Sustainable and Efficient Route for the Regeneration of Carbonyl Compounds from Oximes Using Aqueous Extract of *Sapindus laurifolia* under Microwave Radiation

Debadutta Das,* Ranjan K. Mohapatra, Pankaj K. Parhi, Ashish K. Sarangi, Raghaba Sahu, and Soumya R. Barik

**ABSTRACT:** The synthesis of organic compounds using aqueous medium has become an indispensable tool for modern chemical synthesis strategies because of its ability to produce pure products with higher yield at ambient temperature. The conversion of oxime group into carbonyl group serves as a key step for several organic syntheses. This article describes the regeneration of carbonyl compounds from the oxime group present in various carbon skeletons using I₂ and aqueous extract of *Sapindus laurifolia* under microwave radiation. A correlation has been established between the critical micellar concentration of saponin extracted from *Sapindus laurifolia* and the yield percentage of regenerated different carbonyl compounds. An effortless, competent, and environmentally compassionate protocol for the regeneration of carbonyl compound with a high percent of yield in the range 45–95% could be achieved.

1. INTRODUCTION

Nowadays, a large amount of toxic materials are being produced due to the indiscriminate use of chemicals in different industries and chemical laboratories. These materials are causing serious health and environmental hazards thereby threatening living beings present in the ecosystem. The development of eco-friendly, pollution-free, and less cost-effective chemical methodology is therefore of dire need today for the sustainability of the biosystem. The sustainable methodology primarily means the involvement of green solvents,¹ which in turn conserves the environment. Water is a nontoxic, nonflammable, inexpensive, benign, and abundantly available solvent. Therefore, considerable attentions are now being paid to organic reactions conducted in aqueous media.²⁻⁴ Many of the organic reactions like deoxygenation of nitrones to corresponding imines and oximes to carbonyls have been carried out in hydrated media.⁵ Gogoi et al. reported the selective oxidation of alcohols and deprotonation of oximes and imines to carbonyl compounds in aqueous media.⁶ Surfactant aggregates have been found to be suitable biphasic systems for carrying out a large number of reactions,⁷⁻⁹ and a substantial increase in the yield of products has been reported.

Oxime derivatives serve as an important synthetic intermediate in multistep organic synthesis as they are frequently used for the purification and protection of carbonyl compounds. Some reported methods are useful for the regeneration of carbonyl compounds from oximes, which are produced at nonactivated hydrocarbon sites.¹¹ The literature enumerates a considerable number of methods in hydrolytic oxidative and reductive ways for the conversion of oximes into carbonyl groups. Some of the well-known deoxygenating agents are N₂O₄,¹² pyridinium chlorochromate (PCC),¹³ tert-butyl hydroperoxide (TBHP),¹⁴ KMnO₄/alumina,¹⁵ PhSeO₃O,¹⁶ TMSCl/NaNO₂,¹⁷ Raney nickel,¹⁸ sodium perborate/HOAc,¹⁹ NaHSO₃,²⁰ etc., and several transition-metal salts involve Ti(NO₃)₄,²¹ Cr(OAc)₃,²² Mn(OAc)₃,²³ trimethylsilyl chlorochromate,²⁴ BiBr₃/Bi(OTf)₃,²⁵ 2-nitro-4,5-dichloropyridazin-3(2H)-one,²⁶ and Al(NO₃)₃·9H₂O in the presence of catalytic amounts of NaBr in CH₂Cl₂ at room temperature.²⁷ Furthermore, tetraethyl ammonium chlorochromate (TEACC) in dimethylsulfoxide,²⁸ potassium permanganate–graphite,²⁹ citric acid,³⁰ and many other reagents³¹⁻³⁷ have recently been reported as deoxygenating agents. However, most of these reagents are toxic, corrosive, and expensive and take a longer reaction time for completion. Hence, an effortless, competent, and environmentally compassionate protocol for the regeneration of carbonyl compound with a high percent of yield
within a few minutes using the microwave method\textsuperscript{38} is a big challenge for researchers.

