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# Metal-Free Oxidative Nitration of α-Carbon of Carbonyls Leads to One-Pot Synthesis of Thiohydroximic Acids from Acetophenones

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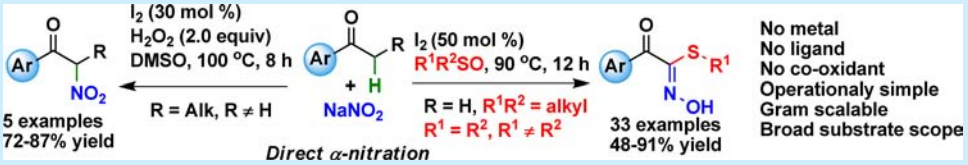
Supporting Information

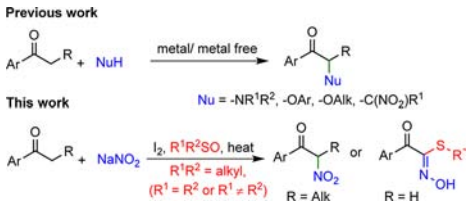



**ABSTRACT:** A metal-free nitration of the α-C−H to carbonyl in propiophenones was achieved with $I_2$/$NaNO_2$ in the presence of an oxidant in dimethyl sulfoxide (DMSO) as the medium. Conversely under similar conditions, reaction of acetophenones produced thiohydroximic acids via a radical-based cascade event which involves oxidative nitration of the α-carbon to a carbonyl followed by Michael addition of the thiomethyl group from DMSO and subsequent rearrangement. Besides DMSO, the scope of the reaction encompasses other symmetrical and unsymmetrical dialkylsulfoxides.

The hypoiodite-mediated oxidative coupling reactions involving a stoichiometric amount of iodine or iodide together with a co-oxidant are considered to be valuable organic transformations. In pioneering work, the Ishihara group utilized in situ generated chiral quaternary ammonium hyopoiodite for oxidative α-phenoxyetherification and α-oxyacylation of carbonyl compounds.[1] Subsequently, diverse oxidative coupling reactions have been investigated employing this approach.[2] Notably, these reactions resulted in C−O, C−N, or C−C coupling at the proximal carbon to the carbonyl group.[3−5] In addition, metal-based α-functionalization of carbonyls under oxidative conditions is also known.[6] However, the oxidative nitration at the α-carbon to the carbonyl group under metal or metal-free conditions remains elusive. We recently demonstrated the $I_2$/$NaNO_2$-mediated oxidative nitration of nitroalkanes for the formation of 3-nitroisoxazoles.[7] Based on the analogy to our work and literature reports about hypoiodite-mediated coupling reactions we reasoned that $I_2$/$NaNO_2$ in the presence of dimethyl sulfoxide (DMSO) as the co-oxidant may induce oxidative nitration of the α-carbon to the carbonyl resulting into α-nitroketones. Such metal-free simple synthesis of α-nitroketones is especially attractive since they are versatile synthons in organic synthesis for obtaining diverse heterocycles and acyclic amides, ketones, aminoketones, and tosyl hydrazones.[8] Here, we disclose synthesis of α-nitro ketones from propiophenones via oxidative nitration of the α-carbon to the carbonyl with $I_2$/$NaNO_2$ in the presence of aq. hydrogen peroxide ($H_2O_2$). Intriguingly under similar conditions, reactions of acetophenones resulted into thiohydroximic acids (Scheme 1).

We commenced the study by treating propiophenone (**1a**) with iodine (30 mol %), $NaNO_2$ (1.2 equiv), and DMSO (5.0 equiv) using DMF as the medium at room temperature.

**Scheme 1. Reported α-C−H Functionalization of Ketones**




Unfortunately, the reaction was unsuccessful, and therefore, it was repeated under heating at 100 °C. Gratifyingly, the reaction at elevated temperature was completed in 12 h furnishing a mixture of products from which the major compound that was isolated in 39% yield was identified as the expected 2-nitro-1-phenylpropan-1-one (**2a**). This result prompted us to optimize the reaction for improving the yield of **2a** (refer to Table 1 in Supporting Information (SI)). Performing the reaction in DMSO as solvent and co-oxidant furnished **2a** in 58% yields. Notably, however, using DMSO as solvent and adding external oxidant not only improved the yield of **2a** but also decreased the reaction time to 8 h. Perhaps the external oxidant facilitated the oxidation of iodide to iodine. The best yield of **2a** (72%) was obtained when $H_2O_2$ (35 wt % in $H_2O$) was employed as the external oxidant whereas with $K_2S_2O_8$, Oxone, TBHP (70 wt % in $H_2O$), and $O_2$ the yield of **2a** ranged between 62% and 70%. We also investigated the reaction in the presence of 30 mol % of TBAI and $H_2O_2$ (2.0 equiv) in DMSO resulting in the formation of **2a** in 43% yield. Conversely, replacing DMSO with DMF as the medium and using $H_2O_2$ as the sole oxidant afforded **2a** in

