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An efficient sonochemical oxidation of benzyl alcohols into benzaldehydes by $FeCl_3/HNO_3$ in acetone

Ramesh Naik [a], Aatika Nizam [a], Aisha Siddekha [b], M.A. Pasha [a,*]

[a] Department of Studies in Chemistry, Central College Campus, Bangalore University, Bengaluru 560 001, India
[b] Department of Chemistry, Smt. V. H. D. Central Institute of Home Science, Bengaluru 560 001, India

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ABSTRACT

Sonochemical oxidation of benzyl alcohols into corresponding aldehydes by $FeCl_3/HNO_3$ in acetone at room temperature has been reported. All substrates give good yield of the products within 10–25 min. The reaction of selected substrates were also studied under reflux and at the room temperature. Further, various Lewis acids were used to evaluate their catalytic efficacy.

1. Introduction

Oxidation of benzyl alcohols into corresponding araldehydes is an important and key transformation [1] since many araldehydes are useful precursors for various organic transformations which find a multitude of industrial applications being intermediates for the synthesis of pharmaceutical and agricultural chemicals. In particular, the oxidation of benzyl alcohol to benzaldehyde, is an important organic transformation as benzaldehyde is a very valuable chemical which has widespread applications in perfumery, dyestuff and agro chemical industries [2].

As there is a growing need for the synthesis of fine chemicals and pharmaceutical intermediates employing "green" technologies, ultrasound has gained importance as a clean and useful tool in accelerating chemical reactions when compared to traditional methods and hence a large number of organic reactions have been reported employing this technology in the past three decades. [3] Not only does acceleration of a chemical reaction takes place but ultrasound is also beneficial in other ways like (i) less purified or cruder reagents can be employed; (ii) avoids forcing conditions like high temperature and high pressure; (iii) improves yields of the products; (iv) reactions occur in shorter durations and (v) is helpful in reducing the number of steps in a reaction thereby simplifying the process, hence, making the protocol green and cost effective.

We, in our lab, have been working on the synthesis and functional group transformations using ultrasound. A few important reports include, the synthesis of δ-chloroesters [4], reduction of nitroarenes to anilines, [5] reduction of nitroarenes to azoarenes, [6] regioselective synthesis of β-iodoethers from olefin-I_2-alcohol, [7] esterification of phenols [8] and very recently the synthesis of amidoalkyl-2-naphthols [9].

Representative oxidants for the oxidation of benzyl alcohols to the corresponding benzaldehydes include use of chromium(VI) reagents, [10] transition metal nitrates on solid supports, [11] hypervalent iodine [12], and dimethyl sulfoxides/HBr [13]. In addition Luzzio et al. employed a modified Corey-Suggs protocol [14] and Stefan Toma used a heterogeneous mixture of $KMnO_4$, $CuSO_4{\cdot}5H_2O$ in dichloromethane [15] for the purpose. Other reports include use of metal complexes such as $RuCl_2(PPh_3)_3$, [16] and $ZrO(OAc)_2$/PhIO or *tert*-butylhydroperoxide as oxidants, [17] and SeO_2-bis(4-anisyl) selenoxide [18]. The disadvantages associated with the above protocols are: (i) many of the methods are incompatible with other functional groups in the substrates; (ii) require stoichiometric amounts of catalyst; (iii) long duration of reaction; (iv) purification of products due to the formation of byproducts, and (iv) heavy metal wastes are left out after the reaction. Hence, in continuation of our ongoing project on developing efficient and environmentally friendly methods for different organic transformations under different conditions, [19] we wish to report a facile route for the oxidation of benzyl alcohols into corresponding aromatic aldehydes under ultrasound irradiation using a mixture of $FeCl_3$ and HNO_3 in acetone (Scheme 1) as an efficient oxidizing agent. The advantages associated with the present method are: (i) the catalyst used is readily available, (ii) is inexpensive and environmentally compatible; (iii) the reaction takes place in a shorter duration;

* Corresponding author. Tel.: +91 80 22961337; fax: +91 80 22961331.
E-mail address: m_af_pasha@ymail.com (M.A. Pasha).

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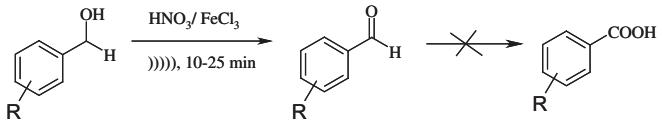


Scheme 1. Synthesis of substituted benzaldehydes.

(iv) gives very good yield of the desired products; and (v) does not give the over-oxidized/undesired nitrated products.

2. Methods

2.1. Materials and instruments

All starting materials were commercial products, and all were used without further purification. Yields refer to yield of the isolated products. Melting points were measured on a Raaga, Chennai, Indian make melting point apparatus. Boiling points were measured using open capillary method and are corrected. Nuclear magnetic resonance spectra were obtained on a 400 MHz Bruker AMX instrument in DMSO-d_6 using TMS as standard. Infrared spectra were recorded using Shimadzu FT-IR-8400s spectrophotometer. All the reactions were studied using SIDILU, Indian make sonic bath working at 35 kHz of power 120 W (constant frequency) maintained at room temperature (by circulating water) without mechanical stirring.

