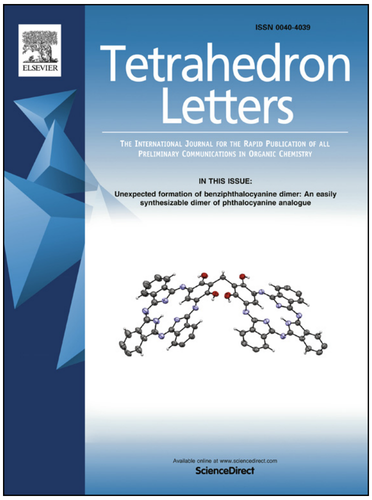

A TEMPO-like nitroxide combined with an alkyl-substituted pyridine: an efficient catalytic system for the selective oxidation of alcohols with iodine

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Graphical Abstract

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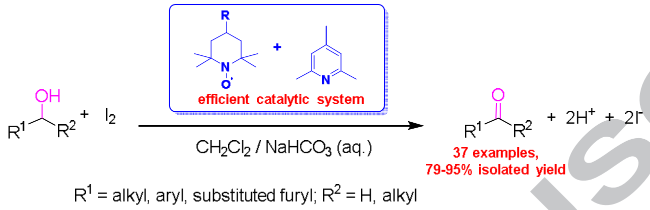

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A TEMPO-like nitroxide combined with an alkyl-substituted pyridine: an efficient catalytic system for the selective oxidation of alcohols with iodine

Vera P. Kashparova,[a] Victor A. Klushin,[a] Irina Yu. Zhukova,[a,b] Igor S. Kashparov,[a] Daria V. Chernysheva,[a,b] Irina B. Il'chibaeva,[a] Nina V. Smirnova,[a] Efim Sh. Kagan,[a] Victor M. Chernyshev,[a]∗

[a] *Platov South-Russian State Polytechnic University (NPI), Prosveschenya 132, 346428 Novocherkassk, Russia*
[b] *Don state technical university, Gagarin square 1, Rostov-on-Don, 344000, Russia*

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ABSTRACT

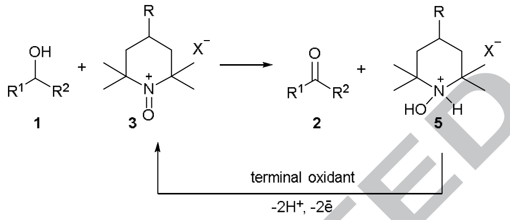
An efficient method for the oxidation of alcohols to aldehydes or ketones in a two-phase $CH_2Cl_2/NaHCO_3$ (aq.) system, using iodine and catalytic amounts of 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl and 2,4,6-trimethylpyridine, was developed. The performance of the method was demonstrated by the selective oxidation of 37 variously substituted alcohols in ≥90% yield, including the gram-scale synthesis of the important chemical 2,5-diformylfuran from biomass-derived 5-hydroxylmethylfurfural.

∗ Corresponding author. e-mail: chern13@yandex.ru; phone/fax : +7(8635)-25-55-68

1. Introduction

The oxidation reactions of primary and secondary alcohols to aldehydes and ketones, respectively, have played pivotal roles in organic synthesis.[1-4] Aldehydes and ketones are highly demanded functional groups in a variety of laboratory-scale and industrial processes for the production of pharmaceuticals, dyes, materials and other fine chemicals.[3] However, particularly for primary alcohols, insufficient selectivity is a common problem due to the tendency of aldehydes to undergo over oxidation to carboxylic acid derivatives.[5] Therefore, the selective oxidation of alcohols continues to attract significant attention.[1-4]

