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ARTICLE TYPE

# Base–Catalyzed Synthesis of Amides and Imines *via* C–C and C=C Bond Cleavage

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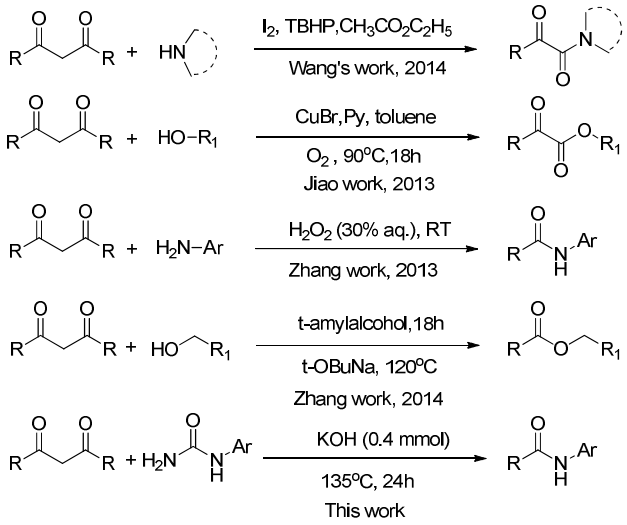
**A transition metal free base catalyzed approach for C–N bond formation *via* C–C and C=C bond activation has been developed. The *N*-arylureas were reacted smoothly with 1,3-dicarbonyls and α,β-unsaturated ketones to furnish the corresponding amides and imines respectively in moderate to excellent yields.**

## Introduction

Amides are one of the abundant and important units present in pharmaceuticals, polymers, agrochemicals, natural products and biological systems.[1] In addition, they have wide application as versatile building blocks in the organic synthesis.[2] Hence, the development of efficient and versatile practical methods for the synthesis of amides has always been an important topic in the organic chemistry. The main synthetic route for amide bond formation is condensation of amines with activated carboxylic acid derivatives.[3] Other methods for amide synthesis are transition metal catalyzed amidation of aryl halides with nitrogen containing reagents,[4] the oxidative amidation of aldehydes,[5] ketones,[6] alcohols,[7] amines,[8] Schmidt rearrangement,[9a] Curtius rearrangement,[9b] Beckmannn rearrangement,[10] aminocarbonylation of haloarenes and alkynes,[11] transition metal catalyzed cleavage of carbon–carbon bond with a nitrogen source.[12] However, these protocols suffer from one or more drawbacks such as use of transition metals, unstable starting compounds, toxic solvents, costly reagents. Hence, the development of simple, efficient and environmentally friendly protocol for the synthesis of amides would be highly desirable.

Recently, selective carbon–carbon bond cleavage (activation) by transition metals have attracted great scope in organic and organometallic chemistry.[13] To facilitate C–C bond activation different methods have been developed such as chelation assistance,[14] the relief of ring strain[15] and employing functional fragmentation as the leaving groups includes carboxylic acids,[16a,b] nitriles,[16c,d] and carbonyls.[16e] The 1,3-diketones have emerged as an important substrates for C–C bond activation in the organic synthesis.[17] Firstly, carbon–carbon bond activation of 1,3-diketones with aryl halides to acyl ketones was reported by Lei in 2010.[18] Subsequently, various protocols have been developed for carbon–carbon bond activation of 1,3-diketones.[19] Recently, $H_2O_2$ mediated oxidative reaction of aromatic amine with 1,3-diketone was reported for the amide synthesis.[20] Nowadays, much attention have been made on the base catalyzed one pot synthesis of various organic compounds.[21] Hence, to perform various transformations by using inexpensive and easily available base is a promising research area. Most recently Zhang's group have reported the base catalyzed C–C bond cleavage of 1,3-diketones to furnish the corresponding esters.[22] The results inspire us to investigate whether amides could be synthesized *via* C–C bond cleavage of 1,3-diketones by using base. The *N*-arylureas are stable, easy to store, handle and can be easily prepared. Moreover, it has been extensively employed as a new type of coupling partners in the organic synthesis.[23] Hence, *N*-arylureas could be used as other alternatives to amines for the preparation of nitrogen containing compounds. To our knowledge, *N*-arylureas have never been used for the synthesis of amides with 1,3-diketones. Here, we report a novel, simple, efficient, solvent and transition metal free methodology for the synthesis of amides from *N*-arylureas and 1,3-diketones by using inexpensive and easily available base (Scheme 1).




