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Application of natural feedstock extract: the Henry reaction

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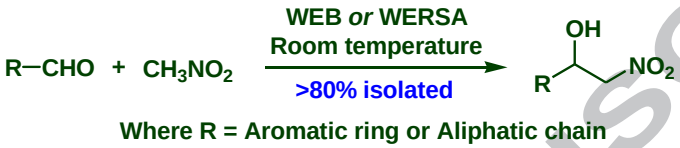

Where R = Aromatic ring or Aliphatic chain

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ABSTRACT

For the first time, we have successfully performed the Henry reaction in neat '*Natural Feedstock Extract*' at room temperature. Herein, we used two most abundant natural feedstock extracts such as '*Water Extract of Banana*' (WEB) and '*Water Extract of Rice Straw Ash*'' (WERSA). This protocol is highly advantageous owing to the employment of natural feedstock as green reaction media results significant novelty and advance with respect to green and sustainable chemistry.

The construction of carbon–carbon bonds is an essential aspect of synthetic organic chemistry. The Henry reaction which is also referred to as the nitro-aldol reaction is a classic carbon–carbon bond formation reaction in organic chemistry.[1] Essentially, this reaction describes the coupling of a nucleophilic nitro alkane with an electrophilic aldehyde or ketone to produce a highly synthetically useful *β*-nitro alcohol.[2] Nowadays, the important aspect which is receiving growing attention is the use of alternative reaction media that avoid the problems associated with many of the traditional volatile organic solvents.[3] The use of hazardous solvents in chemical industry is associated with a variety of indirect environmental impacts such as non-renewable resource reduction as a result of petrochemical solvent production, air emissions due to solvent incineration or high energy investment for solvent recycling processes.[4] Therefore, the ability to efficiently carry out organic reactions in more environmentally friendly solvents remains an important object of green chemistry research. It means that wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to animal health and the environment.[5] Our interest is using highly abundant natural feedstock extract[6] to replace organic solvents in Henry reaction because feedstock extract endows the reaction with green and safe properties. The strategy to use *Water Extract of Banana*' (WEB)[6a,6b] and '*Water Extract of Rice Straw Ash*'' (WERSA)[6c] in catalysis is the key challenge of this work and represent an enormous potential feedstock extracts for the production of chemicals. The preparation of these natural feedstock extracts often involves three steps: drying the banana parts/rice straw followed by burning them to ash and subsequent addition of water to the ash, mixed well and then filtered. The filtrates are abbreviated as WEB and WERSA. Literature reports reveal that these extracts (WEB and WERSA) contain potassium, sodium, carbonate and hydroxide and therefore they are basic in nature.[7,8]

Wang *et al*. have reported a nitro-aldol (or Henry) reaction in aqueous solution using double-stranded DNA of natural origin.[9a] It should also be mentioned that nitroaldol (Henry) reaction of aromatic aldehydes with nitromethane using human serum albumin (HSA) in water has been reported by Matsumoto and his co-workers.[9b] Similarly, Pawar's group has reported the cesium fluorides in ionic liquid [bmim][BF_4] promoted Henry reaction.[9c] Besides, Le and his co-workers developed another method for the Henry reaction of aromatic aldehydes and nitroalkanes performed by catalyst of Lipase A from *Aspergillus niger* in organic/water medium.[9d] Recently Asano *et al*. reported for the first time an *R*-selective hydroxy nitrile lyase from *Arabidopsis thaliana*. However, a maximum of 30% yield was achieved and the reaction is highly substrate dependent.[9e] Lin *et al*. found *d*-aminoacylase from *E. coli* to be the most effective catalyst for the addition of either nitromethane *or* nitroethane to a range of aliphatic, aromatic and heteroaromatic aldehydes.[9f] Practical application of these methods was limited owing to the relatively harsh reaction conditions such as the utilization of toxic organic solvents, long reaction time, elevated reaction temperature, use of expensive, less abundant catalysis, requirement of large amount of catalysts loading, use of additives/promoters and limited substrate scope.