Various reagents and catalytic systems have been developed for the oxidation of alcohols **1** to aldehydes and ketones **2**.[1-6] However, many of these systems suffer from high reagent costs, instability, employment of hazardous metals or oxidants, harsh reaction conditions or operational complexity. Oxoammonium salts **3**, the oxidized derivatives of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), have received wide application in the high-yielding oxidation reactions of primary and secondary alcohols **1** to aldehydes or ketones **2** (Schemes 1, 2).[7-14] While oxoammonium salts **3** have been successfully applied as stoichiometric oxidants, their relatively high price has prompted the development of numerous processes based on the application of catalytic oxoammonium salts **3** or their precursors, nitroxide free radicals **4** (Scheme 2), using various inexpensive secondary oxidants.[1-6,9,15-20] In the absence of a transition-metal co-catalyst (typically Cu^+), these processes usually involve a catalytic cycle in which the oxoammonium cation acts as a two-electron oxidant and is reduced to the corresponding hydroxylamines **5** (Scheme 1).[8,9,21]



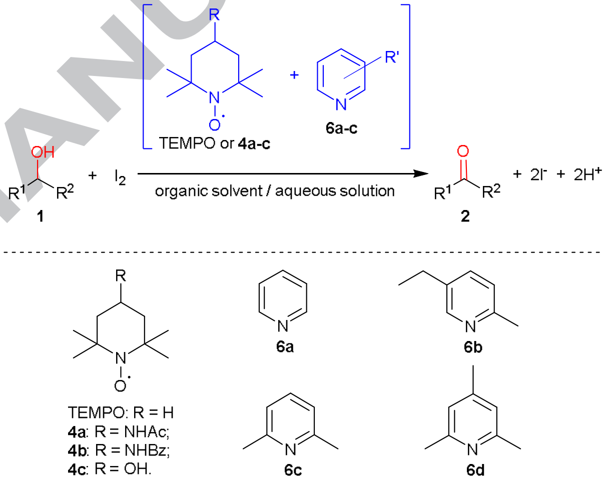
Scheme 1. Simplified catalytic cycle for oxoammonium- and TEMPO-based oxidation pathways.

Various inexpensive, transition-metal-free secondary oxidants, such as sodium hypochlorite or halogens have been successfully applied to the nitroxide-catalyzed oxidation of alcohols to carbonyl compounds.[9,15,18-20,22,23] Several methods in which halogen oxidants are generated electrochemically in "one-pot" have also been developed as potential industrial-scalable nitroxide-catalyzed processes.[9,17,24,25]

Among halogen-based oxidants, elemental iodine has attracted attention as a mild, stable, and inexpensive oxidant.[15,17,20,24] Various chlorine- and bromine-based oxidation systems have also been reported to show low selectivities in the oxidation of susceptible substrates.[9,15,17,26] A nitroxide-catalyzed oxidation of alcohols with elemental iodine was first reported by Cottier and co-workers in a two-phase CH_2Cl_2/KOH (aq.) system with low yields.[26] Miller and Hoerrner reported a more selective oxidation of various alcohols in a toluene/$NaHCO_3$ (aq.) system.[15] An electrochemical method for the oxidation of alcohols in a two-phase CH_2Cl_2/$NaHCO_3$/KI (aq.) system was also reported.[17,24] In our opinion, the nitroxide-catalyzed oxidation of alcohols with iodine in a two-phase system consisting of an "organic solvent/aqueous solution of a base" has potential to serve as a versatile general method for the laboratory and small-scale industrial syntheses of various aldehydes and ketones. However, thus far, this approach has been studied for only a narrow substrate scope which was confined to mainly benzylic-type alcohols **1** (R^1 = aryl or aromatic heterocycles, R^2 = H)[15,17] and a small series of aliphatic alcohols which was examined using an electrochemical mode of oxidation.[24]

Pyridine and alkyl-substituted pyridines **6** have been proposed as effective catalysts for the selective stoichiometric oxidation of alcohols to aldehydes or dimeric esters using oxoammonium salts.[12] Pyridine and some pyridine derivatives were also shown to be effective co-catalysts for the nitroxide-catalyzed oxidation of primary aliphatic alcohols into dimeric esters using certain secondary oxidants.[27-29] However, pyridines have not been studied as co-catalysts for the selective nitroxide-catalyzed oxidation of various types of alcohols to aldehydes or ketones using iodine.