**Scheme 1**: Various C–C bond cleavage reactions.

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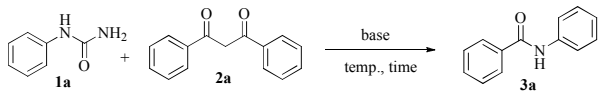
## Results and discussion

To optimize the reaction conditions *N*-phenylurea (**1a**) and 1,3-diphenyl propane-1,3-dione (**2a**) was chosen as a model substrate for the base-catalyzed synthesis of amide. A series of experiments were carried out to study the effect of various reaction parameters such as base, temperature and time (Table 1). Initially, we have screened various bases such as KOH, NaOH, $K_2CO_3$, $Na_2CO_3$, LiOH, *t*-BuONa, *t*-BuOK and $Cs_2CO_3$ for the synthesis of *N*-phenylbenzamide (**3a**) (Table 1, entries 1–8). It was observed that among the various bases, KOH gave the best yield of the desired product **3a** and hence was used for further studies (Table 1, entry 1). However, other bases like NaOH, $K_2CO_3$, $Na_2CO_3$, LiOH, *t*-BuONa, *t*-BuOK and $Cs_2CO_3$ furnished the **3a** in moderate to good yields (Table 1, entries 2–8). However, the product formation was not observed in the absence of the base (Table 1, entry 9). Subsequently, we studied the effect of base loading and it was found that 0.4 mmol of KOH furnished **3a** in excellent yield (Table 1, entry 10). Consequently, we have also examined the effect of reaction time and temperature for the effective progress of the reaction, and observed that 24 h was the optimum time required for completion of the reaction (Table 1, entry 11). It was found that the yield of **3a** decreases with decrease in reaction temperature from 135 °C to 125 °C (Table 1, entry 12). Furthermore, for the possibility of involvement of trace amount of transition metal in the reagent grade KOH, we have also examined the reaction by using KOH 99.99% (metal basis) (Alfa Aesar) and no change in the yield of **3a** was observed (Table 1, entry 13).

**Table 1**: Optimization of the reaction conditions[a]

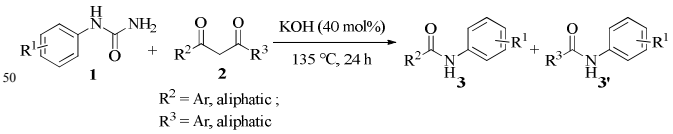



| Entry | Base (mmol) | Time (h) | Yield (%)[b] **3a** |
|---|---|---|---|
| 1 | KOH | 24 | 76 |
| 2 | NaOH | 24 | 71 |
| 3 | $K_2CO_3$ | 24 | 68 |
| 4 | $Na_2CO_3$ | 24 | 63 |
| 5 | LiOH | 24 | 58 |
| 6 | *t*-BuONa | 24 | 68 |
| 7 | *t*-BuOK | 24 | 70 |
| 8 | $Cs_2CO_3$ | 24 | 75 |
| 9 | - | 24 | 0 |
| 10 | KOH (0.4) | 24 | 92 |
| 11 | KOH (0.4) | 20 | 78 |
| 12[c] | KOH (0.4) | 24 | 73 |
| 13[d] | KOH (0.4) | 24 | 92 |

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.5 mmol), Base (0.2 mmol), 135 °C, 24 h. [b] GC yield. [c] 125 °C. [d] KOH 99.99% (metal basis).

With these optimized reaction conditions in hand, we have studied the scope of developed protocol for the synthesis of various kinds of structurally diverse amides from *N*-arylureas and 1,3-diketones. Firstly, different *N*-arylurea derivatives were examined for the synthesis of amides. The *ortho*-substituted *N*-arylurea derivative (**1b**) exhibits the steric effect and provided corresponding *N*-(*o*-tolyl)benzamide (**3b**) in 68% yield (Table 2, entry 2). The reaction of *N*-arylureas bearing electron donating groups such as (–$CH_3$, –OMe) afforded the corresponding products **3c–3d** in excellent yields (Table 2, entries 3–4). Furthermore *N*-arylurea derivatives bearing halo-substituents (–Cl, –Br) also provided the corresponding products **3e–3f** in