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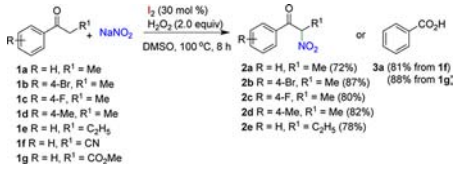
48% yield. Thus, the optimized conditions that produced the best yield of **2a** was propiophenone (**1a**, 1.5 mmol), $NaNO_2$ (1.2 equiv), $I_2$ (30 mol %), and $H_2O_2$ (2.0 equiv) in DMSO (5.0 mL) at 100 °C for 8 h (see SI).

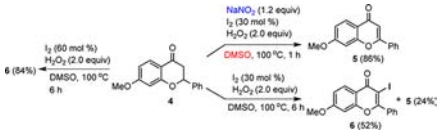
Subsequently, we tested the generality of the protocol by subjecting other substrates (**1b−e**) in the reaction and found that in each case the transformation was successful, affording the corresponding products **2b−e** (Scheme 2). Next, we investigated

**Scheme 2. Oxidative Nitration of the α-C−H to Carbonyl**




substrates **1f** and **1g** bearing an electron-withdrawing group and discovered both substrates (**1f** and **1g**) gave benzoic acid **3a** exclusively which was in agreement with the literature.[9] We examined the scope of the reaction with a representative cyclic substrate 7-methoxy-2-phenylchroman-4-one **4** as well and found that, under the optimized conditions, **4** was dehydrogenated only to afford the 7-methoxy-2-phenyl-4*H*-chromen-4-one **5** in 86% yield (Scheme 3). On the other hand, performing

**Scheme 3. Results of Reaction with 7-Methoxy-2-phenylchroman-4-one (4)**

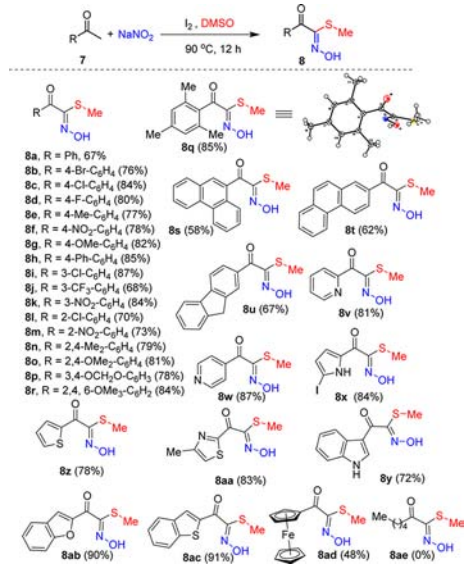



the reaction of **4** in the absence of $NaNO_2$ resulted in a mixture of two products from which the major product (52%) was identified as 3-iodo-7-methoxy-2-phenyl-4*H*-chromen-4-one (**6**) whereas the minor product (24%) was identified to be compound **5**. Increasing the loading of iodine to 60 mol % however furnished **6** in 84% yield exclusively.

To overcome the limited commercial availability of propiophenones and in our efforts to expand the scope of the protocol, we considered probing the methodology with acetophenones which are cheap and readily available and were expected to afford α-nitroacetophenones. Accordingly, (4-bromophenyl)acetophenone (**7b**) was treated with $I_2/NaNO_2$ under the standardized conditions leading to the formation of a mixture of two products in 42% and 21% yields. The major product was identified to be the corresponding benzoic acid **3b** whereas the minor product after detailed spectroscopic analysis was delineated to be methyl 2-(4-bromophenyl)-*N*-hydroxy-2-oxoethanimidothioate **8b**. The formation of benzoic acid may be attributed to transformation of acetophenone to phenylglyoxal or glyoxalic acid followed by degradation[10] while the isolation of **8b** may be explained via simultaneous generation of α-nitroacetophenone followed by addition of the methyl sulfide group from DMSO (vide infra). It may be noted that the nitronate ion produced by 2-nitroacetophenone is susceptible to nucleophilic attack due to the presence of an α-hydrogen but such an opportunity is unavailable in 2-nitropropiophenone. Given the importance of thiohydroximic acids,[11] we were invoked to optimize the reaction to improve the yields of **8b**. In this context, the reaction of **7b** was screened under different conditions (for summary of results refer to Table 2 in the SI). Replacing the external oxidant $H_2O_2$ with TBHP improved the overall yield, but the two products **8b** and **3b** were formed in 38% and 41% yields. The yield of the products, however, decreased in the presence of oxone. Enhancing the amount of iodine to 50 mol % and using TBHP as the oxidant boosted the overall yield of the mixture. Subsequently performing the reaction at 120 °C completed it in 6 h but produced more benzoic acid whereas at 90 °C it gave a 2:1 mixture of **8b** and **3b**. Next the reaction was conducted in the absence of an external oxidant maintaining the temperature at 90 °C. Although the reaction was now completed in 12 h, gratifyingly **3b** was formed in a minor quantity only. Increasing the amount of iodine further to 1.0 equiv was found to have a detrimental impact on the formation of **8b**. Alternating iodine with NIS gave the product in 63% yield with no detection of acid. We also screened the reaction in the presence of copper salts but without any success. Screening the reaction in different mediums revealed that in water **3b** (64%) was the sole product whereas in MeCN the reaction failed. Replacing DMSO with DMF produced 2-hydroxy-1-(4-bromophenyl)ethan-1-one (**9**) (52%) with recovery of the starting substrate (26%) (see SI Table 2). Thus, for conversion of acetophenones to thiohydroximic acids, the optimized conditions were **7b** (0.2 g, 1.01 mmol), $NaNO_2$ (1.2 equiv), and iodine (50 mol %) in DMSO (5 mL) under heating at 90 °C for 12 h.