Herein, we report an efficient method for the oxidation of various alcohols to aldehydes or ketones using iodine in a two-phase system consisting of an "organic solvent/aqueous solution" catalyzed by TEMPO-like nitroxides in combination with substituted pyridines (Scheme 2).



Scheme 2. Oxidation of alcohols with I_2 catalyzed by TEMPO-like nitroxides **4a-c** in combination with pyridine bases **6a-d**.

2. Results and Discussion

Typically, the oxidation reactions of alcohols to carbonyls in biphasic water-organic reaction systems favor the simple separation of lipophilic organic products from inorganic water-soluble reagents and wastes.[17] However, the selectivity of the nitroxide-catalyzed oxidation is sufficiently influenced by the applied solvent.[7,9,12,13,30] To determine an appropriate solvent for the organic phase of the biphasic system, the oxidation reactions of 1-octanol (**1a**), 2-hexanol (**1b**) and 5-hydroxymethylfurfural (**1c**) were studied (Fig. 1) using various organic solvents in the absence of a pyridine co-catalyst, under similar conditions to those used in the work of Miller and Hoerrner applying nitroxide **4a** as a catalyst.[15] The highest conversions and yields were achieved in CH_2Cl_2 (ESI, Table S01). Considering the successful application of CH_2Cl_2 in numerous nitroxide-catalyzed oxidation reactions and the simplicity of product isolation, this solvent was chosen for further investigations.

Various TEMPO-like radicals and their derivatives have been applied as catalysts for the oxidation of alcohols.[9] The oxidation of alcohol **1a** catalyzed by TEMPO or various 4-substituted 2,2,6,6-tetramethyl-1-oxyls **4a-c** revealed that the structure of the nitroxide had no significant effect on the reaction rate or selectivity (ESI, Table S02). Therefore, 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl (**4a**),[31] a low-cost, readily accessible TEMPO derivative, was applied as the catalyst in further experiments.

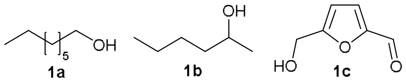


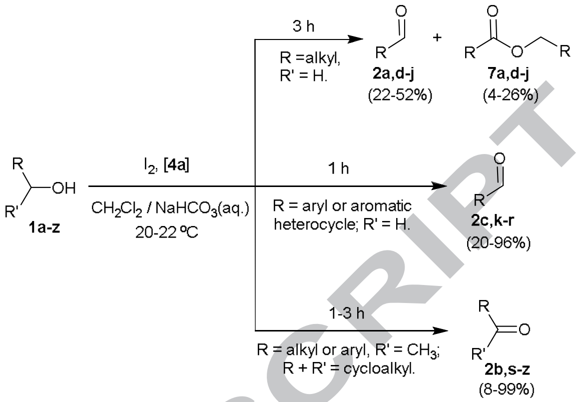
Figure 1. Structures of alcohols **1a-c**.

The effect of the pH of the aqueous solution on the oxidation of alcohols **1a,c** was also studied (ESI, Table S03). In agreement with the literature data for nitroxide-catalyzed alcohol oxidation,[9] high conversions were observed in a basic medium (aq. $NaHCO_3$ or Na_2CO_3). At pH ~5.6, the reaction rates and selectivities were low. When using a Na_2CO_3 solution (pH ~11.3), high conversions of both alcohols **1a,c** were attained; however, the selectivity for the oxidation of **1c** was low. Only the $NaHCO_3$ solution (pH ~8.7) provided appropriate rates and selectivities for the oxidation reactions of both alcohols **1a,c**. Therefore, $NaHCO_3$ was selected as a mild inorganic base for the aqueous phase of the system.

A molar ratio of alcohol:I_2:**4a** = 1:2:0.05 was selected as a starting point for further investigations based on comparative experiments for the oxidations of alcohols **1a,c** (see ESI, Table S04 for results and further discussion).

