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Journal Name

COMMUNICATION

H₂O₂ in WEB: a highly efficient catalyst system for Dakin reactionBishwajit Saikia^{*a}, Parinita Borah^b and Nabin Chandra Barua^cReceived 00th January 20xx,
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Transition metal catalyst, ligand, base, toxic or hazardous reagent, additives/promoters and organic solvent free greener Dakin reactions have been successfully carried out by using H₂O₂ in natural feedstock extract. The reaction proceeds in neat 'Water Extract of Banana' (WEB) at room temperature under aerobic conditions in very short reaction times and therefore, it is an evergreen and environmentally sound alternative to the existing protocols for the Dakin reaction. In our system, the reaction was found to afford excellent yield for the desired product with different electron-withdrawing and electron-donating hydroxylated benzaldehydes.

In Dakin reaction, an aromatic aldehyde or ketone is converted to a phenol on treatment with alkaline hydrogen peroxide, but there must be an –OH group in the *ortho*- or *para*- position.¹ Dakin's conventional procedure utilized excess H₂O₂ and NaOH at elevated reaction temperatures. The Dakin oxidation is a variation of the Baeyer–Villiger oxidation (BVO) that converts benzaldehydes to phenols by BVO and followed by hydrolysis of the intermediate aryl formate, effectively oxidizing both aryl and acyl sp² carbons.² In organic synthesis, dihydric phenols and their derivatives are important substrates and are used extensively in various fields such as agrochemicals, antioxidants, pharmaceuticals, flavoring agents, polymerization inhibitors, photographic processes *etc.*³ During the last decade, a number of research papers have been published on Dakin reaction under different reaction conditions.^{4,5} Although, majority of these techniques were found to be effective in carrying out this transformation, most of these systems are associated with several drawbacks such as the use of expensive ligands, use of stoichiometric alkylperoxides, use of toxic or hazardous reagents, requirement of large amount of catalysts, use of transition metal complex catalyst often requiring activation by elevated temperatures, use of organometallic compounds, expenditure, harsh reaction conditions, longer reaction times, use of organic

solvents, use of H₂O₂ activator and generation of toxic byproducts. Therefore, there is a continued interest in developing an efficient and safer protocol employing mild and green reaction conditions. The designer of a chemical process must choose from alternative raw materials, auxiliary materials such as solvents and catalysts, reaction pathways as well as reaction conditions and these design choices can have a very significant impact on the overall environmental performance of a chemical process.⁶ The urgent need for the development of green and sustainable processes for the use of natural 'feedstocks' in chemical synthesis as an alternative to hazardous organic solvents or other metal-based catalysts is widely recognized.⁷ Continuing our research with the aim to lower the environmental impact of this oxidation, we turned our attention to 'Water Extract of Banana' (WEB)⁸, a highly abundant natural feedstock. To the best of our knowledge this is the first simplest report for the Dakin oxidation employing H₂O₂ in neat WEB at room temperature without using any transition metal catalyst, ligand, base, toxic or hazardous reagent, additives/promoters and organic solvent. In this communication, we report on the use of water extract of banana as an all in one mixture of solvent, catalyst, ligand, base, additives/promoters *etc.* for the Dakin oxidation.

We started the aerobic Dakin oxidation of various substituted hydroxylated benzaldehydes by applying this truly non-toxic conditions using natural feedstock WEB as a neat reaction media (**Scheme 1**). During our study, the different parts (such as banana trunk, rhizome and peels) of banana ashes were extracted with water. Initially, banana ash was suspended in distilled water in a glass beaker and carefully stirred for few minutes (10–15 min) at room temperature. The mixture was then filtered and the filtrate was abbreviated as WEB here. Literature reports reveal that in WEB potassium, sodium carbonate and chloride are the major constituents along with a host of other trace elements.⁹ Similarly, the role of H₂O₂ in organic synthesis has developed increasingly over the years¹⁰ because the use of this oxidant is particularly attractive, both for its high oxygen content and the formation of water as a byproduct. Therefore, we strongly believed that this novel and greener approach represents an efficient and highly

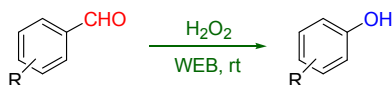
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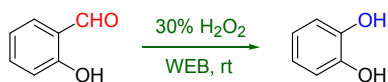
appealing alternative to the existing protocols for this significant synthetic conversion because synthetically challenging aromatic hydroxylations can be formally achieved by Dakin oxidation.



Scheme 1. Dakin oxidation of hydroxylated benzaldehydes to hydroxylated phenols

Our initial efforts focused on identifying the optimal reaction conditions for our proposed reaction and are shown in Table 1. In order to carry out this synthetic protocol, a model reaction of salicylaldehyde by using 30% H_2O_2 in neat WEB at room temperature and it was smoothly and rapidly converted into catechol in excellent yields within a very short reaction time. The conversion of salicylaldehyde to catechol was calculated by NMR, utilizing CDCl_3 as an internal standard. We firstly studied the impact of the amount of 30% H_2O_2 equivalent with respect to the substrate on this reaction. Initial reaction was conducted at room temperature using 0.092 mL (1 equiv.) of 30% H_2O_2 in WEB. We are quite satisfied to see that our reaction proceeded at room temperature and up to 80% product was isolated after a reaction time of 1 h (Table 1, entry 1). A quantitative coupling yield (98%) was obtained when the amount of 30% H_2O_2 reached to 0.185 mL (2 equiv.) (Table 1, entry 3). We were pleased to observe that all of the conditions (with different 30% H_2O_2 equiv.) we attempted resulted in the formation of catechol in good to excellent yields, establishing the feasibility of our proposed oxidation process (Table 1, entries 1–3). Mild reaction conditions, shorter reaction time, cost-effectiveness, operational simplicity and very high yields make this transformation a method of alternative for the straightforward preparation of numerous hydroxylated phenols. Within the set of previous methods⁴ highlighted herein, a solution is offered to this problem in the form of a novel, mild and green alternative for this key transformation.