With the optimized conditions in hand, we turned our attention toward testing the scope of the protocol with a variety of acetophenones (**7**) including heteroaromatic variants. Therefore, in the first set of reactions several substituted acetophenones (**1a−r**) were evaluated, and it was found that all substrates irrespective of the electronic nature of the substituents present on the phenyl ring afforded thiohydroximic acids (**8a−8r**) in 67−87% yields (Scheme 4). The structure of these products was secured unambiguously by carrying out X-ray analysis of the crystal of one of the analogues **8q**. The phenanthridine-based acetophenones also furnished the products **8s** and **8t** in good yields. Different heteroaromatic acetophenones (**7v−z**, **7aa−ac**) also underwent the reaction to

**Scheme 4. Scope of the Protocol with Acetophenones[a]**




[a]All reactions were performed at 0.2 g of acetophenones.



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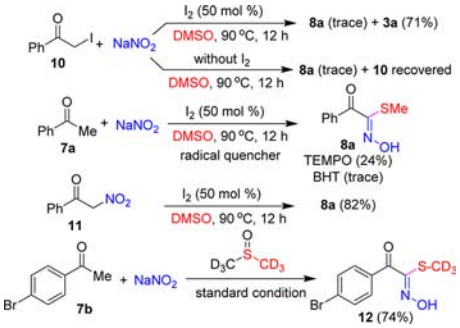
give respective products (**8v−z**, **8aa−ac**) in 72−91% yields. For **7x**, the pyrrole ring was iodinated at the 5-position leading to **8x**. The reaction with ferrocene-2-acetophenone **7ad** was successful as well affording the product (**8ad**) in 48% yields. Scaling up the reaction to the gram scale using **7b** as the reactant produced **8b** without any attenuation in yield. However, when acetophenone was replaced by 2-heptanone (**7ae**) the reaction failed to afford the corresponding product (**8ae**).

In a classical event,[4a,6a] the reaction of **7a** with iodine is expected to produce 2-iodo-1-phenylethanone **10** that may undergo nucleophilic substitution with $NaNO_2$ to afford 2-nitro-1-phenylethanone **11** which on addition of dimethyl sulfide produces **8a**. In support of the suggested mechanism control experiments were carried out. Treating **10** with $I_2/NaNO_2$ under the standardized conditions gave **8a** in a trace amount only with the major product being the acid **3a**. A similar reaction of **10** in the absence of $I_2$ also resulted in trace formation of **8a** while most of the starting **7a** was recovered unreacted. These results suggested that perhaps **10** is not the possible intermediate and the proposed nucleophilic substitution pathway may not be operating. Consequently, as reported by Guo et al.,[4d] the possibility of a radical mechanism was probed. Accordingly, acetophenone **7a** was treated with $I_2/NaNO_2$ in DMSO in the presence of TEMPO or 2,6-di-*tert*-butyl-4-methylphenol (BHT). Whereas the reaction of TEMPO afforded **8a** in 24% yield, the reaction with BHT gave **8a** in a trace amount only (Scheme 5). Simultaneously treating 2-nitro-1-phenylethanone

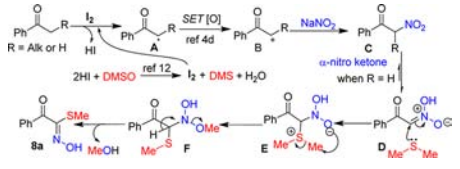
**Scheme 5. Control Experiments**




**11** with iodine in the presence of DMSO furnished **8a** in 82% yield indicating **11** as the possible intermediate in this transformation. Although in the recent past there have been several reports related to the introduction of the SMe group from DMSO,[13,14] to independently gain supporting evidence we performed the reaction of **7b** in the presence of deuterated DMSO to obtain **12** containing a deuterated thiomethyl moiety.