The oxidation of several primary and secondary alcohols with iodine catalyzed by nitroxide **4a** in the absence of a pyridine co-catalyst revealed that the features of the reaction were similar to non-catalytic stoichiometric oxidations of alcohols with oxoammonium salts (Scheme 3; ESI, Table S05).[7,10] Thus, sterically unhindered benzyl alcohols and secondary aliphatic alcohols were oxidized at reasonable rates, while primary aliphatic alcohols required prolonged reaction times. Within the range of homologs of linear primary aliphatic alcohols, the rate of oxidation decreased successively with increasing hydrocarbon chain length. Interestingly, these results differ sufficiently from the results of analogous nitroxide-catalyzed oxidation reactions of alcohols with bleach (NaOCl) in a two-phase $CH_2Cl_2/NaHCO_3$ (aq.) system, for which the oxidation of primary alcohols proceeded with higher rates than the oxidation of secondary ones.[22,32] Bleach oxidation provided sufficiently higher overall rates for the oxidation reaction of all types of alcohols;[22,23] however, the formation of various by-products was reported.[9,23]

Surprisingly, in the nitroxide-catalyzed oxidation of primary aliphatic alcohols with iodine, we observed sufficiently high yields of dimeric esters **7** in molar ratios of **7**:**2** up to 0.7:1 (Scheme 3; ESI, Table S05). These results differ from the stoichiometric oxidation of primary aliphatic alcohols with oxoammonium salts, for which the formation of dimeric esters was detected only in minor yields (3-5%).[7,10,33] The formation of dimeric esters **7** in relatively high yields prompted us to assume that the non-catalytic oxidation of the alcohol with iodine has a considerable contribution to the overall reaction. For example, the oxidative esterification of alcohols with iodine is a well-known reaction.[34] However, experiments regarding the oxidation of various alcohols with iodine in a two-phase $CH_2Cl_2/NaHCO_3$ (aq.) system revealed, in the absence of the nitroxide, that the oxidation proceeds slowly and that the yields of carbonyl compounds are 5-10 times lower (ESI, Table S06) in comparison with the nitroxide-catalyzed oxidation under the same conditions (ESI, Table S05). Interestingly, the formation of dimeric esters as major products was recently described in the TEMPO/$CaCl_2$-catalyzed oxidation of primary alcohols with oxone in the presence of water;[35] however, this oxidation system was quite different from the system described here.



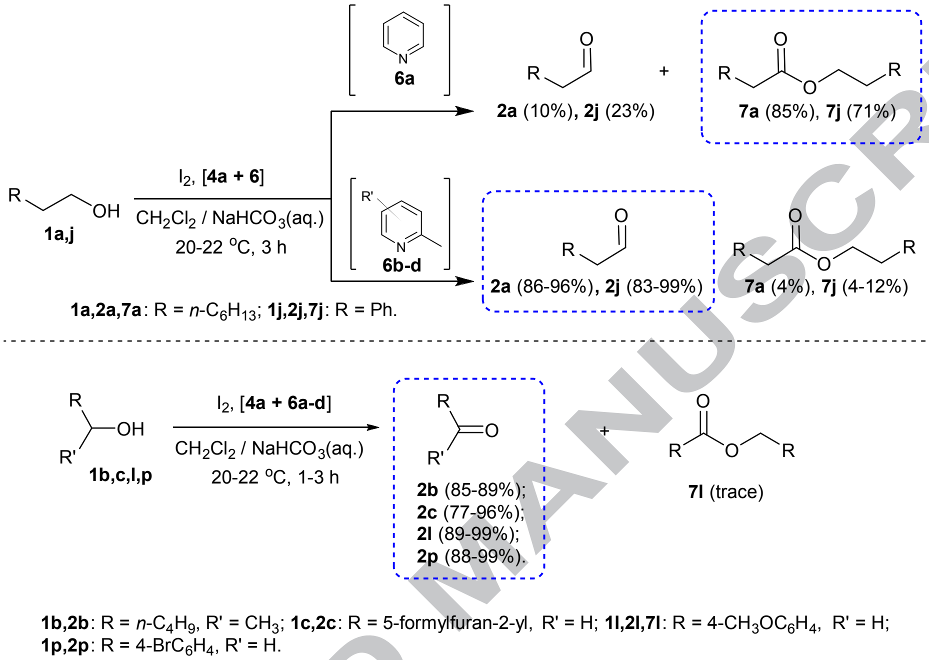
Scheme 3. Oxidation of alcohols **1a-z** with I_2 catalyzed by compound **4a** in the absence of a pyridine co-catalyst (for details, see ESI, Table S05; for the structures of R and R′, see Table 1).

