	72	88
2	2.0 (27.2)	64	62
3	1.5 (20.4)	48	54
4	1.0 (13.6)	36	39
5	0.5 (6.8)	24	33

[a] The reactions were performed as follows: the mixture of benzaldehyde (**1a**, 0.6 mmol), acetone (**2a**), and $Ba(OH)_2$ (20 mol%) was stirred in a sealed tube at 80°C for the time given in the table. [b] At this moment, enone **3aa** was fully consumed and the reaction mixture was then worked up. [c] Isolated yield.

Table 4. Reaction process.



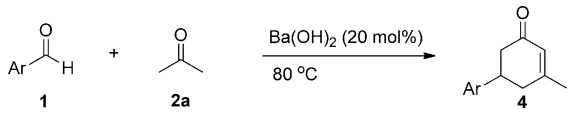
Entry[a]	t [h]	Yield of **3aa** [%][b]	Yield of **4aa** [%][b]	**3aa**+**4aa** [%][b]
1	1	96	0	96
2	4	84	12	96
3	12	67	26	93
4	24	58	34	92
5	36	33	57	90
6	48	24	67	91
7	60	10	79	89
8	72	0	88	88

[a] The reactions were performed as follows: the mixture of benzaldehyde (**1a**, 0.6 mmol), acetone (**2a**, 3.0 mL), and $Ba(OH)_2$ (20 mol%) was stirred in a sealed tube at 80°C for the time given in the table. [b] Isolated yield.

In order to further investigate the domino reaction, the yields of products **3aa** and **4aa** were investigated during the whole process of the transformation (Table 4). It was found that benzaldehyde (**1a**) disappeared after only an hour and at this moment linear enone **3aa** was obtained in up to 96% yield without the formation of cyclic enone **4aa** (Table 4, entry 1). After 4 h, the yield of enone **3aa** decreased to 84% and the yield of cylcohexenone **4aa** increased to 12% (Table 4, entry 2). Furthermore, it was confirmed by the experimental results that enone **3aa** transformed into cyclohexenone **4aa** gradually in the subsequent reaction process (Table 3, entries 3–7). As a result, linear enone **3aa** totally transformed into cyclic enone **4aa** after 72 h and cyclohexenone **4aa** was obtained in 88% yield (Table 4, entry 8). Importantly, the total yield of enone **3aa** and **4aa** was affected slightly during the whole reaction process, which indicated that a high yield of cyclohexenone **4** could be obtained via this method.

Under the optimised reaction conditions, the scope of the reaction was explored. The results of the domino reactions between acetone (**2a**) and a series of aromatic aldehydes

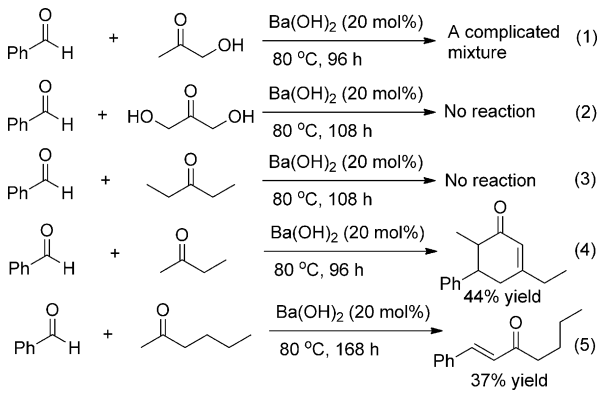
Table 5. Scope of the aldehyde.



Entry[a]	1	Ar	t [h][b]	Yield of **4** [%][c]
1	**1a**	Ph	72	88, **4aa**
2	**1b**	2-ClPh	72	75, **4ba**
3	**1c**	2-BrPh	68	72, **4ca**
4	**1d**	2-MePh	72	82, **4da**
5	**1e**	2-MeOPh	72	77, **4ea**
6	**1f**	3-BrPh	60	65, **4fa**
7	**1g**	3-NO_2Ph	64	65, **4ga**
8	**1h**	3-MePh	72	76, **4ha**
9	**1i**	3-MeOPh	72	86, **4ia**
10	**1j**	4-FPh	72	80, **4ja**
11	**1k**	4-ClPh	72	85, **4ka**
12	**1l**	4-BrPh	68	77, **4la**
13	**1m**	4-NO_2Ph	64	64, **4ma**
14	**1n**	4-MePh	72	89, **4na**
15	**1o**	4-MeOPh	68	83, **4oa**
16	**1p**	naphthalen-2-yl	96	47, **4pa**
17	**1q**	2-thienyl	192	59, **4qa**
18	**1r**	4,5-dimethylfuran-2-yl	96	75, **4ra**
19	**1s**	styryl (PhCH=CH)	189	71, **4sa**
20[d]	**1t**	–	72	85, **4aa**

[a] The reactions were performed as follows: the mixture solution of aldehyde (**1**, 0.6 mmol), acetone (**2a**, 3.0 mL), and $Ba(OH)_2$ (20 mol%) was stirred in a sealed tube at 80°C for the time given. [b] At this moment, linear enone **3** was fully consumed and the reaction mixture was then worked up. [c] Isolated yield. [d] (*E*)-4-Phenylbut-3-en-2-one was used as reactant.

