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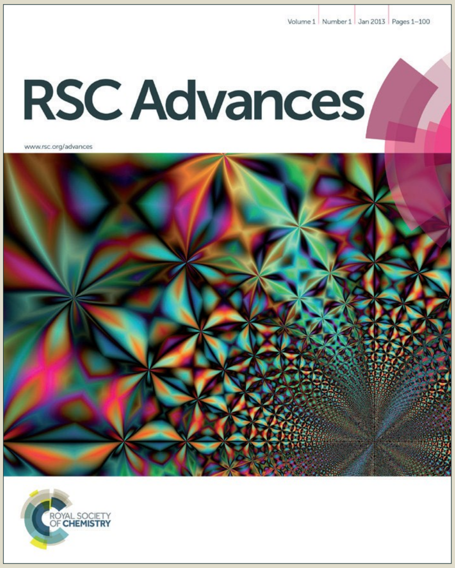

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A new avenue to Dakin reaction in H_2O_2–WERSA

Bishwajit Saikia*[a] and Parinita Borah[b]

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We have developed a novel protocol to realize Dakin reaction in a more greener way. In fact, by the using of H_2O_2–WERSA, we can oxidize aromatic arylaldehydes to phenols at room temperature. It is remarkable that the catalytic system does not require activation or any toxic ligand, additive/promoter, transition metal catalyst, base, organic solvent and so on. A range of substituted hydroxylated benzaldehydes were screened to investigate the scope of this protocol.

Conversion of *o*-and *p*-hydroxybenzaldehydes to dihydric phenols using alkaline hydrogen peroxide is generally known as Dakin oxidation.[1] Dihydric phenols and their derivatives are practically important substrates and are used extensively in various fields particularly in agrochemicals, antioxidants, pharmaceuticals, flavoring agents, polymerization inhibitors, photographic processes *etc.*[2] Dakin's original procedure utilized excess hydrogen peroxide and sodium hydroxide at elevated temperatures.[1a] Till date many methods have been investigated to perform this transformation.[3] The propagation of methods available to undertake this particular transformation indicates to the synthetic usefulness; and, yet, major problems remain to anyone wishing to apply these methods within an effortless synthetic context, mostly arising from the harshness. Most of these reactions were performed in traditional organic solvents and resulted in considerable environmental pollution, often requiring activation by metal catalysts and use of H_2O_2 activator. Moreover, health, safety and environmental issues associated with the use of many conventional organic solvents have led to their use being strictly curtailed. Due to environmental, economical, and safety concerns, it is highly desirable to develop green, cheap and easy procedure with high durability and activity for Dakin reaction. Similarly, the design of efficient catalysts system producing high yields under aerobic conditions continues to be an important challenge. In this report we offered a solution to this problem in the form a novel and highly mild green alternative for this key transformation (**Figure 1**).