Therefore, despite some similarities to stoichiometric oxidation reactions with oxoammonium salts,[7,10] the nitroxide-catalyzed oxidation of alcohols with iodine in $CH_2Cl_2/NaHCO_3$ (aq.) differs in terms of the rate and selectivity compared to the majority of nitroxide-catalyzed oxidation reactions in two-phase systems.[9,18,22,32,36] From the results described above, it became apparent that additional provisions were needed to enhance the oxidation rate and selectivity, particularly in the case of primary aliphatic alcohols. Therefore, catalysis with various pyridines was investigated.

We studied the effects of catalytic amounts of pyridine **6a** and alkyl-substituted pyridines **6b-d** on the oxidation reactions of various alcohols (Scheme 4; ESI, Table S07). It was revealed that the addition of compounds **6a-d** accelerated the oxidation sufficiently compared to experiments without the addition of the pyridine, in particular for the oxidation of primary aliphatic alcohols **1a,j**. However, the selectivity for the reactions of alcohols **1a,j** was highly susceptible to the structure of the co-catalyst: unsubstituted pyridine **6a** afforded predominantly dimeric esters **7a,j**, while substituted pyridines **6b-d** provided the corresponding aldehydes **2a,j** as the major products (Scheme 4). The highest yields of aldehydes were observed in the presence of 2,6-dimethylpyridine (lutidine, **6c**) and, in particular, 2,4,6-trimethylpyridine (collidine, **6d**).

The observed selectivities for the oxidation of primary aliphatic alcohols in the presence of pyridines **6a-d** (ESI, Table S07) were in agreement with the reported data regarding the effects of the structures of pyridine bases on the selectivities for the stoichiometric oxidation of alcohols using oxoammonium salts: unsubstituted pyridine promotes the formation of dimeric esters, while 2,6-disubstituted pyridines produce aldehydes.[12] The reaction rates reflected by the overall conversions correlate with the basicities of compounds **6a-d** and were highest in the presence of collidine **6d** (ESI, Table S07). Once again, these observations agree with the relative energies calculated for the H-bonded complexes between the oxoammonium cations, alcohols and various pyridine bases, which have been proposed as transition states (**TS-1**) in the pyridine-base catalyzed oxidation of alcohols to aldehydes or ketones (Fig. 2).[12] Therefore, the most likely mechanism for the reaction is analogous to the recently described mechanism for the stoichiometric oxidation of alcohols using oxoammonium salts in the presence of pyridine bases (for details, see ESI, Section 2).[12] According to the proposed mechanism, the pyridine bases **6a-d** catalyze the oxidation of alcohols to aldehydes/ketones *via* **TS-1**. However, unsubstituted pyridine **6a** is prone to the formation of betaines **I-2** with aliphatic aldehydes (Fig. 2). Betaines **I-2** are readily oxidized to *N*-acyl pyridinium ions, which further react with alcohols to form dimeric esters **7**. The steric effects of substituted pyridines **6b-d** deter the formation of betaines **I-2**. Therefore, compounds **6b-d** are more appropriate co-catalysts for the oxidation of primary alcohols to aldehydes.

Among compounds **6**, collidine **6d** was chosen as the best co-catalyst. The reaction conditions were additionally optimized using the oxidation of biomass-derived 5-hydroxylmethylfurfural (**1c**, HMF)[37,38] into dialdehyde **2c** (ESI, Table S08). Considering the overall results, a molar ratio of I_2:**4a**:**6d**:alcohol = 2:0.05:0.1:1 was determined as the optimal ratio for the preparative oxidation of alcohols to aldehydes or ketones.