On the basis of the above experiments a tentative reaction mechanism is delineated in Scheme 6. Initially the molecular iodine decomposes into an iodine radical that abstracts the $\alpha$-hydrogen of the ketone to form the radical intermediate **A** together with liberation of HI which is trapped by DMSO to

**Scheme 6. Plausible Mechanism of Reaction**




regenerate molecular iodine and dimethyl sulfide. The intermediate **A** is transformed to the carbocation intermediate **B** via single electron oxidation.[4d] Subsequent nucleophilic addition of the nitrate anion onto **B** results in $\alpha$-nitro ketone **C**. When R = H, the nitro group tautomerizes to the nitronate **D** succeeded by attack of the in situ formed dimethyl sulfide on the imine carbon leading to **E**. Subsequent rearrangement with loss of methanol in **F** afforded the thiohydroximic acid.

Mechanistic considerations generated interest to investigate the fate of the protocol with respect to other sulfoxides. Therefore, **7b** was treated with different sulfoxides **13a−d**, and it was found that while **13a−c** smoothly furnished the corresponding hydroximic acids **14a−c**, **13d** failed to give **14d** inferring that dialkylsulfoxides are essentially required for the success of the protocol (Scheme 7). Since oxidative conditions were used for

**Scheme 7. Scope of Protocol with Sulfoxides**[a]

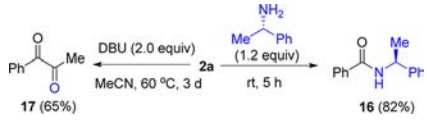

[a]All reactions were performed at 0.1 g of **7b** and 3.0 mL of sulfoxide.

the reaction, for extending the scope, in a model reaction we treated secondary benzyl alcohol **15** under the standardized conditions to expectedly isolate **8a** in 62% yield (Scheme 8).

**Scheme 8. Scope of Protocol with Secondary Alcohol**


Finally, a few synthetic transformations of the $\alpha$-nitration products and thiohydroximic acids using **2a** and **8b** as the model substrates were performed. Treating **2a** with (*S*)-1-phenylethan-1-amine under neat conditions[15] produced the corresponding amide **16** while Nef-reaction of **2a** in the presence of DBU furnished 1-phenylpropane-1,2-dione (**17**) (Scheme 9). For **8b**,

**Scheme 9. Synthetic Transformations of $\alpha$-Nitration Product 2a**[a]




[a]Reactions were carried out with 0.1 g of **2a**.

representative transformations on all three functional groups were attempted. Reducing the ketone in the presence of $NaBH_4$ afforded the alcohol **18** while acetylation and tosylation of the oxime moiety resulted in *N*-acetoxy (**19**) and *N*-tosyloxy (**20**) derivatives, respectively (Scheme 10). Oxidizing the thiomethyl group of **8b** in the presence of $H_2O_2$ gave the methylsulfinyl derivative **21** in 82% yield.[16]

In summary, we have demonstrated $I_2/NaNO_2$/DMSO to be an effective reagent for $\alpha$-nitration of carbonyls. In contrast to propiophenones or higher homologues wherein $\alpha$-nitroketones were isolated, acetophenones afforded thiohydroximic acids.



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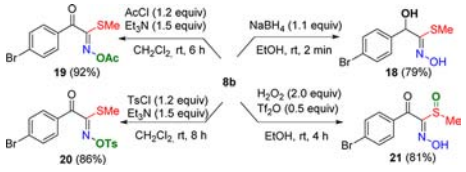
**Scheme 10. Synthetic Transformations of Thiohydroximic Acid 8b**[a]




[a]Reactions were carried out with 0.1 g of **8b**.

Mechanistically the formation of thiohydroximic acid is suggested to proceed via a radical mechanism, and the protocol is amenable to other dialkyl sulfoxides beside DMSO. Attractive attributes of this protocol include that it is metal-free, uses commercially available starting substrates, and is of general nature and scalable. Further utility of the $I_2/NaNO_2$ system for diverse synthetic objectives is being explored and will be reported in the future.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01807.

Experimental details, spectroscopic data, X-ray data for **8q**, and copies of $^1H$ and $^{13}C$ NMR data for all compounds (PDF)

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### Author Contributions

[∥]S.U.D. and S.M. contributed equally.


### Notes

The authors declare no competing financial interest.

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