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Ceric Ammonium Nitrate (CAN) Catalyzed Modification of Ketones *via* Two C−C Bond Cleavages with the Retention of the Oxo-Group

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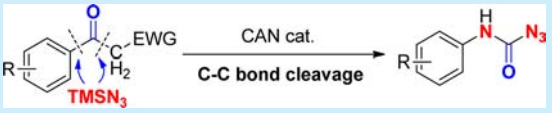
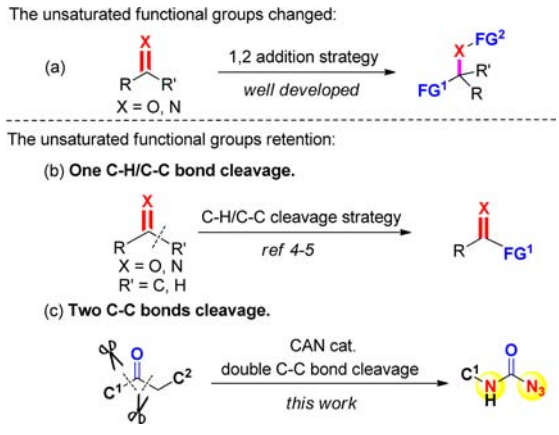
Supporting Information

ABSTRACT: A simple ceric ammonium nitrate (CAN) catalyzed functionalization of ketones through double C−C bond cleavage strategy has been disclosed. This reaction provides a mild, practical method toward carbamoyl azides, which are versatile intermediates and building blocks in organic synthesis. Based on relevant mechanistic studies, a unique and plausible C−C bond and N−O bond cleavage process is proposed, where the oxyamination intermediate plays an important role in this reaction.



Aldehydes, ketones, and imines are among the most important and fundamental organic functional groups. Their transformation and modification are the most common strategy in organic synthesis to prepare complex and value-added chemicals.[1] As the reactive functional groups, aldehydes, ketones, and imines mainly participate in transformations through a 1,2-addition strategy,[1] in which the unsaturated bonds are converted into saturated functional groups (Scheme 1a). In contrast, the functionalization of these groups with the retention of these unsaturated chemical bonds is an undoubtedly attractive but challenging issue. One or two C−H/C−C bond cleavages would be involved for this kind of functionalization. Although the direct C−H[2] and C−C[3] bond functionalization has been significantly developed in the past decades, the functionalization of ketones through C−H/C−C bond cleavage is still a challenging issue (Scheme 1b).[4,5] Especially, the direct transformation of ketones through two C−C bond cleavages in one step is still unknown.

Scheme 1. Functionalization of Unsaturated Aldehydes, Ketones, and Imines



Herein, we disclose a novel CAN catalyzed functionalization of ketones for the efficient synthesis of carbamoyl azides with the retention of the oxo-group through two C−C bond cleavages (Scheme 1c). The significances of the present method is threefold: (1) To the best of our knowledge, this chemistry presents a novel direct transformation of ketones to carbamoyl azides with the retention of the oxo-group. This inexpensive CAN catalyzed process is easily handled under mild conditions. (2) The transformation *via* unstrained C−C bond cleavage[6] under mild conditions presents one of the most challenging reactions due to their inactivity and selectivity, but remains a very attractive process. Two C−C bond cleavages are achieved in this transformation including the insertion of a N-atom into a C−C bond, as well as the azidation of a C−C bond. (3) Organic azides have assumed an important position at the interface between chemistry, biology, medicine, and materials science.[7] This chemistry provides a direct approach from simple ketones to carbamoyl azides, which are also versatile intermediates and building blocks in organic synthesis.[7c]

Our research commenced with the reaction of methyl 3-oxo-3-phenylpropanoate (**1a**) as the model substrate with $TMSN_3$ in the presence of catalysts and oxidants. Gratifyingly, carbamoyl azide **2a** was obtained when the reaction was carried out in the presence of CAN (Table 1). After extensive screening of different parameters, it is interesting to note that only a catalytic amount of CAN is required for this transformation. The reaction under the optimized conditions, which includes 20 mol % CAN, 1.0 equiv of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), under O_2 at 60 °C, could afford the desired product **2a** in 77% yield (entry 1). Both CAN and