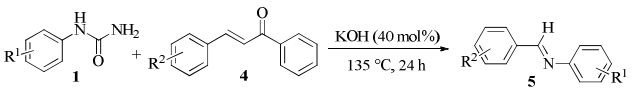
**Table 2**: Substrate study for the synthesis of amides[a]

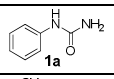
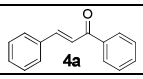
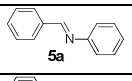
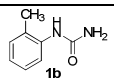
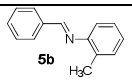
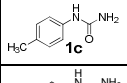
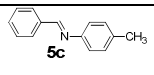
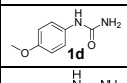
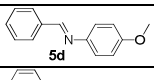
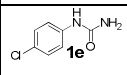
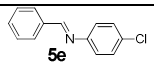
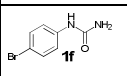
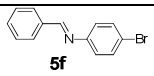
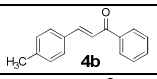
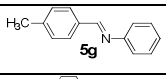
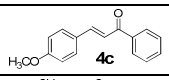
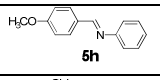
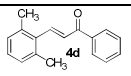
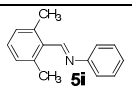
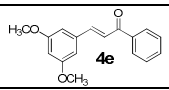
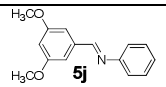
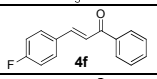
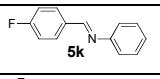
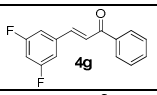
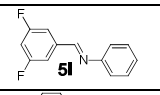
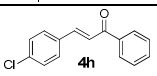
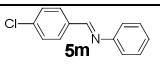
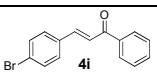
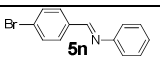
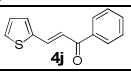
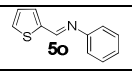



| Entry | *N*-arylurea | 1,3-diketone | Product | Yield (%)[b] 3 |
|---|---|---|---|---|
| 1 | 1a | 2a | 3a | 90 |
| 2 | 1b | 2a | 3b | 68 |
| 3 | 1c | 2a | 3c | 92 |
| 4 | 1d | 2a | 3d | 93 |
| 5 | 1e | 2a | 3e | 74 |
| 6 | 1f | 2a | 3f | 65 |
| 7 | 1a | 2b | 3g | 82 |
| 8 | 1a | 2c | 3h | 85 |
| 9 | 1a | 2d | 3i | 87 |
| 10 | 1a | 2e | 3j | 60 |
| 11 | 1a | 2f | 3k | 63 |
| 12 | 1a | 2g | 3a + 3l | 35:40 |
| 13 | 1a | 2h | 3l + 3m | 36:43 |
| 14 | 1a | 2i | 3l + 3n + 3o | 20:24:31 |
| 15 | 1a | 2j | 3a + 3n | 30:38 |

[a] Reaction conditions: *N*-arylureas (1 mmol), 1,3-diketones (1.5 mmol), KOH (0.4 mmol ), 135 °C, 24 h. [b] isolated yield.

**Table 3**: Substrate study for the synthesis of imines[a]



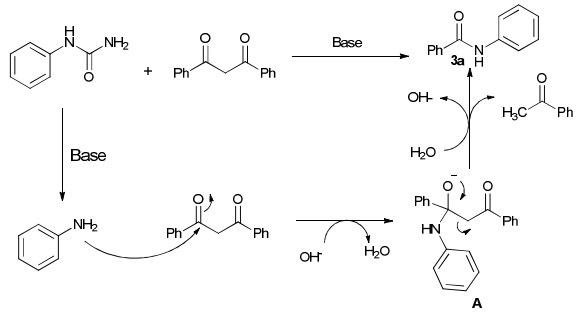

| Entry | *N*-arylurea | α,β-unsaturated ketone | Product | Yield (%)[b] 5 |
|---|---|---|---|---|
| 1 |  |  |  | 77 |
| 2 |  | **4a** |  | 62 |
| 3 |  | **4a** |  | 78 |
| 4 |  | **4a** |  | 80 |
| 5 |  | **4a** |  | 65 |
| 6 |  | **4a** |  | 63 |
| 7 | **1a** |  |  | 76 |
| 8 | **1a** |  |  | 79 |
| 9 | **1a** |  |  | 65 |
| 10 | **1a** |  |  | 81 |
| 11 | **1a** |  |  | 63 |
| 12 | **1a** |  |  | 61 |
| 13 | **1a** |  |  | 64 |
| 14 | **1a** |  |  | 68 |
| 15 | **1a** |  |  | 71 |

[a] Reaction conditions: *N*-arylureas (1 mmol), α,β-unsaturated ketones (1.5 mmol), KOH (0.4 mmol ), 135 °C, 24 h. [b] isolated yield.