*Sapindous laurifolia* is one type of soap nut tree mostly available in South Asia. Saponin isolated from *S. laurifolia* is a complicated mixture of saccharin derivatives and belongs to a class of naturally occurring nonionic surfactants.\textsuperscript{39,40} The hydrophilic part of the molecule called glycon consists of saccharides such as glucose, galactose, rhamnose, xylose, pentose, etc., and the hydrophobic part called aglycon consists of steroids or triterpene. The hydrophobic part is bonded through oxygen to the hemiketal or hemiacetal carbon of the saccharide residue, which in turn is linked through oxygen linkages to other saccharide residues. Due to its amphiphilic nature, it can solubilize organic molecules in water. Hence, it can be a suitable replacement for many organic solvents in chemical reactions. The general structure of saponin is shown in Figure 1.

Herein, we describe a simple and neutral method by which regeneration of carbonyls proceeds efficiently with good yield and reduced reaction time under mild reaction conditions. A method using iodine (I\textsubscript{2}) and an aqueous extract of natural surface active agent *S. laurifolia* under microwave radiation for the regeneration of carbonyl compounds from oxime is established.

**2. RESULTS AND DISCUSSION**

**2.1. Effect of *S. Laurifolia* Concentration on the Regeneration of Carbonyl Compounds.** *S. laurifolia* is a saponin-rich plant that consists of two parts: one part is polar sugar chain and the other part is nonpolar triterpene ring. Due to the lipophilic nature of saponin, it can solubilize the nonpolar organic molecule in aqueous medium\textsuperscript{41−44} (Scheme 1). The rate enhancement in the aqueous extract of *S. laurifolia* pods might be attributed to its surfactant property and acidic pH. The saponins, which are acidic, solubilize the reactant species strongly by hydrogen-bond formation in aqueous medium. This increases the number of favorable collisions between the reactant species.

It has been observed from Figure 2 that the percentage of regeneration of carbonyl compounds increases with an increase in *S. laurifolia* concentration up to 0.017 g/cm\textsuperscript{3}, which is the critical micellar concentration. Above the critical micelle concentration (CMC), there is no appreciable increase in the percentage of regeneration of carbonyl compounds, which may be due to the formation of micelles. Thus, the solubility of reactant species oxime and iodine reaches maximum at CMC. Therefore, 0.017 g/cm\textsuperscript{3} is the optimized concentration for the regeneration of carbonyl compounds from oxime.

**2.2. Mechanism of Reaction.** The electrophilic iodine forms an iodonium ion with the carbon−nitrogen double bond, which promotes the hydration of the carbon−nitrogen double bond of oxime (Scheme 2). This proposed mechanism involves the dismutation of I\textsubscript{2}. Due to the formation of micelle by saponin of aqueous *S. laurifolia*, nonpolar I\textsubscript{2} molecule and oxime are solubilized in the micellar core, which is nonpolar (hydrophobic). Therefore, aqueous extracts of *S. laurifolia* can solubilize both the reactants oxime and iodine. The low yield of the compound 1n (Table 1) may be due to its low solubility in the micellar core. This is because of the large number of nonpolar rings in the molecule. The time duration and yield percentage are given in Table 1.

The basic principle behind the microwave-assisted reaction is that the solvent molecule (here water) absorbs microwave energy, thereby increasing the temperature of the reaction mixture. This leads to a rapid increase in the rate of reaction. The use of microwave radiation has several advantages over conventional heating methods, such as faster reaction rates, higher yields, and reduced reaction times. Additionally, microwave-assisted reactions are often more efficient and environmentally friendly than traditional heating methods.

Figure 1. Structure of saponin, where *R* = sugar unit.

Figure 2. Percentage of regeneration of carbonyl compounds.