Considering the promise of Henry reaction and the need to make industrial processes more environmentally friendly, we advance this catalytic concept to describe the first Henry reaction of various aliphatic/aromatic aldehydes on the use of novel aqueous extract such as WEB and WERSA. To the best of our knowledge this is the first report of the Henry reaction in neat WEB/WERSA at room temperature without using any external

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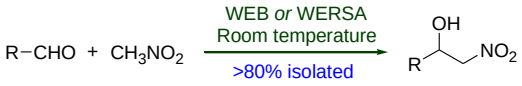
base, toxic or hazardous reagent, additives/promoters and organic co-solvent (**Scheme 1**). It is important to note that we have prepared our catalyst system from natural waste only. Therefore, we strongly believed that our catalyst system (WEB/WERSA) is the best and highly green ever reported. This new Henry variant can be accomplished with excellent yield for a broad range of substrates and that are highly attractive for industrial applications in the near future.

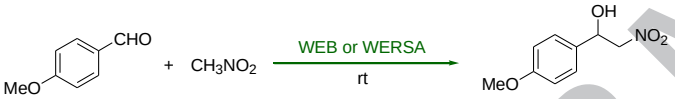


Where R = Aromatic ring or Aliphatic chain

Scheme 1. Henry reaction in Natural Feedstock Extract at room temperature

We started to explore the method on the model reaction of 4-methoxybenzaldehyde and nitromethane in neat WEB and WERSA separately at room temperature. We first studied the influence of nitromethane equivalent on the reaction yield as well as the reaction time. In both the extracts (WEB; $P^H \approx 10.5$ and WERSA; $P^H \approx 10$) we found good to excellent product yields at room temperature within a very short reaction time (**Table 1**; entries 1–5). It was observed that enhancing the equivalent of CH_3NO_2 increased the product yield with slightly increased in reaction time (**Table 2**, entries 1–5).

Table 1. Effects of the nitromethane equiv. and time in the Henry reaction in neat WEB/WERSA at room temperature[a]

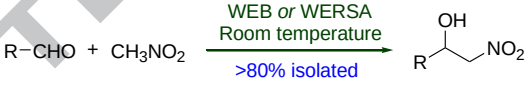


Entry	CH_3NO_2	Time (h)	Yield[b] (%)
1	1.5 equiv.	1[c] 1[d]	50[c], 40[d]
2	2.5 equiv.	1[c] 1[d]	60[c], 50[d]
3	5 equiv.	1[c] 2[d]	70[c], 60[d]
4	10 equiv.	2[c] 3.5[d]	80[c], 75[d]
5	10 equiv.	3[c] 6[d]	85[c], 82[d]

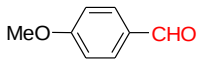
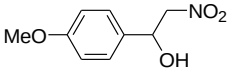
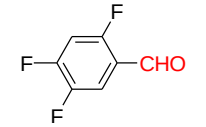
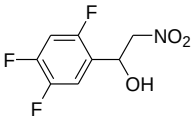
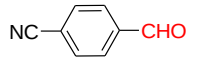
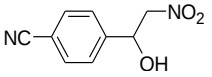
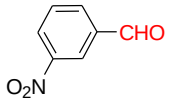
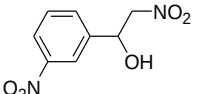
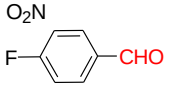
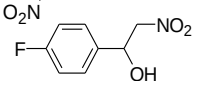
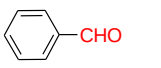
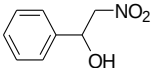
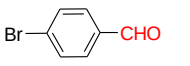
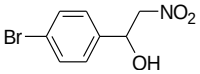
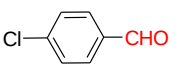
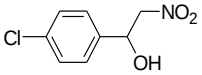
[a]Reaction conditions: Reaction conditions: 4-methoxybenzaldehyde (1 mmol), nitromethane (10 mmol) in WEB or WERSA (3 mL) at room temperature..
[b]Yields refer to isolated yields.
[c]WEB
[d]WERSA

Based on the optimized results, we first examined the applicable scope of Henry reaction by using different aromatic and aliphatic aldehydes in both the systems. The results from this section were shown in Table 2. Gratifyingly, a wide range of aromatic aldehydes that incorporate electron-donating and electron-withdrawing groups such as $–CH_3$, $–OCH_3$, –Cl, –F, –Br, –CN, –OH and $–NO_2$ at the *ortho*-, *meta*- and *para*- positions are readily tolerated (**Table 2**, entries 1–5 & 7–13). Notably, electron-withdrawing substituents on the phenyl ring of aromatic aldehydes slightly favoured the reaction (**Table 2**, entries 2–5). Aliphatic aldehydes, such as pentanal and octanal, also generated the desired Henry reaction products with excellent yields (**Table 2**, entries 16 & 17). It is interesting to note that both the Henry and Michael products were found for the case of cinnamaldehyde and the yields in both the systems (WEB/WERSA) were similarly good (**Table 2**, entry 21). This feature would allow the present method to prepare a wide range of nitroalcohols. Therefore, the present method opens a new avenue to the Henry reaction, and should be helpful for exploring further usages of these unusual compounds.