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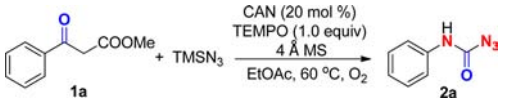
Table 1. Examination of Reaction Conditions[a]



entry	change from the "standard conditions"	yield (%)[b]
1	none	77
2	no CAN	0
3	no TEMPO	17
4	no 4 Å MS	70
5	PIDA instead of TEMPO	trace
6	NHPI instead of TEMPO	10
7	DMF instead of EtOAc	trace
8	CH_3CN instead of EtOAc	45
9	Air instead of O_2	56
10	Ar instead of O_2	50
11	$Mn(OAc)_3{\cdot}3H_2O$ instead of CAN	65
12	$FeCl_3$ instead of CAN	35
13	$CuCl_2$ instead of CAN	35
14	the amount of $TMSN_3$ was 2.0 equiv	29
15	the amount of TEMPO was 0.2 equiv	26

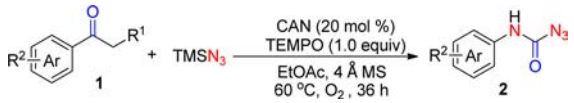
[a]Reaction conditions: 0.4 mmol of **1a**, 1.4 mmol of $TMSN_3$ (azidotrimethylsilane), 20 mol % CAN (ceric ammonium nitrate), 1.0 equiv of TEMPO, 3 mL of EtOAc, 100 mg of 4 Å MS, stirred at 60 °C under O_2 for 36 h. [b]Isolated yields. PIDA (phenyliodine diacetate), NHPI (*N*-hydroxyphthalimide).

TEMPO were essential for this direct transformation (entries 2, 3). The reactions with other oxidants showed low efficiencies (entries 5−6). The reaction did not work well in strong polar solvents such as DMF (entry 7) and gave a moderate yield in CH_3CN (entry 8). Further studies indicated that moderate yields were achieved in the presence of Ar or air, suggesting that oxygen is not essential (entries 9−10). Yet, O_2 is still the most suitable choice to improve the efficiency of this transformation. It is interesting that when $FeCl_3$ or $CuCl_2$ was used as the catalyst instead of CAN, **2a** was obtained in 35% and 35% yields, respectively (entries 12−13), which indicates that CAN may play a role as both a single electron oxidant and Lewis acid to catalyze this transformation.

With the optimal conditions in hand, the scope of the substrate was investigated. It is noteworthy that the arylketones at the *β*-position of a ketone, ester, and amide group performed well under these conditions (entries 1−4, Table 2). Interestingly, the desired carbamoyl azide products could be obtained when *β*-cyano, nitro, phospholipid substituted ketones were employed, albeit in low yields (entries 5−7). The substrates containing an electron-donating group at the aryl ring could be transformed to the desired products in good yields (entries 8−10). Meanwhile, substrates with electron-deficient aryl substituents showed moderate efficiencies (entries 11−15). It is noteworthy that the substrates with aromatic halides performed well in this transformation generating halo-substituted products (60−72%, entries 11−13), which offer opportunities for further transformations. In addition, substituents at different positions of the aryl group did not affect the efficiency (entries 18−21). Gratifyingly, the heteroaryl substituted ketone **1x** gave the desired carbamoyl azide product in 63% yield under the standard conditions (entry 24).

To illustrate the synthetic utility of this difunctionalization reaction, a variety of transformations of carbamoyl azide are displayed in Scheme 2. It is noteworthy that carbamoyl azide is an economical intermediate for the synthesis of tetrazoles (**3**),[8]

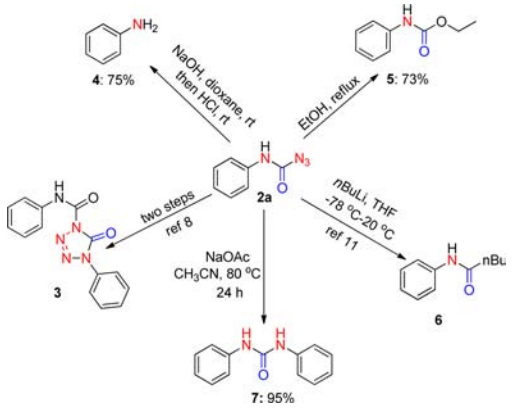
Table 2. Substrate Scope of Ketones[a]



