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A Novel Access to Carbonyl and Acetylated Compounds: the Role of *tetra-n*-Butylammonium Bromide/Sodium Nitrite Catalyst⁺

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A novel aerobic oxidation of alcohols without the use of any oxidants was developed. An equimolar catalytic mixture of *tetra-n*-butylammonium bromide and sodium nitrite catalyzes the aerobic selective oxidation of benzylic alcohols under oxidant-free, base-free and metal-free conditions. The mild reaction conditions allow oxidation of a wide range of benzylic alcohols, chemo-selectively to their carbonyl compounds (68-93% isolated yields). More importantly, high selectivity among different kinds of alcohols (aromatic *vs* aliphatic alcohols, primary *vs* secondary alcohols as well as alcohols having neutral rings *vs* electron-deficient rings) is available by this approach. The method surprisingly switched over to be an efficient acetylation approach in the case of aliphatic alcohols without the use of any transition metal, phosphorous or other toxic reagents or any need for using toxic acyl halides, sulfonyl halides, anhydrides, etc by the utility of only acetic acid as reagent.

Introduction

With a quick search into the processes used for the synthesis of intermediates and chemicals of industrial interest, one can find selective catalytic oxidation of alcohols as one of the most important transformations.¹ Traditionally, various oxidants, from toxic chromium and manganese oxides ² to hydrogen peroxide,³ *tert*-butylhydroperoxide,⁴ hypervalent iodine reagents,⁵ NaOCI/TEMPO,⁶ Swern reagent ⁷ ozone,² etc., were used for this transformation.

About two centuries after the Berzelius classification of aerobic oxidation of ethanol in contact with platinum as his explanation about catalysis, use of "air" in oxidation of alcohols has gained much interest especially because of the evolutions related to *'Green Chemistry guideline to reach sustainable development*".⁸ Although aerobic oxidation is the most atom-economical and environmentally benign oxidation of alcohols, since H₂O is produced as the only by-product, there are some limitations such as the need for pure oxygen,⁹ requirement of activating the O=O bond due to the large energy-gap between O₂ and organic compounds, and use of halogenated solvents¹⁰ that must be addressed.

Numerous palladium homogeneous and heterogeneous catalysts have been introduced for this purpose since the late 1990s.¹¹ In addition, some other noble metals such as gold, ruthenium, platinum, copper and rhodium as well as their



Our research was inspired by the results of the $Br_2/AcOH$ oxidation system by Crimmins et al.,¹⁸ the NaBr-NaBrO₃ system by Joshi et al.,¹⁹ the NaNO₂/DDQ/AcOH system by Wang et al. ²⁰ and the TEMPO/Br₂/NaNO₂ system by Liu and co-workers.²¹ In two first procedures, the bromine as well as *in situ* generated bromonium ion acted as a mild selective oxidant for the oxidation of alcohols. In the third, it was shown that sodium nitirite was able to produce NO, which was oxidized to NO₂ by the air. However, from the Liu work, re-oxidation of HBr to Br₂ by NO₂ was shown. We reasoned that if HBr can be oxidized to regenerate Br₂ by NO₂ and if NO/NO₂-cycle could

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be formed by molecular oxygen, thus a sodium nitritecatalyzed process with a catalytic amount of Br anion in the presence of the air could be established. With respect to the growing need for development of clean and benign catalytic processes, this research is concerned with the design of an extremely efficient and more importantly *a greener* catalytic way for the aerobic oxidation of alcohols free from any transition metal, as well as any oxidants such as DDQ, TBHP, TEMPO, etc. Herein, a novel access to acetate esters is introduced as well.

Results and discussion

With the eliminating of external oxidants in mind, initial investigation of sodium nitrite-catalyzed aerobic oxidation was carried out using benzyl alcohol as substrate with 5 mol % of TBAB, 2.5 mol % of sodium nitrite and an air balloon under 80 $^{\circ}$ C for 6 h. The preliminary result (62% conversion by GC) clearly showed that the overall plan was true (Scheme 1).



Scheme 1 Initial investigation of NaNO2-catalyzed aerobic oxidation of benzyl alcohol

Reducing the reaction time to 2 h, did not decrease the conversion of the reaction. In the absence of sodium nitrite, only about 6% conversion was observed. It proved that $NaNO_2$ acted as a bridge between O_2 and Br_2 oxidation-reduction cycles.¹⁸

The reaction was repeated under 100 °C, 70 °C and 50 °C. In all three cases the reaction led to the desired product but the best result was achieved at 70 °C. Indeed, the invented catalytic system exhibited high chemoselectivities at investigated conditions. Systematic screening of the reaction conditions was done precisely by using various "NO₂" sources, various "halide" sources and different kinds of solvents (Table 1). When pure oxygen gas was used to replace air, no detectable change in the isolated yield was achieved. Proving the role of molecular oxygen of the air as oxidant was also examined. Under a nitrogen atmosphere, the reaction was conducted and no notable product was observed even after 24 h.