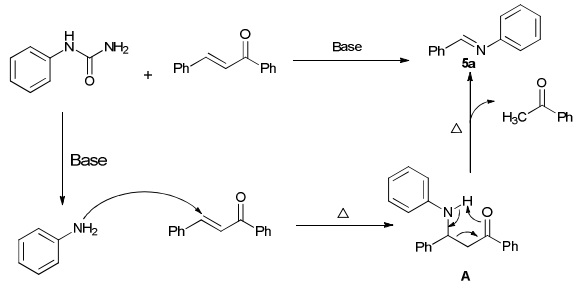
moderate yields (Table 2, entries 5–6). Next, various 1,3-diketone derivatives were also studied for the synthesis of amides. It was found that **2a** bearing electron donating substituents (–$CH_3$, –OMe) furnished the desired amides **3g–3i** in excellent yields (Table 2, entries 7–9). Furthermore, the reaction of **1a** with **2a** bearing halo substituents also provided the respective amides **3j–3k** in good yields (Table 2, entries 10–11). Next, the unsymmetrical 1-phenylbutane-1,3-dione (**2g**) was also studied with **1a** and it was found that mixture of amides **3a** and **3l** were obtained (Table 2, entry 12). However, the reaction of **1a** with aliphatic diketone such as acetylactone (**2h**) provided the mixture of *N*-phenylacetamide (**3l**) and β-enaminone (**3m**) products (Table 2, entry 13). Furthermore, the reaction of **1a** with aliphatic β- keto ester (**2i**) provided the mixture of amide (**3l**), carbamate (**3n**) and ethyl 3-(phenylamino)but-2-enoate (**3o**) products (Table 2, entry 14). Subsequently, aromatic β- keto ester (**2j**) was also studied with **1a** and it was found that mixture of amide **3a** and carbamate **3n** were obtained (Table 2, entry 15).

Imines are important intermediates in the synthesis of nitrogen heterocycles, fine chemicals, pharmaceuticals and agricultural chemicals.[24,25] In addition, they also act as a electrophiles in various transformations including addition reactions, condensations, reductions and cyclization.[25] Moreover, imines also display wide range of biological activities such as anti-inflammatory, anti-bacterial, anti-fungal, anti-viral properties.[26] Thus, the progress toward newer methods for the synthesis of imines is also significant interest among the organic synthetic community. The literature study reveals that α,β-unsaturated ketone undergoes thermal decomposition in the presence of aniline at very high temperature to provide the corresponding imine derivative.[27] So, the scope of developed protocol was further expanded for the synthesis of imines by using *N*-arylureas and α,β- unsaturated ketones. It was observed that the reaction of **1a** with chalcone (**4a**) under the optimized reaction conditions furnished the desired *N*-benzylideneaniline (**5a**) in 77% yield (Table 3, entry 1). Next, *N*-arylurea bearing *ortho*-substituent exhibits steric-effect on the reaction yield and gave corresponding *N*-benzylidene-2-methylaniline (**5b**) in 62% yield (Table 3, entry 2). Furthermore, *N*-arylureas having electron donating substituents at *para*-position (–$CH_3$, –OMe) were converted into corresponding imine derivatives **5c–5d** in good yields (Table 3, entries 3–4). Next, it was observed that **1a** bearing halogen substituents (–Cl, –Br) were also well tolerated and gave respective imine products **5e–5f** in moderate yields (Table 3, entries 5–6). Furthermore, we have also examined the substituted chalcone derivatives with **1a** and it was observed that **4a** with electron donating substituents (–$CH_3$, –OMe) provided the corresponding imines **5g–5h** in good yields (Table 3, entries 7–8). Subsequently, the reaction of **1a** with disubstituted chalcone derivatives provided respective imine derivatives **5i–5j** in good yields (Table 3, entries 9–10). Furthermore, the reaction of **1a** with **4a** bearing halo substituents also furnished the corresponding imine derivatives **5k–5n** in moderate yields (Table 3, entries 11-14). Next, the reaction of **1a** with **4j** provided corresponding *N*-(thiophen-2-ylmethylene)aniline (**5o**) in 71% yield (Table 3, entry 15).

