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Copper-Assisted Direct Nitration of Cyclic Ketones with Ceric Ammonium Nitrate for the Synthesis of Tertiary α-Nitro-α-substituted Scaffolds

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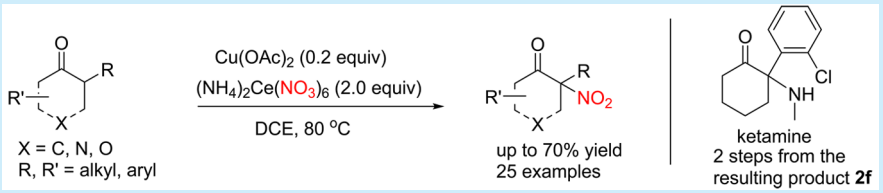
Supporting Information



ABSTRACT: An efficient and direct Cu-assisted nitrating approach to create synthetically valuable and challenging tertiary α-nitro-α-substituted moieties has been developed using ceric ammonium nitrate as a nitrating reagent, oxidant, and Lewis acid. Notably, the commonly used clinical drug ketamine was smoothly synthesized in four steps.

Nitration of aliphatic C−H bonds has been a challenging topic in modern organic synthesis,[1] especially nitration of C−H bond at the α-position of the carbonyl group. Consequently, many synthetic methods have been developed to efficiently prepare α-nitro ketones and simultaneously meet the requirements for green chemistry, such as preformation under mild reaction conditions, use of relatively low-toxicity nitrating reagents, and simple manipulation.[2] However, the nitration of the C−H bond at the α-position of the carbonyl group for the construction of aza-quaternary carbon centers containing NO_2 groups remains an unexploited avenue.[3]

Tertiary α-nitro, α-substituted ketones are unique moieties in organic synthesis, pharmaceutical molecules, and materials science. These scaffolds not only exist in bioactive compounds used as herbicides but also serve as intermediates for the syntheses of natural products and functional molecules based on diverse transformations of the nitro and carbonyl groups.[4] For example, the selective reduction of the nitro group provides the tertiary amine,[5] which is a common moiety of bioactive molecules including erythraline alkaloids[6] and the drug ketamine.[7] The simultaneous reduction of nitro and carbonyl groups could generate the privileged 1,2-amino alcohol ligands for asymmetric catalysts (Figure 1). Owing to their difficult construction using conventional nitrating methods, the methods for their preparation to date have been rarely reported, especially for the preparation of α-nitro α-aryl ketone moieties. To the best of our knowledge, only two approaches have been developed to prepare challenging α-nitro α-aryl ketone moieties. One is the arylation of α-nitro ketone using tributylphenylstannane (Scheme 1a).[8a] The other is the nitration of highly active 1,3-dicarbonyl compounds (Scheme 1b).[8b] However, from green and step-economic points of view, there are some disadvantages in the developed methods, such as the relative toxicity of the arylating stannane, $Hg(OAc)_2$ and $Pb(OAc)_4$ reagents, the extra chemical transformation for the preparation of suitable precursors, and the narrow substrate scope. Therefore, the development of a direct, efficient, and general method for the preparation of these moieties is essential.

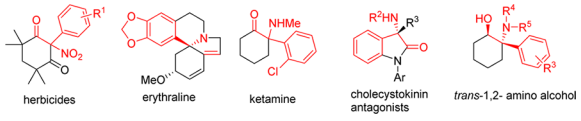
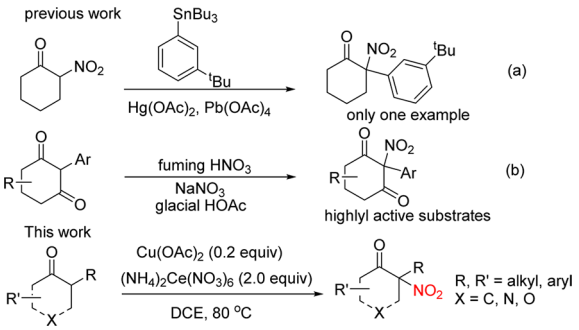


Figure 1. Selective functional molecules related to tertiary α-nitro α-aryl ketone moieties.