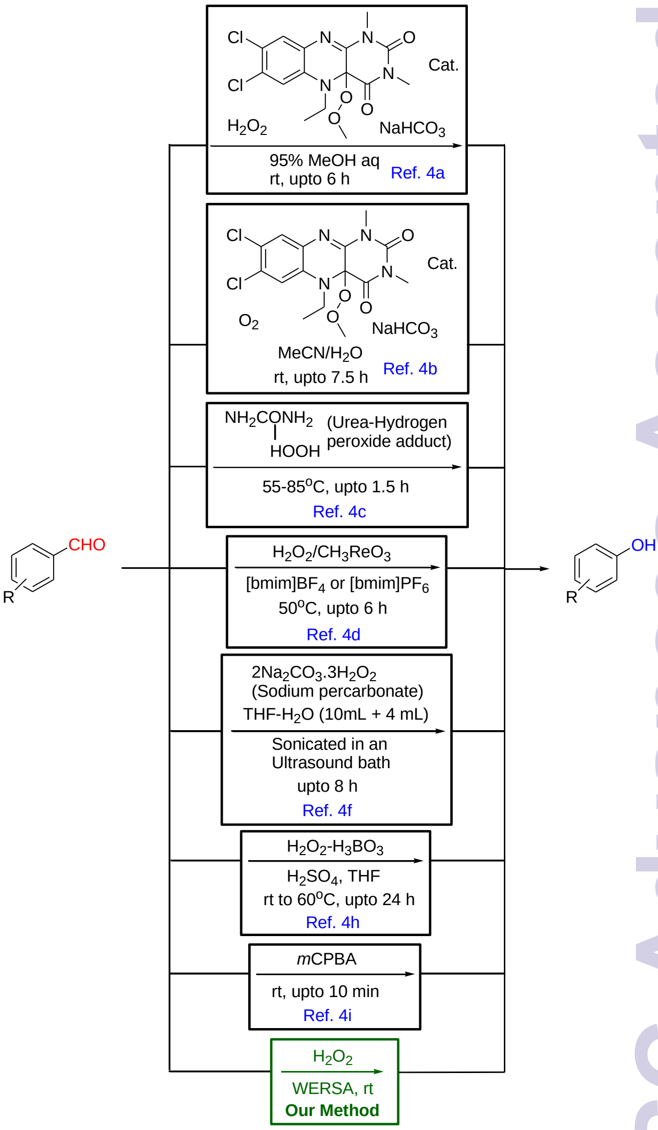

Fig. 1 Previous works *vs* our work

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Experiments should involve the use of alternative solvents which are not only eco-friendly but also be easily available anywhere in bulk quantities at very cheap price. Rice straw is a highly abundant natural waste material across the world and therefore, its application in organic synthesis as reaction medium will draw significant awareness from the point of environmental issues. Because green chemistry efficiently utilises (preferably renewable) raw materials, eliminates waste and avoids the use of toxic/hazardous solvents and reagents in the manufacture and application of chemical products.[4] In our effort toward developing green and sustainable catalytic methods, we now wish to report an extended study of the catalytic behaviour of "*Water Extract of Rice Straw Ash*" (WERSA)[5] as catalysts as well as reaction medium in the Dakin oxidation involving hydroxylated benzaldehydes. We are utilizing WERSA as a cheap, non-toxic, and green catalytic media in this important synthetic conversion. WERSA has been prepared by burning rice straw to ashes and that ash was suspended in distilled water in a glass beaker and mechanically stirred for a few minutes at room temperature. Finally, the mixture was filtered and the filtrate was abbreviated as WERSA here (**Figure 2**). Likewise, hydrogen peroxide is one of the cheapest environmentally friendly and easy to handle oxidizing agents widely used for a range of oxidative transformations over the years.[6]

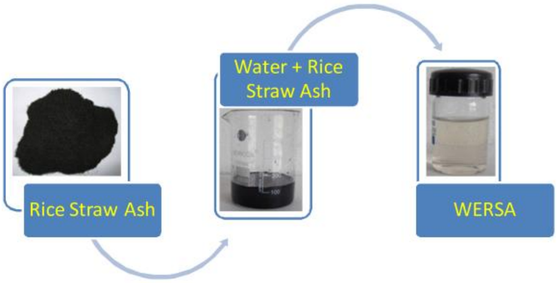
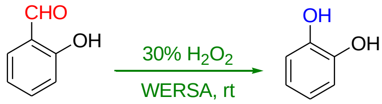


Fig. 2 Preparation of WERSA

The catalytic activity of H_2O_2–WERSA system in the Dakin oxidation was tested by using salicylaldehyde in the presence of 1 equiv. of H_2O_2 in WERSA at room temperature. The reaction after 4 h gave the product catechol in 75% yield (**Table 1**, entry 1). On using 1.5 to 2.0 equiv. of H_2O_2, the yield of the desired product was increased (88 and 98% respectively) (**Table 1**, entries 2 & 3). We have calculated the conversion of salicylaldehyde to catechol by NMR spectroscopy, utilizing $CDCl_3$ as an internal standard. Subsequently the Dakin oxidation of variety of hydroxylated benzaldehydes, including activated and deactivated ones (**Table 2**; entries 1–16), was examined using H_2O_2–WERSA as the catalyst system and yields were excellent. Results were very consistent with reactions achieved with high yields and purities regardless of the substituent's such as –OH, $–OCH_3$, $–CH_3$, $–C_2H_5$, $–NO_2$, –Br, –Cl *etc.* on the aromatic ring and again with all reactions run in air (**Table 2**; entries 1–16). Therefore, this is the simplest example for Dakin oxidation among all other oxidation systems so far reported. The method in general provides good to excellent yields of oxidized products. Interestingly, the formation of undesired benzyl alcohols or benzoic acids was not detected in this reaction condition.[7] Our findings reflect that the goal of carrying out the Dakin reactions can be successfully achieved when H_2O_2–WERSA is used as catalyst system even in the case of species that are deactivated.[3] In comparison to existing reagents, this aerobic oxidation of hydroxylated benzaldehydes with this novel H_2O_2–WERSA system appears to be a superior alternative in terms of shorter reaction time, cleaner product formation, commercially feasibility as well as environmental sustainability.