Based on our experimental observation and literature report,[28] we propose a plausible reaction mechanism for the synthesis of amide (Scheme 2). Firstly, when *N*-arylurea is heated with base at 135 °C, it undergoes thermal decomposition to provide aniline and its formation was confirmed by GC-MS, $^1$H and $^{13}$C NMR spectroscopic techniques. However, aniline formation was not observed in the absence of the base. This confirms that under the thermal condition and in the presence of basic medium, **1a** was converted into corresponding aniline. Next, the aniline derivative reacts with carbonyl derivative to form the corresponding intermediate **A** which finally undergoes C–C bond cleavage to furnish the desire product **3a** and acetophenone as a side product. Furthermore, based on literature report[27] and our observation, we have also found that α,β-unsaturated ketone reacts with aniline formed from *N*-arylurea under optimized reaction condition to furnish corresponding imine derivative (Scheme 3).



**Scheme 2**: Proposed mechanism for the synthesis of amide.



**Scheme 3**: Proposed mechanism for the synthesis of imine.

## Conclusion

In conclusion, we have developed a novel base catalyzed approach for the synthesis of amides and imines *via* C–C and C=C cleavage of 1,3-diketones and α,β-unsaturated ketones with *N*-arylureas. Here, we have firstly demonstrated that *N*-arylureas can be envisioned as a new type of coupling partners for 1,3-diketones and α,β-unsaturated ketones. The various amides and imines could be efficiently synthesized by this method in good to excellent yields. Due to the generality of the process, the developed protocol will cover a wide application in organic synthesis. Hence, the developed protocol sounds to be highly efficient, novel methodology for the synthesis of amides as well as imines and have wide substrate applicability.

## Experimental Section

**A typical experimental procedure for the synthesis of amide from *N*-arylurea and 1,3-dicarbonyl:**

A 20 mL schlenk tube equipped with magnetic stirring bar was charged with *N*-arylurea (1 mmol), 1,3-dicarbonyl (1.5 mmol), KOH (0.4 mmol) and was placed in a preheated oil bath for 24 h at 135 °C. After cooling down reaction mixture to room temperature, it was extracted with ethyl acetate (3×5 mL) and the combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated under reduce pressure. The crude product was directly purified by column chromatography (silica gel, 100-200 mesh, PE–EtOAc) to furnish the corresponding pure product. The identity of product was confirmed by $^1H$ and $^{13}C$ NMR spectroscopic analysis.

**A typical experimental procedure for the synthesis of imine from *N*-arylurea and α,β-unsaturated ketone:**

A mixture of *N*-arylurea (1 mmol), α,β-unsaturated ketone (1.5 mmol), KOH (0.4 mmol) was heated at 135 °C for 24 h in a sealed 20 mL schlenk tube. After cooling the reaction mixture to room temperature, it was extracted with ethyl acetate (3×5 mL), combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated under reduce pressure to afford the crude product. The crude product was purified by column chromatography (basic alumina saturated with $Et_3N$, 100-200 mesh, PE) to provide the desired pure product. The identity of product was confirmed by $^1H$ and $^{13}C$ NMR spectroscopic analysis.

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# Base–Catalyzed Synthesis of Amides and Imines *via* C–C and C=C Bond Cleavage

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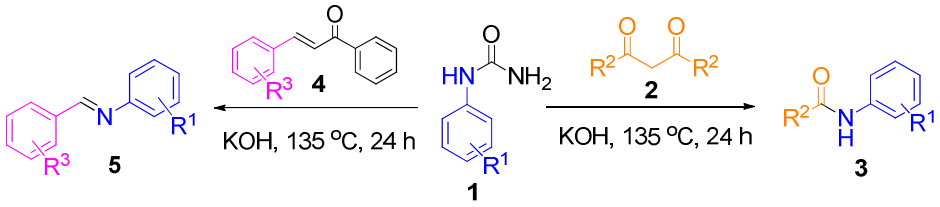


A simple and efficient protocol has been developed for the synthesis of amides and imines from 1,3-dicarbonyls and α,β-unsaturated ketones respectively with *N*-arylureas in the presence of inexpensive and easily available KOH base under solvent free condition.