Table 1 Screening the reaction conditions



Entry	NO ₂ source (mol %)	Halide source (mol %)	Solvent (0.5 mL)	Isolated Yield % ^a	Selectivity%
1	NaNO ₂ (2.5)	TBAB (5)	AcOH	67	100
2	NaNO ₂ (5)	TBAB (5)	AcOH	93	100
3	NaNO ₂ (10)	TBAB (5)	AcOH	75	100
4	NaNO ₂ (5)	TBAB (2.5)	AcOH	58	100
5	NaNO ₂ (5)	TBAB (10)	AcOH	90	100
6	AgNO ₂ (5)	TBAB (5)	AcOH	83	100
7	NaNO ₂ (5)	KBr (5)	AcOH	44	100
8	NaNO ₂ (5)	NaBr (5)	AcOH	51	100
9	NaNO ₂ (5)	TBAI (5)	AcOH	57	100
10	NaNO ₂ (5)	TBAB (5)	Toluene	<5	-
11	NaNO ₂ (5)	TBAB (5)	DCM	<5	-
12	NaNO ₂ (5)	TBAB (5)	Acetonitrile	<9	-
13	NaNO ₂ (5)	TBAB (5)	AcOH/DCM (1:2)	17	100
14	-	TBAB (5)	AcOH	<5	-
15	NaNO ₂ (5)	-	AcOH	<10	-
16	-	-	AcOH	<5	-
17 ^b	NaNO ₂ (5)	TBAB (5)	AcOH	92	100
18 ^c	NaNO ₂ (5)	TBAB (5)	AcOH	<5	-

^{a)} Determined after isolation by flash chromatography.^{b)} Under pure O₂ balloon.^{c)} Under N₂ atmosphere after 24 h.

Under the optimized conditions (1 mmol of alcohol, 5 mol % of NaNO₂, 5 mol % of TBAB, an air balloon and in 0.5 mL of acetic acid at 70 $^{\circ}$ C), reactivity of various benzylic alcohols as well as

aliphatic alcohols was investigated during 2-16 h and the results were recorded (Table 2).

The best results were obtained with benzyl alcohol itself in addition to methyl and halide substituents on the aromatic

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ring (entries 1-5). In the case of *ortho*-bromobenzyl alcohol, a more bulky alcohol, the reaction led to the desired product in 73% isolated yield (entry 6). Electron-withdrawing groups such as nitro- and trifluoromethyl groups slightly reduced the rate and yield of the reaction (entries 7-12). The reaction of both *ortho* and *para*-methoxybenzyl alcohols simply led to a mess of products. Repeating the reactions at room temperature, however, led to the same result (entries 13-14). Both lowering the reaction time to 10 minutes in one additional try and decreasing the amounts of acetic acid from 0.5 mL into 0.08 mL in another brought about no change and the same dirty mixture of products were obtained. Fortunately, 4-

phenoxybenzyl alcohol oxidized in the reaction conditions resulted in 4-phenoxybenzaldehyde in about 82% isolated yield (entry 15).

The method worked well for the aromatic alcohols, with the exception of 5-(hydroxymethyl)furan-2-carbaldehyde, a heteroaromatic alcohol, in which the reaction surprisingly led to the acetylated alcohol, that is, (5-formylfuran-2-yl)methyl acetate in 90% isolated yield (entry 16, see supporting information S16). 1-phenylethanol, a secondary benzylic alcohol, was also oxidized to acetophenone, a ketone, in 68% isolated yield (entry 17).

Table 2 Oxidation of Benzylic Alcohols Catalyzed by TBAB/NaNO $_2$



Reaction conditions: Alcohol (1 mmol), TBAB (5 mol %), NaNO₂ (5 mol %), AcOH (0.5 mL), 70 °C under air balloon. Just the isolated yields are reported. ^{a)} The acetylated alcohol was obtained.

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Another outstanding outcome was gained when primary aliphatic alcohols with or without aromatic moiety were exploited instead of benzylic alcohols. Surprisingly, in these cases, the process that observed in the case of 5-(hydroxymethyl)furan-2-carbaldehyde (entry 16, table 2) was repeated. Indeed, the reaction of cyclohexylmethanol, 3-phenylpropan-1-ol, 3-cyclohexylpropan-1-ol, 2-ntolylethanol, 4-phenylbutan-1-ol, 5-phenylbutan-1-ol and 2-(N-benzyl-N-methylamino)ethanol led to the corresponding 'acetylated alcohols' in excellent isolated yields (Table 3, entries 1-7, see supporting information) without production of oxidation products. The reaction of cinnamyl alcohol as an allyl alcohol resulted in the production of cinnamaldehyde in 8% isolated yield (entry 8). Because a double bond is present, it was thought that the addition product (bromoacetate product) would be the main product, but more detailed investigations showed that it was not the case. Instead, it was again the acetylated cinnamyl alcohol that was formed (60% isolated yield). Interestingly, in the case of cyclohexanol and cyclopentanol, *secondary aliphatic alcohols*, no product was obtained after 16 h. With increasing the amount of the catalyst to 10 mol %, no improvement in the yield was observed (entries 9 and 10).