Table 1. Optimization of reaction conditions[a]

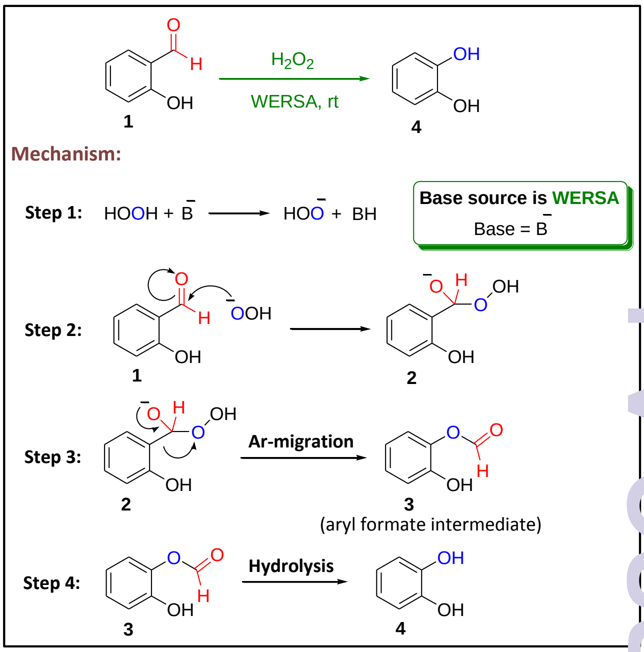


Entry	H_2O_2 (equiv.)	Time (h)	Yield[b] (%)
1	1	4	75
2	1.5	3	88
3	2	2	98

[a] Reaction conditions: salicylaldehyde (1 mmol), H_2O_2 in WERSA (3 mL) at room temperature.

[b] Isolated yields.

Dakin oxidation is a variation of the Baeyer–Villiger oxidation (BVO) that converts benzaldehyde (**1**) to phenol (**4**) by BVO (migration of aryl group) followed by hydrolysis of the aryl formate intermediate (**3**), effectively oxidizing both aryl and acyl sp^2 carbons. Literature report reveals that rice straw ash consists of oxides of SiO_2 (74.31%), Al_2O_3 (1.40%), Fe_2O_3 (0.73%), TiO_2 (0.02%), CaO (1.61%), MgO (1.89%), K_2O (11.30%), Na_2O (1.85%), P_2O_5 (2.65%) *etc.*[8] Oxides of potassium, sodium, magnesium and calcium react with water to produce hydroxides of these metals and therefore, we strongly believe that these alkali metal hydroxides (particularly KOH and NaOH) work as internal bases here to assist the Dakin reactions smoothly at room temperature in absence of any H_2O_2 activators or organic co-solvents. The possible H_2O_2–WERSA catalysed Dakin oxidation mechanism is illustrated in **Scheme 1**.