1 are listed in Table 5. The results showed that the domino reaction proceeded smoothly to form the cyclohexenones **4** in good to high isolated yields. Both electron-withdrawing (Table 5, entries 2–3, 6–7, 10–13) and electron-donating substituents (Table 5, entries 4–5, 8–9, 14–15) could be introduced into the aromatic ring, and most of the reactions of these substrates afforded cyclohexenones **4** in good to high yields. The nitro group on the aromatic ring was found to strongly affect the reaction, and the reactions furnished cyclic enones **4** in moderate yields (Table 5, entries 7 and 13). Other aromatic aldehydes were also surveyed. When 2-naphthaldehyde (**1p**) was used as reactant, 3-methyl-5-(naphthalen-2-yl)cyclohex-2-enone (**4pa**) was obtained in 47% yield (Table 5, entry 16). Thiophene-2-carbaldehyde (**1q**) was found to react with acetone quite slowly and afforded 3-methyl-5-(thiophen-2-yl)cyclohex-2-enone (**4qa**) in 59% yield (Table 5, entry 17). The use of 4,5-dimethylfuran-2-carbaldehyde as the reactant led to the formation of 3-methyl-5-(4,5-dimethylfuran-2-yl)cyclohex-2-enone (**4ra**) in 75% yield (Table 5, entry 18). It should be noted that cinnamaldehyde (**1s**) was also compatible under these reaction conditions and was successfully transformed into 3-methyl-5-styrylcyclohex-2-enone (**4sa**) in 71% yield (Table 5, entry 19). When (*E*)-4-phenylbut-3-en-2-one (**3aa**) was used as the starting material, the Michael-aldolisation reaction proceeded smoothly to afford cyclohexenone **4aa** in 85% yield (Table 5, entry 20).

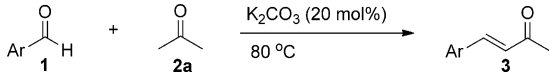


Scheme 2. Scope of ketones.

Apart from acetone, we have also attempted to extend the synthetic method to other ketones. The preliminary results are displayed in Scheme 2. A complicated mixture was obtained from the $Ba(OH)_2$-catalyzed reaction between benzaldehyde and acetol (Scheme 2, Eq. 1). No reaction took place between benzaldehyde and 1,3-dihydroxypropan-2-one (Scheme 2, Eq. 2). Pentan-3-one also failed to react with benzaldehyde (Scheme 2, Eq. 3). Interestingly, butan-2-one (**2b**) reacted with benzaldehyde (**1a**) to afford 3-ethyl-6-methyl-5-phenylcyclohex-2-enone (**4ab**) in 44% yield (Scheme 2, Eq. 4). When hexan-2-one (**2c**) was used, 1-phenylhept-1-en-3-one (**3ac**) was obtained in 37% yield as the main product (Scheme 2, Eq. 5).

With these data in hand, we then investigated the potassium-carbonate-catalysed Claisen–Schmidt reaction between aldehydes and acetone for the synthesis of acyclic α, β-unsaturated ketones **3**. Representative results are displayed in Table 6. In the presence of K_2CO_3 at 80 °C, benzaldehyde reacted with acetone smoothly to furnish enone **3aa** in 95% yield (Table 6, entry 1). Aromatic enones bearing either electron-withdrawing (Table 6, entries 2–3) or electron-donating substituents (Table 6, entries 4–5) were obtained in high yields from the corresponding aldehydes. Heteroaromatic aldehydes were also used in this transformation and the reactions afforded aldol adducts with more than 90% yield (Table 6, entries 6–7).

Table 6. Potassium-carbonate-catalysed Claisen–Schmidt reaction.



Entry[a]	1	Ar	t [h][b]	Yield of 3 [%][c]
1	**1a**	Ph	120	95, **3aa**
2	**1l**	4-BrPh	180	91, **3la**
3	**1m**	4-NO_2Ph	36	85, **3ma**
4	**1n**	4-MePh	180	84, **3na**
5	**1o**	4-MeOPh	220	87, **3oa**
6	**1q**	2-thienyl	60	90, **3qa**
7	**1r**	4,5-dimethylfuran-2-yl	84	94, **3ra**

[a] The reactions were performed as follows: the mixture of aldehyde (**1**, 0.6 mmol), acetone (**2a**, 3.0 mL), and K_2CO_3 (20 mol%) was stirred in a sealed tube at 80 °C for the time given. [b] At this moment, aldehyde **1** was fully consumed and the reaction mixture was then worked up. [c] Isolated yield.

Conclusions

In summary, we have successfully developed an efficient catalytic cascade reaction for the synthesis of cyclohexenone derivatives. In the presence of $Ba(OH)_2$, a series of aldehydes reacted with acetone smoothly to furnish 3,5-disubstituted cyclohex-2-en-1-ones in 47-89% yields. Moreover, α, β-unsaturated methyl ketones were obtained as the sole product in 84–95% yield from the K_2CO_3-catalyzed Claisen–Schmidt reaction between aldehydes and acetone. Compared with Ghorai's report,[13] broad substrate scope and high yields of cyclohexenone derivatives were achieved. Further applications of these reactions are currently under investigation.

Experimental Section

General Procedure for the Synthesis of Cyclohexenones via a Domino Reaction

In a sealed tube, the reaction mixture of aldehyde (0.6 mmol), acetone (3.0 mL), and $Ba(OH)_2$ (20 mol%) was heated from room temperature to 80 °C for 60–192 h, and was monitored by TLC. Acetone was removed and the crude reaction mixture was purified by column chromatography on silica gel to yield the desired product.

General Procedure for the Synthesis of α,β-Unsaturated Methyl Ketones

In a sealed tube, the reaction mixture of aldehyde (0.6 mmol), acetone (3.0 mL), and K_2CO_3 (20 mol%) was heated from room temperature to 80 °C for 36–220 h, and was monitored by TLC. Acetone was removed and the crude reaction mixture was purified by column chromatography on silica gel to yield the desired product.

Acknowledgements

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