Scheme 4. Oxidation reactions of alcohols **1a,b,c,j,l,p** with I_2 using nitroxide **4a** as a pre-catalyst and various pyridines **6a-d** as co-catalysts. The highest yields achieved for each co-catalyst **6a-d** are shown (for further details, see ESI, Table S07).

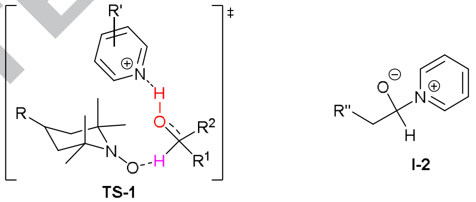
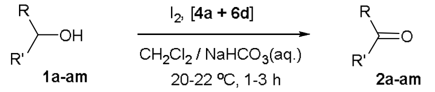
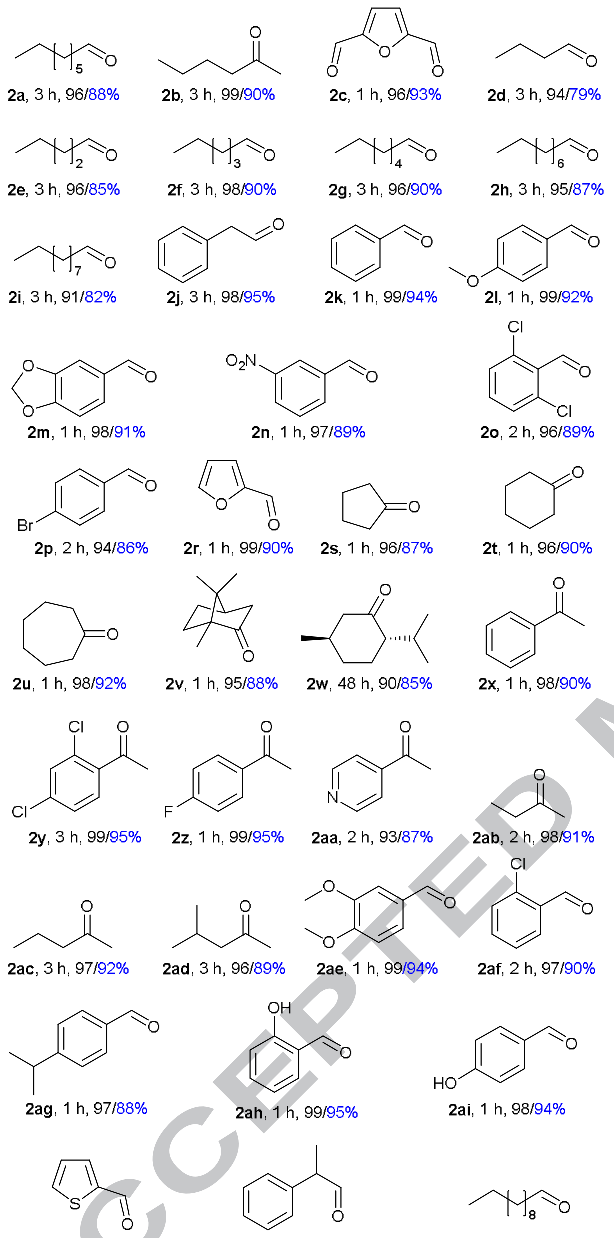


Figure 2. Structures of the transition state (**TS-1**) for the pyridine-base-catalyzed oxidation of alcohols to aldehydes/ketones and the key intermediate **I-2** for the adverse pyridine-catalyzed formation of dimeric esters during the oxidation of primary aliphatic alcohols (for further details, see ESI, Section 2).