2.2. Procedure for the oxidation of benzyl alcohol

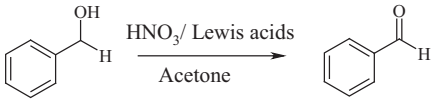
Benzyl alcohol (1 mmol), HNO_3 (0.5 mmol) and $FeCl_3$ (0.5 mmol) in 5 mL acetone was sonicated at 35 kHz for 10 min. After complete conversion (monitored on TLC), acetone was evaporated, diluted with water and extracted with ether (3 × 10 mL). The ether extract was washed with saturated $NaHCO_3$, dried over anhyd. Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography using EtOAc/ Pet. Ether (5:95) to get benzaldehyde (94%).

3. Results and discussion

A mixture of benzyl alcohols, $FeCl_3$ and HNO_3 in acetone were sonicated at 35 kHz for 10 min to convert benzyl alcohols into corresponding aldehydes (Scheme 1). Experimental evidences showed that, for every equivalent of benzyl alcohol 0.5 equivalent of HNO_3 and 0.5 equivalent of $FeCl_3$ is required to get maximum yield of the aldehyde. Use of nitric acid alone at room temperature gave the aldehyde as well as nitration product. Further, use of only $FeCl_3$ does not give the expected product and the starting compound was recovered intact. Hence, $FeCl_3$ in conjugation with HNO_3 was employed for oxidation and we found that neither ring nitration nor nitrate esters were formed.

In order to achieve the maximum yield using the above protocol, various reactions were carried out using benzyl alcohol as the representative substrate. Firstly, the reaction was done without any catalyst under several reaction conditions, as no desired product was obtained, a mixture of HNO_3/$FeCl_3$ was used as catalyst under different reaction conditions such as silent and reflux, formation of product was observed after longer duration, hence the reaction was subjected to ultrasonic irradiation initially for 2 min, but no product was detected, sonication was then continued for 4 min, product formation was noticed, the reaction was continued further to 6 min, 8 min and 10 min, and after 10 min complete conversion of benzyl alcohol into benzaldehyde occurred. Continuation of sonication for 20 min, did not affect the yield or gave over-oxidized product – benzoic acid. After this, various other Lewis acids along with HNO_3 under sonic condition were taken up and the result of all these studies are presented in the Table 1.

Table 1
Use of different Lewis acids in the oxidation of benzyl alcohol by HNO_3 under different conditions.



Trial	Lewis acid	Condition	Time	Conversion (%)	Yield (%)
1	$FeCl_3$	)))))	10 min	100	94
2	$FeCl_3$	Silent	12 h	100[a]	50
3	$FeCl_3$	Reflux	4 h	100[b]	20
4	–	)))))	80 min	5	–
5	–	Silent	12 h	–	–
6	–	Reflux	5 h	100[c]	–
7	CuCl	)))))	1 h	20	5
8	$CuCl_2$	)))))	1 h	30	5
9	$ZnCl_2$	)))))	25 min	70	45
10	$SnCl_2$	)))))	0.5 h	70	40
11	$MgCl_2$	)))))	1.5 h	10	–
12	$CoCl_2$	)))))	40 min	70	40
13	$NiCl_2$	)))))	1.5 h	20	5
14	–	)))))[d]	1 h	–	–

[a] 1:1 benzaldehyde and benzoic acid.
[b] Benzoic acid with trace of benzaldehyde.
[c] Only benzoic acid.
[d] In the absence of HNO_3.

From the Table 1 it is clear that, FeCl3 is the best catalyst for the complete conversion of benzyl alcohol into benzaldehyde under ultrasonic condition, as the desired product yield is obtained is 94% within 10 min. It is noted that, when a similar reaction was carried out under silent and reflux condition, after 12 h and 4 h the product yield was only 50% and 20% respectively. From these results it is evident that ultrasound has a great role in enhancing the rate of the reaction and the yield of the desired product.