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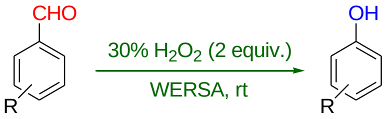
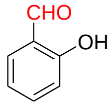
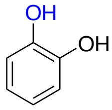
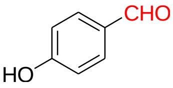
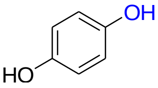
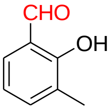
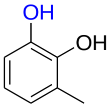
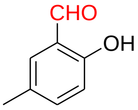
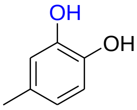
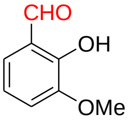
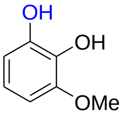
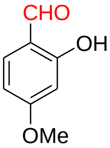
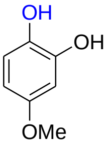
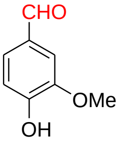
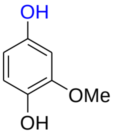
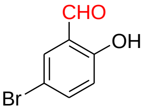
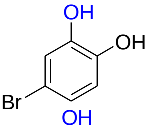
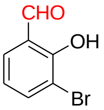
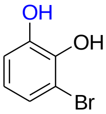
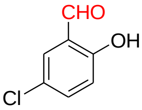
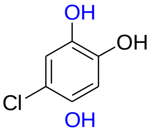
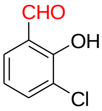
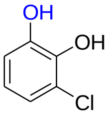
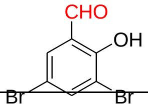
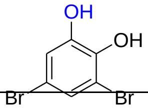
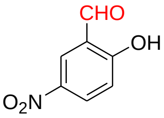
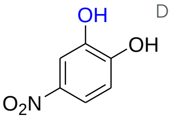
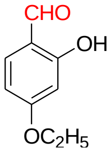
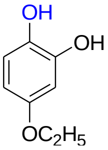
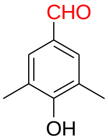
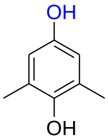
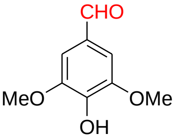
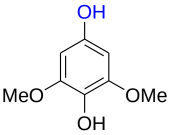
Scheme 1. Possible H_2O_2–WERSA catalysed Dakin oxidation mechanism.

Table 2. Conversion of arylaldehydes to phenols in H_2O_2–WERSA system at room temperature[a]



Entry	Starting Material	Product	Time (h)	Yield[b] (%)
1			2	98
2			2	98
3			2	96
4			2	95
5			2.5	92
6			2.5	92
7			3	90
8			2	96
9			2	94
10			2	94
11			2	92
12			3	88
13			3	90
14			3	90
15			3	88
16			3	85

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[a] Reaction conditions: arylaldehydes (1 mmol), H_2O_2 (2 equiv relative to the amount of substrates) in WERSA (3 mL) at room temperature.

[b] Isolated yields.

Conclusions

In conclusion, we have described a novel Dakin oxidation protocol with 30% H_2O_2 in "Water Extract of Rice Straw Ash" (WERSA) at room temperature. This system works with a wide scope of substrates, without using any other ligands, bases, additives, organic co-solvents and higher yields compared to those reported earlier with various Dakin oxidation systems. Since Dakin oxidation is a widely used reaction in industry, this cheap and simple system definitely will attract attentions and find potential application in near future. Our strategy would be a potential tool for the direct utilization of WERSA for attaining different industrially important catalytic reactions.

Acknowledgment

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Graphical Abstract:

A new avenue to Dakin reaction in H_2O_2–WERSA

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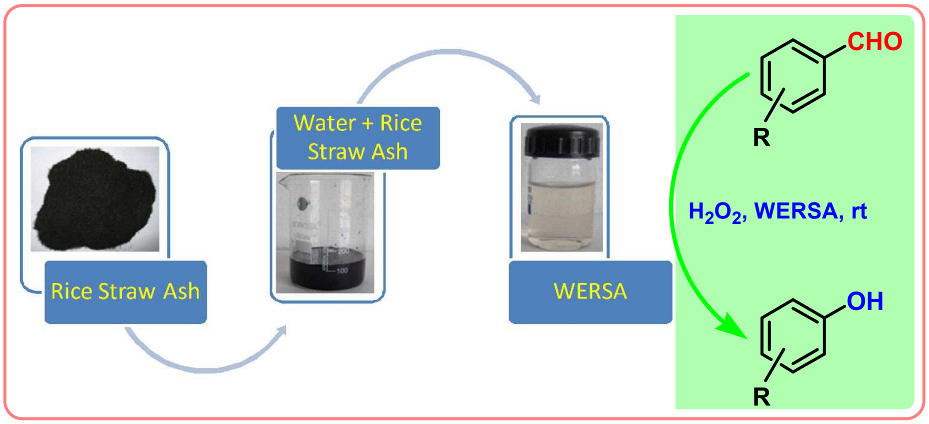
We have developed a novel protocol to realize the Dakin reaction in H_2O_2–WERSA at room temperature. It is highly remarkable that the catalytic system does not require activation or any toxic ligand, additive/promoter, transition metal catalyst, base, organic solvent and so on.



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