Scheme 1. Outline of Preparation of α-Aryl α-NO_2 Cyclic Ketones



Ceric ammonium nitrate (CAN) has been widely applied in organic synthesis, especially as a special single-electron-transfer oxidant.[9] Due to its low toxicity, low cost, safety, air and moisture

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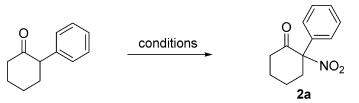
stability, and ease of handling, it has received increasing attention in recent decades. Notably, either combined with excess of $NaNO_2$ as a NO_2 source or alone, CAN can promote the nitration of the C (sp^2)−H bond for the preparation of nitroalkenes, nitroamides, or nitroarenes.[10] However, CAN used as a NO_2 source has been rarely reported for the nitration of C(sp^3)−H bonds, especially the preparation of tertiary α-nitro ketones. Continuing our research interests in "three birds with one stone" chemical reagents,[11] we speculated that CAN could serve as Lewis acid, oxidant, and nitrating reagent for the nitration of a C−H bond at the α-position of a cyclic ketone, resulting in the construction of the challenging tertiary α-nitro-α-substituted scaffolds under suitable conditions. Here, we report our research on this topic based on the multifunctional properties of CAN (Scheme 1).

Initially, we selected commercially available 2-phenylcyclohexanone as a model substrate to test our designed nitration using CAN as a multifunctional reagent. However, competitive side reactions needed to be suppressed, such as the nitration of the C(sp^2)−H bond on the phenyl ring,[12] the formation of benzyl nitrates,[13] the cleavage of the C−C bond at the ketone α-position,[14] and the self-coupling of 2-phenylcyclohexanone.[15] After some attempts, to our delight, the desired product **2a** was isolated in 43% yield when the reaction was performed in 1,2-dichloroethane (DCE) at 80 °C for 12 h (entry 1). Inspired by this initial result, further screening of other additives was conducted.[16] The results showed that both Cu(I) and Cu(II) salts gave moderate yields (entries 2−8), and the highest yield (60%) of product **2a** was obtained using $Cu(OAc)_2$ as the additive (entry 6). The equivalents of CAN, the reaction temperature, and the solvents were varied, and no better results could be obtained.[16] Other nitro sources were then investigated. When $Bi(NO_3)_3 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, or $Cu(NO_3)_3 \cdot 3H_2O$ was applied, a slightly decreasing yield was obtained because the hydroxylation side product at the α-position was observed (entries 9−11); using $AgNO_3$ or $AgNO_2$ to replace CAN led to obviously decreasing yields (entries 12 and 13). Interestingly, *tert*-butyl nitrite and isopentyl nitrite, two commonly used organic nitrating reagents, were applied, and product **2a** was isolated in almost identical yields (entries 14 and 15). Additionally, fuming HNO_3 afforded the desired product **2a** in 50% yield (entry 16), whereas $NaNO_2$ proved to be a completely ineffective reagent (entry 17). Therefore, the combinations listed in entry 6 in Table 1 were selected as the optimal reaction conditions.

With the optimal reaction conditions in hand, we investigated the generality of this novel nitration. Substrates bearing different substituents on the aromatic ring were subjected to the optimal conditions, and the results are shown in Scheme 2. The tested substrates reacted smoothly, affording the corresponding products **2b−j** in moderate to good yields, and the structure of product **2g** was further confirmed by X-ray crystallography.[17] For example, the *p*-F, *o*-F, *m*-F products (**2b−d**) can be isolated in 53%, 51%, and 51% yields, respectively, and the substrates bearing the phenyl group at the *para*-position, the electron-donating group (OMe) at the *meta*-position or the electron-withdrawing group (NO_2) at the *para*-position provided the desired products **2h−j**, respectively. These results demonstrated that the positions or electronic properties of substituents on the aromatic ring had slight effects on this transformation. The 2-naphthalene derivative was an ideal substrate, giving the expected product **2k** in 50% yield. Benzocyclic ketones reacted well, furnishing the desired product **2l** in 70% yield; its analogue bearing a OMe group on the benzocyclic ring was also obtained in an acceptable yield.