Table 3 Acetylation of Aliphatic Alcohols in the presence of Acetic acid as reagent and Catalyzed by TBAB/NaNO2



Reaction conditions: Alcohol (1 mmol), TBAB (5 mol %), NaNO₂ (5 mol %), AcOH (0.5 mL), 70 °C under air balloon. Just the isolated yields are reported. The yields for aerobic oxidation are in parentheses.

To the best of our knowledge, to date there have been many reports of alcohol acetylation which require acetylating agents such as *vinyl acetate* in the presence of 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane in *toluene*,²² *vinyl acetate* in the presence of enzymes,²³ acetic anhydride

in the presence of TiO(OTf)₂ in *dichloromethane*²⁴ or magnesium ²⁵/molybdenum ²⁶/boron compounds.²⁷ In addition, *N*-acetyl heterocycles such as 2-acetyl-4,5-dichloropyridazin-3(2H)-one in *tetrahydrofuran*,²⁸ *acetyl chloride* in the presence of titanium,²⁹ zirconium ³⁰ or

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bismuth compounds,³¹ acetyl acetone in the presence of iron(III) ³² or indium compounds,³³ ethyl acetate in the presence of 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane ³ or $K_5COW_{12}O_{40}$,³⁵ and methyl acetate with N(Et)₄ClO₄³⁶ or $Bu_4N[Fe(CO)_3(NO)]^{37}$ are other examples of reported methods. Among them, there are also some procedures that used acetic acid as the acetylating agent in which toxic/expensive/corrosive reagents and solvents were also utilized over and above acetic acid namely: scandium tris(trifluoromethanesulfonate),³⁸ $K_5COW_{12}O_{40}$,³⁵ perchloric acid,³⁹ ion-exchange resin in *benzene*,⁴⁰ ytterbium perfluorooctanesulfonate in toluene,⁴¹ porous polyphenolsulfonic acid formaldehyde resin,42 silica gel acid,43 immobilized perchloric pyridine/Nbromosuccinmide/triphenylphosphine in dichloromethane $^{\rm 44}$ and $S_4B_{15}W_{12.5}$ borated zirconia modified with ammonium metatungstate in toluene.45

In fact, the most fundamental problem of all foregoing methods can be summarized into the 'environmental issue'.

Part 1:

Having toxic/carcinogenic/corrosive/inaccessible reagents often in *toxic solvents* are among these drawbacks.

As shown in table 3, the method introduced a novel strategy for *selective acetylation of primary aliphatic alcohols* free from any toxic/corrosive acetylating agent or solvent and/or expensive and toxic heavy metal. Acetic acid is the only reagent used in this method.

Based on the results obtained from the electron-rich rings, and the acetylation of primary aliphatic alcohols, we proposed a mechanism which could interpret all of the observations of the invented method. A conceivable mechanism of this new metal-free aerobic oxidation of benzylic alcohols and acetylation of aliphatic alcohols is illustrated in Scheme 2.



Scheme 2 Proposed mechanism for the aerobic oxidation of benzylic alcohols and acetylation of primary aliphatic alcohols in the reaction conditions

Generation of the nitrosonium ion from the NaNO₂ in the presence of acetic acid, 13e,46 initiates the overall reaction.

The reaction smoothly continues by oxidation of NO⁺ to NO₂⁺ by the air,^{13a,13e,46c} followed by oxidation of Br⁻ to Br₂

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via the *in situ* generated NO₂^{+.13a,47} Finally, in part 2, for the benzylic alcohols, oxidation of alcohol by the *in situ* generated Br₂ occurs via a conjugation forced E2 elimination mechanism and a new and efficient metal- and oxidant-free aerobic oxidation of alcohols is formed.

In part 2, for the primary aliphatic alcohols, it seems that since there is no conjugation driving force for the E2 reaction, the bimolecular nucleophilic substitution reaction between the acetate anion and the intermediate occurs and results in the acetylated products. This mechanism can also explain why the reaction is not successful in the case of the secondary aliphatic alcohols. They are unreactive in the reaction conditions because neither the conjugation driving force, as is the case for the benzylic alcohols, nor the absence of the steric hindrance, as is ideal for the primary aliphatic alcohols, are present.