Table 2. Conversion of aryl/alkylaldehydes to nitroalcohols in neat WEB/WERSA system at room temperature[a]



Where R = Aromatic ring or Aliphatic chain

Entry	Aldehyde	Product	Time (h)	Yield [a,b]
1			3[c], 6[d]	85[c], 82[d]
2			2[c], 4[d]	92[c], 89[d]
3			3[c], 4[d]	88[c], 84[d]
4			3[c], 4[d]	86[c], 83[d]
5			2[c], 4[d]	87[c], 84[d]
6			3[c], 4[d]	82[c], 80[d]
7			3[c], 4[d]	85[c], 82[d]
8			2[c], 4[d]	90[c], 85[d]
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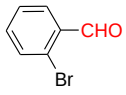
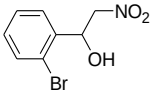
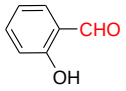
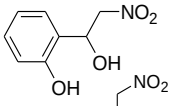
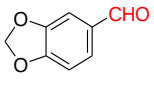
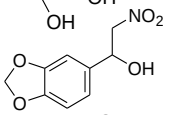
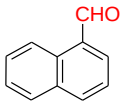
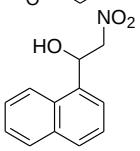
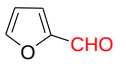
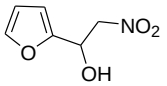
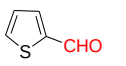
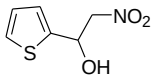
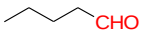
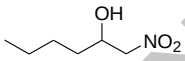
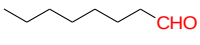
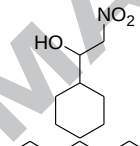
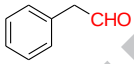
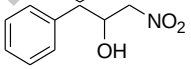
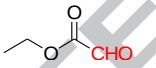
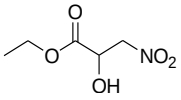
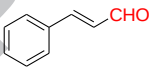
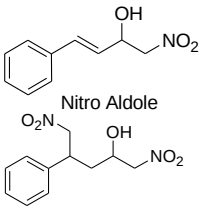
10			2[c], 4[d]	95[c], 90[d]
11			3[c], 5[d]	80[c], 75[d]
12			3[c], 5[d]	75[c], 70[d]
13			3[c], 6[d]	76[c], 70[d]
14			3[c], 6[d]	90[c], 85[d]
15			3[c], 6[d]	80[c], 76[d]
16			3[c], 6[d]	90[c], 85[d]
17			3[c], 6[d]	90[c], 85[d]
18			3[c], 6[d]	91[c], 84[d]
19			4[c], 7[d]	81[c], 78[d]
20			3[c], 7[d]	80[c], 78[d]
21		 Nitro Aldole Michael and Nitro Aldole	3[c], 4[d]; 3[c], 4[d]	41[c], 39[d]; 40[c], 38[d]

[a]Reaction conditions: arylaldehydes (1 mmol), nitromethane (10 mmol) in WEB or WERSA (3 mL) at room temperature.
[b]Yields refer to isolated yields.
[c]WEB
[d]WERSA

In conclusion, we have reported an environmentally friendly reaction protocol for aqueous Henry reaction under air at room temperature, which is applicable to a broad range of substrates. No organic co-solvents, external base or other additives/promoters are required, isolation of substrates in excellent yields. This study not only demonstrates a new method to synthesize *β*-nitro alcohols, but also supplies a new, efficient green catalyst for the Henry reactions of challenging aliphatic aldehydes. All these advantages make WEB/WERSA a competitive catalyst and thus can be a clean and convenient alternative for other industrially important reactions. Further work is in progress to exploit these abundant natural feedstock extracts (WEB & WERSA) in different valuable organic transformations.

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Highlights

1. Henry reaction assisted by most abundant and renewable natural feedstock extract.
2. No heat/ligand/external base/toxic reagent/additive and organic solvents.
3. Use of WEB/WERSA greatly increases the green credentials of the method.
4. WEB/WERSA surpasses the criteria in terms of novelty/high scientific integrity.
5. Protocol is efficient in terms of reactivity, cost-effective and air-stability.