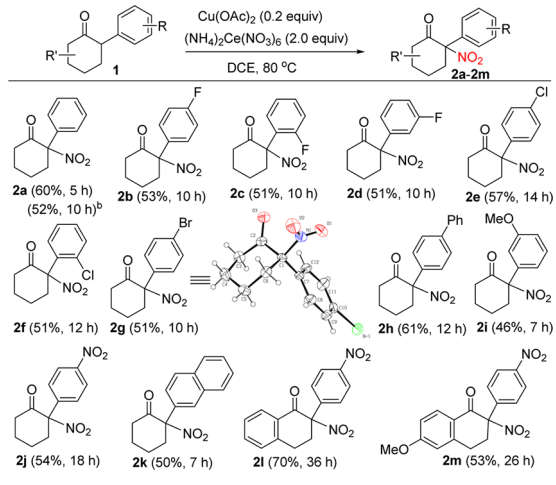
Table 1. Optimization of the Reaction Conditions[a]



entry	reagent (equiv)	additive	solvent	temp (°C)	yield[b] (%)
1	CAN (2.0)		DCE	80	43
2	CAN (2.0)	CuO	DCE	80	53
3	CAN (2.0)	$CuSO_4$	DCE	80	46
4	CAN (2.0)	$CuCl_2$	DCE	80	45
5	CAN (2.0)	$Cu(acac)_2$[c]	DCE	80	50
6	CAN (2.0)	$Cu(OAc)_2$	DCE	80	60
7	CAN (2.0)	$Cu(OTf)_2$[d]	DCE	80	55
8	CAN (2.0)	CuCl	DCE	80	50
9	$Bi(NO_3)_3 \cdot 5H_2O$ (2.0)	$Cu(OAc)_2$	DCE	80	41
10	$Fe(NO_3)_3 \cdot 9H_2O$ (2.0)	$Cu(OAc)_2$	DCE	80	45
11	$Cu(NO_3)_3 \cdot 3H_2O$ (2.0)	$Cu(OAc)_2$	DCE	80	43
12	$AgNO_3$ (2.0)	$Cu(OAc)_2$	DCE	80	27
13	$AgNO_2$ (2.0)	$Cu(OAc)_2$	DCE	80	27
14	^tBuONO (2.0)[e]	$Cu(OAc)_2$	DCE	80	48
15	isopentyl nitrite (2.0)[e]	$Cu(OAc)_2$	DCE	80	49
16	fuming HNO_3 (2.0)	$Cu(OAc)_2$	DCE	80	50
17	$NaNO_2$ (20.0)	$Cu(OAc)_2$	DCE	80	0

[a]Reactions were performed using 2-phenylcyclohexanone (0.2 mmol) in 2.0 mL of solvent at the noted temperature under an argon atmosphere in a 15 mL sealed tube. [b]isolated yield. [c]acac = acetyl acetonate. [d]Tf = trifluoromethanesulfonyl. [e]Under an oxygen atmosphere.

Scheme 2. Scope of Substituted Cyclohexanones[a]



[a]Reaction conditions: **1** (0.2 mmol), additive (0.04 mmol), CAN (0.4 mol) in DCE (2.0 mL). [b]The reaction was performed on a 1 g scale.