Unexpected results gained from the electron-rich ortho and para-methoxybenzyl alcohol as well as the acetylation of alcohol on the electron-rich furan ring, led us to the hypothesis that in these cases, however, the ring helps the loss of leaving group in the intermediate and consequently, instead of $S_N 2$, that is the unimolecular nucleophilic substitution reaction which wins its competition with E2 mechanism. Therefore, one can interpret the polymerization of the reaction mixture in the case of strongly electron-rich methoxybenzyl alcohols and acetylation of alcohol on the moderate electron-rich furan ring (scheme 3).



Scheme 3 The proposed mechanism for the polymerization of methoxybenzyl alcohols and unexpected acetylation of aromatic 5-(hydroxymethyl)furan-2-carbaldehyde

Competitive reactions between different alcohols were also investigated (Table 4). When a mixture of 4-methylbenzyl alcohol and 4-methyl-2-nitrobenzyl alcohol was applied simultaneously, 4-methylbenzyl alcohol was oxidized in 68% yield as the major product but conversion of nitrocontaining alcohol proceeded only about 23% (entry 1). The same trend was observed when competitive reaction was conducted between 4-methylbenzyl alcohol and 4nitrobenzyl alcohol (entry 2). In this respect, when competition was hold between a primary benzyl alcohol, 4methylbenzyl alcohol, and a secondary benzyl alcohol, 1phenylethanol, oxidation occurred in favour of the former with high selectivity (entry 3). Fortunately, the same excellent selectivity was observed in the case of the competition between 4-methylbenzyl alcohol and the aliphatic alcohols (entries 4, 5 and 7). However, there is an exception in entry 6, in which the benzylic alcohol used did not show a reliable selectivity.

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^{a)} Reaction conditions: alcohols (1 mmol each), TBAB (5 mol %), NaNO₂ (5 mol %), AcOH (0.5 mL), 70 °C, air balloon, quenched after 2 h. ^{b)} Determined based on the isolated yields. ^{C)} Determined after isolation by the iodine-treated preparative TLC chromatography method.

Regarding important guiding principle of green chemistry, the design of environmentally benign processes (benign by design), it is better to prevent wastes than to treat wastes.⁴⁸ By this method, selective aerobic oxidation of benzylic alcohols and acetylation of primary aliphatic alcohols were accessible without using any oxidants (unless air)/any toxic acetylation agents/expensive transition metal complexes nor an *equimolar* amounts of halide sources.

Conclusions

In summary, we have introduced a solution to eliminate the use of toxic and/or explosive oxidants in aerobic oxidation

of benzylic alcohols for the first time. A variety of benzylic alcohols selectively converted to their carbonyl compounds (14 examples, 68-93% isolated yields) under air and without the use of any harsh and environmentally unbenign oxidant such as DDQ, TBHP, TEMPO, etc, even in catalytic amounts. More importantly, the method works successfully for the oxidation of alcohols having electron-withdrawing groups at *ortho-, meta-* and *para-*positions as well as bulky groups even at *ortho-*position. In addition, a high selectivity among different kinds of alcohols is provided by this method. One can oxidize a benzyl alcohol having a neutral group in the presence of a benzyl alcohol having an electron-withdrawing group. Similarly, selective oxidation of primary alcohols in the presence of secondary ones as well as

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selective oxidation of benzyl alcohols in the presence of aliphatic alcohols is available. The observed high selectivity of the reaction results from such a mild oxidant-free condition.

Furthermore, the method also worked well to acetylate primary aliphatic alcohols selectively and solely by the utility of acetic acid as reagent (instead of carcinogenic acyl halides, mutagenic sulfonyl halides, anhydrides, etc). This is the first report of significant contribution of catalytic sodium nitrite/air system to design environmentally benign processes. The simplicity in running, reduction in the cost and toxicity of the reagents, reduction of the wastes and more importantly, high selectivity of the function introduce a novel and sustainable catalytic system for organic chemical synthesis.

Experimental Section

General Procedure for the aerobic oxidation of benzylic alcohols and acetylation of primary aliphatic alcohols

A mixture of alcohol (1 mmol), sodium nitrite (0.05 mmol, 5 mol %), tetra-n-butylammonium bromide (TBAB, 0.05 mmol, 5 mol %), and acetic acid (0.5 mL) was prepared in a two-necked flask and then the flask filled with air by use of a balloon. The reaction mixture stirred at 70 °C and the progress of the reaction was monitored by means of TLC. After completion of the reaction followed by addition of dichloromethane (5 mL) to the reaction flask, the mixture was centrifuged and the solute was separated and dried with sodium sulfate. After evaporation of dichloromethane and chromatographic purification, the structures of carbonyl/acetylated products were proved by the comparison of their ¹HNMR by related literatures.

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