Table 1. Synthetic scope for preparation of aldehydes and ketones **2a-al** *via* the optimized procedure[a]





2a, 3 h, 96/88%
2b, 3 h, 99/90%
2c, 1 h, 96/93%
2d, 3 h, 94/79%
2e, 3 h, 96/85%
2f, 3 h, 98/90%
2g, 3 h, 96/90%
2h, 3 h, 95/87%
2i, 3 h, 91/82%
2j, 3 h, 98/95%
2k, 1 h, 99/94%
2l, 1 h, 99/92%
2m, 1 h, 98/91%
2n, 1 h, 97/89%
2o, 2 h, 96/89%
2p, 2 h, 94/86%
2r, 1 h, 99/90%
2s, 1 h, 96/87%
2t, 1 h, 96/90%
2u, 1 h, 98/92%
2v, 1 h, 95/88%
2w, 48 h, 90/85%
2x, 1 h, 98/90%
2y, 3 h, 99/95%
2z, 1 h, 99/95%
2aa, 2 h, 93/87%
2ab, 2 h, 98/91%
2ac, 3 h, 97/92%
2ad, 3 h, 96/89%
2ae, 1 h, 99/94%
2af, 2 h, 97/90%
2ag, 1 h, 97/88%
2ah, 1 h, 99/95%
2ai, 1 h, 98/94%
2aj, 1 h, 97/91%
2ak, 2 h, 98/91%
2al, 2 h, 99/90%

[a] Reagents and conditions: **1a-am** (8 mmol), nitroxide **4a** (0.4 mmol), collidine **6d** (0.8 mmol), CH_2Cl_2 (10 mL), $NaHCO_3$ (24 mmol), water (10 mL), I_2 (16 mmol), 20-22 °C, 1-3 h; corresponding reaction times and GC/isolated yields are shown under each product (for details, see ESI, sections 1.9-1.10).

Thus, with the optimized reaction conditions in hand, we performed the preparative synthesis of 2,5-diformylfuran (**2c**, DFF), a monomer of great utility,[17,38,39] from biomass-derived 5-hydroxylmethylfurfural (**1c**, HMF)[37,38,40] on a 10 g scale. Crude dialdehyde **2c** was obtained in 93% yield with 97% purity, and recrystallization from water afforded **2c** (99% purity) in 88% yield (Table 1).

The synthetic scope of the developed method was demonstrated using 37 examples of primary and secondary alcohols (Table 1). Most of the carbonyl compounds **2a-al** were obtained in 85-95% isolated yields (GC yields up to 99%), even in the case of highly susceptible electron-rich furan and phenol derivatives.

3. Conclusion

In conclusion, an efficient method for the selective oxidation of primary and secondary alcohols to aldehydes and ketones, respectively, in a two-phase $CH_2Cl_2/NaHCO_3$ (aq.) system was developed. The key features of the method are (i) the use of elemental iodine as a mild oxidant, preventing the halogenation of electron-rich substrates, and (ii) the application of a catalytic system comprising of 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl (or the analogous nitroxides) in combination with collidine. The catalytic system not only accelerates the oxidations of alcohols, but also prevents the formation of dimeric esters from the corresponding primary aliphatic alcohols. The advantages of the method are the wide synthetic scope, the simplicity of the synthetic and isolation procedures, and the low-cost of the transition-metal-free catalytic system and oxidizing reagent. The scalability of the method was demonstrated by the high-yielding synthesis of DFF, a valuable monomer and chemical, from biomass-derived HMF.

Acknowledgments

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Supplementary Material

Supplementary data (synthetic procedures and characterization of isolated compounds, discussion of reaction mechanism, NMR spectra and GC-MS data) associated with this article can be found in the online version at doi:.

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Highlights

- Selective catalytic oxidation of alcohols to aldehydes or ketones.
- Elemental iodine as a mild oxidant.
- TEMPO-like nitroxide combined with 2,4,6-collidine as an efficient catalytic system.
- Wide synthetic scope and the simplicity of the synthetic and isolation procedures.
- Gram-scale synthesis of 2,5-diformylfuran (DFF) from 5-hydroxylmethylfurfural (HMF).