Next, a series of benzyl ketone derivatives were subjected to the optimal reaction conditions; the results are shown in Scheme 3. Both cyclopentanone and cycloheptanone derivatives reacted smoothly, affording the corresponding products **2n** and **2o**. Both 3-phenylchroman-4-one and 1-methyl-3,4-dihydronaphthalen-2(1*H*)-one were ideal substrates, and their expected products **2p** and **2q** were isolated in moderate yields. Since 3-alkyl-3-amino-2-oxindoles are a key skeleton in bioactive alkaloids and clinical drugs,[18] 3-methylindolin-2-ones bearing different *N*-protecting

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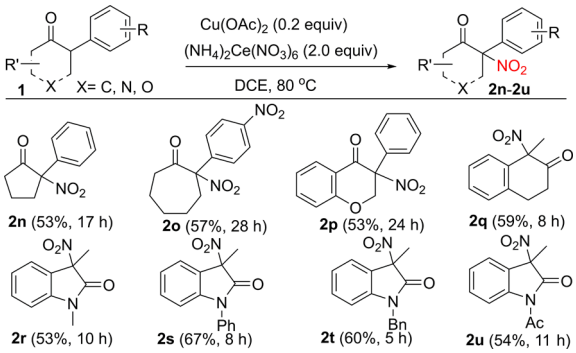
Scheme 3. Scope of Benzyl Ketones[a]

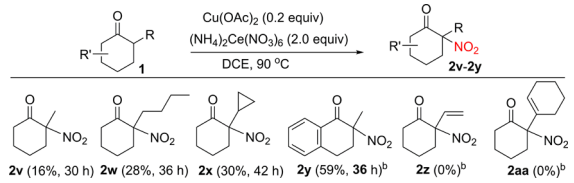


[a]Reaction conditions: substrate **1** (0.2 mmol), additive (0.04 mmol), CAN (0.4 mmol) in 2.0 mL of DCE.

groups were tested. The nitrating reactions proceeded smoothly under the optimal conditions, and the desired products **2r**–**u** were obtained in 53–67% yield. These results indicated that diverse protecting groups at the *N*-1 position of 3-methylindolin-2-one could be tolerated. Hence, these transformations can provide various choices in further chemical transformations of these important indolin-2-one skeletons.

Other cyclic ketone substrates were also tested, and the reaction results are enumerated in Scheme 4. To our pleasure, the

Scheme 4. Scope of Alkyl-Substituted Substrates[a]



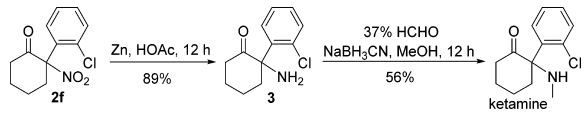
[a]Reaction conditions: substrate **1** (0.2 mmol), additive (0.04 mmol), CAN (0.4 mmol) in 2.0 mL of DCE. [b]Reaction at 80 °C.

desired products **2v**–**y** were obtained. The 2-methyl-, 2-butyl-, or 2-cyclopropyl-substituted cyclohexanones reacted well and led to the expected products in relatively low yield, albeit with longer reaction times at 90 °C. Notably, 2-methyl-1-tetralone proved to be an ideal substrate, providing the desired product **2y** in 59% yield. Unfortunately, the alkenyl-substituted substrates failed to afford the corresponding products **2z** and **2aa**, resulting in complex mixtures.

In these novel transformations, versatile functional groups, such as halogens, NO_2, and OMe on an aryl ring, could be further reacted with other partners to increase the diversity and complexity of products, a universal strategy for medical chemistry and materials science. To further demonstrate the synthetic utility of these transformations, the model reaction was carried out in gram scale and afforded the expected product **2a** in slightly lower 52% yield (Scheme 2). This result suggests that the current protocol can be used to synthesize α-nitro α-aryl cyclic ketones derivatives on a large scale.