entry	substrate	yield(%) of 2[b]	entry	substrate	yield(%) of 2[b]
1	**1a**: R^1 = COOMe	**2a** 77	18	**1r**: R^1 = COOMe, R^2 = 3,4-Me_2	**2r** 63
2	**1b**: R^1 = COMe	**2a** 63	19	**1s**: R^1 = COOMe, R^2 = 2-Me	**2s** 50
3	**1c**: R^1 = COOEt	**2a** 70	20	**1t**: R^1 = COOEt, R^2 = 4-Me	**2h** 64
4	**1d**: R^1 = CONHPh	**2a** 46	21	**1u**: R^1 = COMe, R^2 = 4-Me	**2h** 50
5	**1e**: R^1 = NO_2	**2a** 11	22	**1v**	**2v** 70
6	**1f**: R^1 = CN	**2a** 31	23	**1w**	**2w** 43
7	**1g**: R^1 = $P(OEt)_2$	**2a** 34	24	**1x**	**2x** 63
8	**1h**: R^2 = Me	**2h** 72			
9	**1i**: R^2 = OMe	**2i** 78			
10	**1j**: R^2 = OEt	**2j** 75			
11	**1k**: R^2 = F	**2k** 69			
12	**1l**: R^2 = Cl	**2l** 72			
13	**1m**: R^2 = Br	**2m** 60			
14	**1n**: R^2 = CF_3	**2n** 63			
15	**1o**: R^2 = CN	**2o** 51			
16	**1p**: R^2 = *t*Bu	**2p** 68			
17	**1q**: R^2 = Ph	**2q** 65			

[a]Reaction conditions: 0.4 mmol of **1**, 1.4 mmol of $TMSN_3$, 20 mol % CAN, 1.0 equiv of TEMPO, 4 Å MS, 3 mL of EtOAc, stirred at 60 °C under O_2 for 36 h. [b]Isolated yields.

Scheme 2. Diverse Transformations of Carbamoyl Azide Products



which are very useful building blocks and common biologically active molecules.[9] Carbamoyl azide can also be easily converted into arylamine (**4**) in 75% yield.[10] Urethane (**5**) was produced in 73% yield when **2a** was refluxed in ethanol. Similarly, with *n*-BuLi and amine as nucleophiles, carbamoyl azide can be transformed into amide (**6**)[11] and urea (**7**)[12] respectively.

When the reaction time was shortened to 60 min, the benzoyl azide (**8**) was isolated in 25% yield (eq 1). Furthermore, when benzoyl azide **8** and isocyanate **9**, which is the Curtius rearrangement[13] product of acyl azide, were used as substrates under the standard conditions, the target products were obtained in 79% and 80% yields, respectively (eqs 2, 3). These results suggest that benzoyl azides and isocyanates might be the intermediates involved in this transformation.

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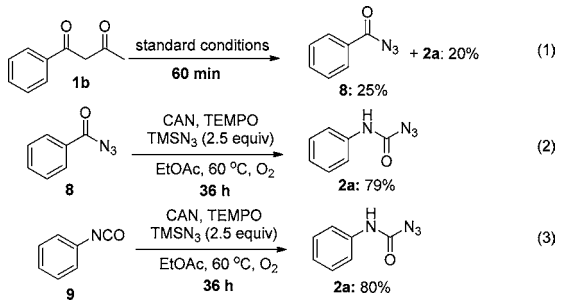
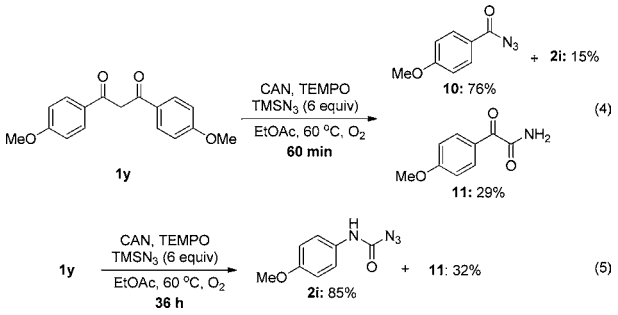
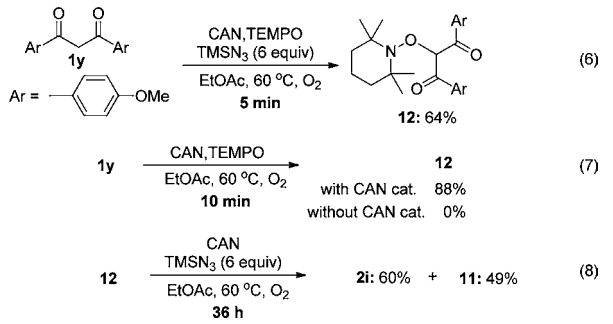