Table 1. Effects of the amount of 30% H_2O_2 and time in the Dakin oxidation of salicylaldehyde in WEB at room temperature^a



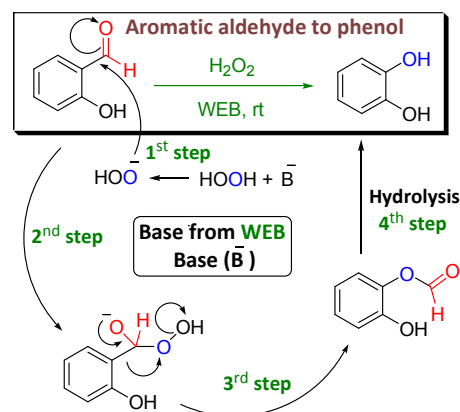
Entry	H_2O_2 (mL)	Time (min/h)	Yield ^b (%)
1	0.092 (1 equiv.)	1 h	80
2	0.139 (1.5 equiv.)	40 min	90
3	0.185 (2 equiv.)	40 min	98

^a Reaction conditions: salicylaldehyde (1 mmol), 30% H_2O_2 in WEB (3 mL) at room temperature.

^b Yields refer to isolated yields.

The mechanism and dramatic acceleration for Dakin oxidation catalyzed by WEB is the subject of much scientific interest and the exact identity of the active species remains unclear. We believe that the alkali metal carbonates such as K_2CO_3 and Na_2CO_3 present in WEB⁹ are acting as internal base here to facilitate the Dakin

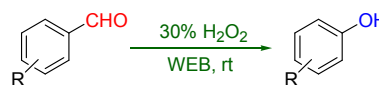
oxidations. The most plausible general mechanism for this reaction in the presence of H_2O_2 –WEB system is given in scheme 2.



Scheme 2. Potential H_2O_2 –WEB catalyzed Dakin oxidation mechanism

With the results of our initial feasibility and optimization study in hand, we turned our attention toward exploring the substrate scope for our newfound hitherto unknown oxidation protocol. A range of commercially available substituted hydroxylated benzaldehydes were screened to investigate the scope of this method (Table 2). We envisioned exploring both substituted electron-poor and electron-rich hydroxylated benzaldehydes to determine the overall robustness of our method. As depicted in Table 2, a wide-range of substrates oxidized efficiently under our optimized conditions to provide the corresponding alcohols. Yields were excellent, across the board, and varied marginally among *ortho*-, *meta*-, and *para*- substituted hydroxylated benzaldehydes (Table 2, entries 1–16). The production of undesired benzyl alcohols or benzoic acids¹¹ was not detected. Moreover, it is amazing that these catalytic oxidations in WEB proceed faster than in conventional solvents. To date, no reported procedure for Dakin oxidation makes use of such a very mild and green environment and leads to such a high product yields. Consequently, the present method appears to be a convenient way of transforming benzaldehydes into the corresponding phenols. In view of the results presented in this paper, we also believe that this is one of the best and greenest procedures ever reported for the title reaction. Therefore, the present synthetic method would be extremely beneficial and more efficient to synthetic chemistry community at all.

Table 2. Conversion of arylaldehydes to phenols in H_2O_2 –WEB system at room temperature^a



Entry	Starting Material	Product	Time (min)	Yield ^b (%)
1			40	98

2		40	98
3		50	95
4		50	92
5		50	95
6		60	95
7		50	94
8		50	94
9		50	96
10		60	91
11		60	94
12		50	98
13		60	92
14		60	90
15		50	95
16		50	94

^a Reaction conditions: arylaldehydes (1 mmol), 30% H₂O₂ (2 equiv. with respect of each substrate) in WEB (3 mL) at room temperature.

^b Yields refer to isolated yields.

Conclusions

In conclusion, we have developed an aerobic and mild catalytic system for the Dakin oxidation. In this manuscript we investigated the applicability of the hydrogen peroxide using natural feedstock WEB for the Dakin oxidation of a wide range of organic compounds. Our method is flexible and is tolerant of various electron-donating and electron-withdrawing groups at the *ortho*-, *meta*-, and *para*-positions on the aromatic ring. It is remarkable that the catalytic system does not require activation or any toxic ligand and additive/promoter. The developed catalyst system represents, so far, the most efficient greener protocol toward the Dakin oxidation in air at room temperature and it provide efficient and safe oxidants to the synthetic community. In terms of both economical and environmental considerations, we believe that the oxidation protocol holds a potential value in laboratory and industry in near future. All these advantages make H₂O₂-WEB a competitive catalyst and thus can be a clean and convenient alternative for other industrially important reactions.

Acknowledgment

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Graphical Abstract:

H₂O₂ in WEB: a highly efficient catalyst system for Dakin reaction

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Transition metal catalyst, ligand, base, toxic or hazardous reagent, additive/promoters and organic solvent free Dakin reactions have been successfully carried out by using H₂O₂ in neat 'Water Extract of Banana' (WEB) at room temperature under aerobic conditions in very short reaction times.