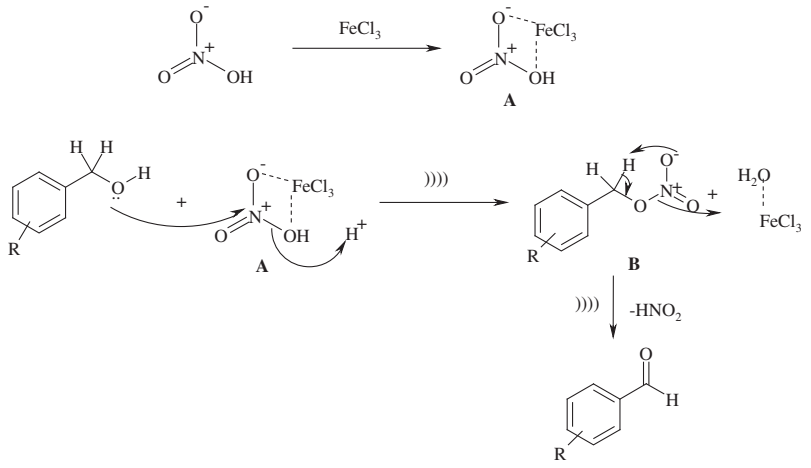
After, establishing the applicability of ultrasound for the oxidation of benzyl alcohols, we then examined the effect of solvent on this reaction; in solvents such as CH_3CN, DMSO, DMF, THF, CH_2Cl_2, $CHCl_3$ and CCl_4 the reaction was comparatively faster and in contrast slow oxidation occurred in solvents like petroleum ether, hexane, benzene and toluene but best results were obtained when reaction was carried out in acetone.

The use of ultrasound in chemistry offers the synthetic chemist a method of chemical activation which has broad applications; and uses equipment which is relatively inexpensive. The driving force for sonochemical reactions is cavitation and so a general requirement is that, at least one of the phases of the reaction mixture should be a liquid.

To generalize our findings, we have extended the reaction conditions over a wide variety of primary benzyl alcohols, and the results of this study are presented in Table 2. From this table it is

Table 2
Sonochemical oxidation of benzyl alcohols by HNO_3 and $FeCl_3$.

Entry	R	Time(Min)	Yield (%)
1	C_6H_5	10	94
2	4-$CH_3C_6H_4$	12	90
3	4-$C_2H_5C_6H_4$	14	95
4	4-$MeOC_6H_4$	10	86
5	2-$MeOC_6H_4$	12	92
6	3-$NO_2C_6H_4$	25	84
7	4-$NO_2C_6H_4$	25	80
8	3-ClC_6H_4	18	88
9	4-FC_6H_4	20	86
10	Furfuryl	14	80
11	3,4-$(MeO)_2C_6H_4$	25	90



Scheme 2. A plausible mechanism for the oxidation of benzyl alcohols under sonic condition.

clear that, electron withdrawing or donating groups does not contribute to towards the rate of the reaction; and sufficiently good yields of the desired products is obtained irrespective of the substitution.

The important achievement of our work is: (i) reduction of the reaction time; (ii) control over generation of over-oxidized products and (iii) increase in the yield of the products.

4. Mechanism

The oxidation of benzyl alcohols to the corresponding aldehydes is expected to proceed *via* the activation of HNO_3 by $FeCl_3$ to give a complex **A**, followed by nucleophillic attack of the various substituted benzyl alcohols onto the complex **A** under sonic condition to give intermediate **B**, subsequent loss of HNO_2 is expected to give the required aldehyde as shown in Scheme 2.

As well known ultrasound enhances chemical reactions in a liquid medium through the generation and subsequent destruction of cavitation bubbles. Here in this study the reaction was carried out in acetone, the complex **A** generated insitu in the solution and the benzyl alcohols used formed a homogeneous mixture. When ultrasound waves propagated through the medium via a series of compression and rarefaction waves, at sufficiently high power, the rarefaction cycle exceeds the attractive forces of the molecules of the liquid and cavitation bubbles are expected to form. These bubbles grow by a process known as rectified diffusion i.e. small amounts of vapour (or gas) from the medium enters the bubble during its expansion phase and is not fully expelled during compression. The bubbles grow over the period of a few cycles to an equilibrium size for the particular frequency applied and then collapse generating high temperatures and pressures. This cavitation bubble collapse is a remarkable phenomenon induced throughout the liquid by the power of ultrasound which provides the energy needed for a chemical reaction [20].

Reaction between the complex **A** and benzyl alcohols in the homogenous mixture under the influence of ultrasound may take place in:

I. the bulk liquid immediately surrounding the bubble which collapses activating the reactants surrounding it, hence exerting force on the reactants thereby enhancing the reaction, and
II. in the bubble itself where the reactants enter during its formation are subjected to extreme conditions of temperature and pressure on collapse leading to chemical reaction between them.
III. unlike cavitation bubble collapse in the bulk liquid, collapse of a cavitation bubble may occur near the surface of the reaction vessel unsymmetrically, because the surface provides resistance to liquid flow from that side. The result is an inrush of liquid predominantly from the side of the bubble remote from the surface resulting in a powerful liquid jet being formed. This high pressure jet may impart activation of the reactants and may increase the rate of the reaction.

All the above processes of bubble collapse may provide sufficient energy required for the present reaction to take place and afford the final product.

5. Conclusion

In conclusion we have developed a simple and efficient method for the oxidation of primary benzyl alcohols into corresponding benzaldehydes using a mixture of HNO_3 and $FeCl_3$ as a catalyst. This works very well under the influence of ultrasound and gives excellent yields of the products with in 10–25 min. The notable feature of this protocol is: over-oxidized, nitrated or nitrate ester products are not formed during the course of the reaction.

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