In order to probe the C−C bond cleavage process, 1,3-bis(4-methoxyphenyl)propane-1,3-dione (**1y**) was employed as the substrate to detect the other half product of this transformation. Interestingly, besides the desired benzoyl azide intermediate (**10**) and difunctional product (**2i**), an α-ketoamide byproduct (**11**) was detected in this transformation (eqs 4, 5).



Furthermore, TEMPH (tetramethylpiperidine) as the reduction product of TEMPO was detected by GC-MS after reaction (see Figure S1). In addition, essential ^{18}O-labeling studies exclude the possibility of an oxygen source such as H_2O and O_2 (see SI). We therefore hypothesized that TEMPO donated an O-atom to this transformation leading to the formation of **11** (eq 4), which can also explain why stoichiometric TEMPO was required in this reaction system (entry 15, Table 1).

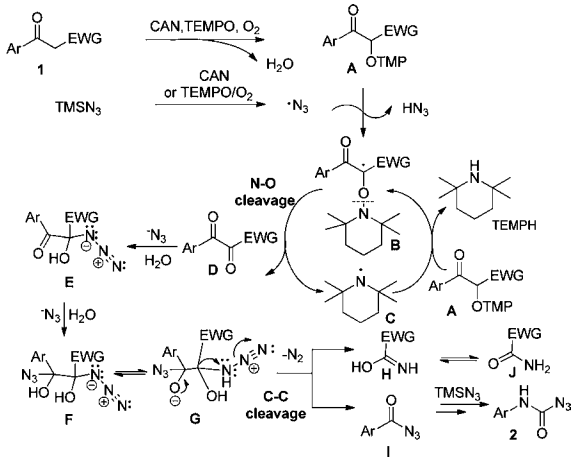
Inspired by the above results, the active oxyamination intermediate (**12**) was detected at a very early step of the reaction (eq 6). In addition, **12** could be obtained in high yield



(88%) in the absence of azide under the optimal conditions (eq 7). It is worthy to note that a similar reaction did not work without the CAN catalyst (eq 7), which explains why CAN is required for this transformation. Furthermore, the control reaction shows that **12** could be converted into the desired products successfully under the standard conditions (eq 8). The above results indicate that TEMPO would initially react with the methylene group of ketones directly to trigger this C−C bond cleavage process.

On the basis of these results, a plausible mechanism is proposed in Scheme 3. TEMPO electrophilic attack at the

Scheme 3. Plausible Mechanism for This Transformation



methylene group of the substrate (**1**) initially occurs to produce the oxyaminated species **A**.[14,15] In this reaction, intermediate **A** could not be formed in the absence of CAN (eq 7). Meanwhile, an azide radical is produced through the oxidation of $TMSN_3$ by CAN,[16,17a,b] or the TEMPO/O_2 oxidative system.[17c] Then the azide radical attacks **A** to produce the unstable intermediate **B**.[18] The radical species **B** undergoes a N−O bond cleavage process through a radical autocatalytic cycle, where the TEMPH and the fragile intermediate **D** are generated.[19] Then the intermediate **E** is generated from **D** which was attacked by the azido nucleophile at the more electrophilic position adjacent to the electron-withdrawing group.[20] The subsequent similar nucleophilic addition of **E** produces intermediate **F** with its resonance structure **G**, which undergoes the fragmentation process to produce benzoyl azide **I** and byproduct **H** for the further formation of an amide byproduct. Finally, **I** undergoes Curtius rearrangement[13] and transforms into the target product carbamoyl azide **2** with an additional amount of azide.

In conclusion, a novel and simple CAN catalyzed direct nitrogenation of ketones through double C−C bond cleavage has been developed. TEMPO not only plays the role of oxidant but also participates in the key C−C activation process. This chemistry offers a simple approach leading to carbamoyl azides which are of versatile reactivity and synthetic value and provides meaningful mechanistic insight into the novel cleavage process. Further studies about the reaction mechanism and the applications of this transformation are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, full characterization of new products, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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