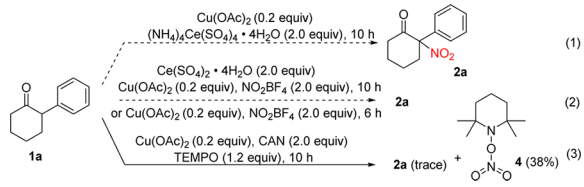
After expansion of the scale synthesis of this transformation, we turned our attention to the synthetic application. Ketamine[7] is a widely used nonopioid anesthetic drug that has attracted the interest of medical and synthetic chemists since the 1950s due to its simple chemical scaffold with diverse clinical values. Starting from the product **2f**, selective reduction afforded the primary amine **3** in 89% yield, which was subsequently monomethylated using the modified methods[7d] to provide the target molecule in 56% yield (Scheme 5). Notably, the current approach for the preparation of ketamine is forward and efficient.

Scheme 5. Short Synthesis of Ketamine



Finally, control experiments were conducted to elucidate a possible mechanism (Scheme 6). Replacement of CAN with

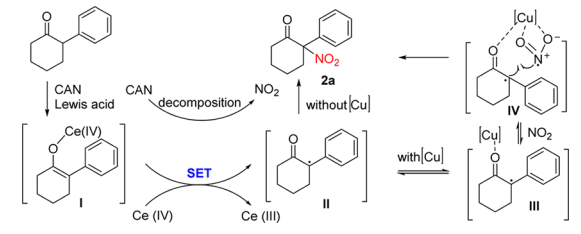
Scheme 6. Some Control Experiments



ammonium cerium(IV) sulfate could not promote the desired transformation, and this result reveals that the NO_2 group is derived from a nitrate anion other than the ammonium ion in CAN (eq 1). In the presence or absence of $Ce(SO_4)_2{\cdot}4H_2O$, using NO_2BF_4 to replace CAN did not provide the desired product **2a**, eliminating the possibility that the electrophilic NO_2 cation was involved in the nitrating process (eq 2). A slight effect of electronic factors of the substitutes on the aryl ring was observed (Scheme 2), partly ruling out the possibility of a carbocation intermediate. Therefore, when (2,2,6,6-tetramethylpiperdin-1-yl)oxyl (TEMPO) was introduced under the optimal reaction conditions, the desired nitration was obviously suppressed, resulting in isolated compound **4** in 38% yield along with trace **2a** (eq 3). This result indicates that NO_2 may be a reactive species in the current transformation. Further support for this speculation was derived from the evolution of brown gas observed in some nitrating cases. The phenomenon is consistent with NO_2 formed through the decomposition of CAN above a certain temperature.[19]

Based on the above-mentioned experimental results and the reported literature,[20–22] a possible reaction mechanism was proposed (Scheme 7). First, the CAN served as a Lewis acid[9,21] to

Scheme 7. Proposed Reaction Mechanism



promote the formation of the enolized intermediate **I**, which was easily oxidized by CAN to generate radical **II**.[20c] The resulting radical **II** either was directly trapped by NO_2 derived from CAN[19] without Cu species or reacted through the possible intermediate **IV** stabilized by Cu species[20e] to afford the desired product **2a**. Certainly, because NO_2 is a highly reactive specie,[22] other reaction pathways cannot yet be excluded.

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In summary, an efficient and direct Cu-assisted nitrating approach toward the synthetically challenging tertiary α-nitro, α-substituted cyclic ketones scaffolds has been developed using CAN as a Lewis acid, oxidant, and nitro source. Ketamine, which has been used as an anesthetic and analgesic in the clinic, was efficiently synthesized by this novel nitration. Additionally, the mechanistic studies proposed a possible radical process. Expansion of this new reaction system for nitration of other compounds is underway in our group and will be reported in the near future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00040.

Experimental procedures, spectroscopic data, and NMR spectra of compounds (PDF)

X-ray crystallographic data of compound **2g** (CIF)

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Notes

The authors declare no competing financial interest.

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(16) For details, see the Supporting Information.

(17) Compound **2g** (CCDC 1524692) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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