![Scheme 1. Solubilization of Oxime and I\textsubscript{2} in Micellar Core of *S. laurifolia*](image1)

![Scheme 2. Mechanism for the Conversion of Oximes into Carbonyl Compounds. (Adapted with Permission from Gogoi et al.,\textsuperscript{4} 2005, American Chemical Society.)(image2)
energy and transfers heat energy to the reactant present in the medium. Thus, the transfer of oximes to corresponding carbonyl compounds enhanced efficiently within a few minutes with I₂ in water under microwave irradiation. The conversion of oximes

| Entry | Substrates 1a-1n | Time (Minutes) | MW (Watts) | Products (2a-2n) | Yield % | Absence of s. laurifolia | Presence of s. laurifolia |
|-------|-----------------|----------------|------------|-----------------|---------|-------------------------|-------------------------|
| 1a    |                 | 6              | 100        | 21              | 91°     |                         |                         |
| 1b    |                 | 12             | 100        | 19              | 94°     |                         |                         |
| 1c    |                 | 05             | 100        | 14              | 75°     |                         |                         |
| 1d    |                 | 06             | 100        | 16              | 72°     |                         |                         |
| 1e    |                 | 10             | 100        | 11              | 65°     |                         |                         |
| 1f    |                 | 10             | 100        | 13              | 74°     |                         |                         |
| 1g    |                 | 12             | 100        | 14              | 81°     |                         |                         |
| 1h    |                 | 12             | 100        | 12              | 82°     |                         |                         |
| 1i    |                 | 12             | 100        | 15              | 85°     |                         |                         |
| 1j    |                 | 10             | 170        | -               | 60°     |                         |                         |
| 1k    |                 | 10             | 170        | 11              | 62°     |                         |                         |
| 1l    |                 | 10             | 170        | -               | 64°     |                         |                         |
| 1m    |                 | 08             | 170        | 10              | 64°     |                         |                         |
| 1n    |                 | 12             | 170        | -               | 45°     |                         |                         |

*Purification by distillation. ¹Purification by column chromatography.
into carbonyl compounds catalyzed by iodine may be represented as follows (Scheme 2).

3. CONCLUSIONS

In a nutshell, a simple, green, and cost-effective protocol for the regeneration of carbonyl compounds using I₂ and aqueous extract of S. laurifolia has been demonstrated. A salient feature of this method is that aqueous extracts of S. laurifolia effectively solubilize oxime and iodine in its micellar core, which can replace common commercial surfactants such as sodium dodecyl sulfate (SDS), cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl benzene sulfonate (SDBS), etc. in organic reactions. This work reports a useful, attractive, and alternative method for the conversion of oximes into corresponding carbonyl compounds with more efficiency compared to the existing conventional method. The activation energy required for the formation of transition state is achieved quickly due to the increase in the frequency of rotation of water molecules, which in turn increases the energy content of oxime molecule.

4. MATERIALS AND METHODS

4.1. Isolation of Saponin from S. laurifolia. Dry fruit of S. laurifolia (10 g) was taken, and the pericarp of the fruit was removed, dried, and powdered. This powder was suspended in the desired volume (100 mL) of water. The aliquot was subjected to agitation for a time duration of 3 h by a magnetic stirrer. Then, the supernatant solution obtained was centrifuged and filtrated to extract out the active component as saponin into the corresponding aqueous medium. This extract was utilized as solvent for the regeneration of carbonyl compound.

4.2. Surface Activity of the Aqueous Extract of S. laurifolia. The surface tension of the aqueous extract was measured by a surface tensiometer (Kyowa-350, Japan). The surface tension of pure water is 72 mN/m, and it gets saturated until a minimum value of 40 mN/m when the concentration of the surfactant reaches 0.017 g/cm³ (1.7 wt %). It is reported that the minimum surface tension is achieved at 0.017 g/cm³, which may be the CMC of the dispersant. This is because, above this concentration, there is no further reduction in the surface tension value.

4.3. Preparation of Oxime and Carbonyl Compound. The chemicals are from Aldrich and purified by the standard procedure whenever necessary. Triple-distilled water is used throughout the experiment. Oxime derivatives are prepared from the corresponding carbonyl compounds. The products were characterized by elemental analyses; determination of melting point, boiling point, etc.; and direct comparison of the spectral data with those of the authentic samples. Infrared (IR) spectra and ¹H NMR (in deuterio solvent chloroform) spectra were recorded on a JASCO FT/IR/S-300 spectrophotometer and JFAL FX-90 instrument, respectively.

4.4. Method of Regeneration of Carbonyl Compound. In a typical procedure, oxime derivatives (1 mmol) iodine (1.5 mmol) and S. laurifolia extract (5 mL) were taken in an Erlenmeyer flask and placed inside a microwave oven (2450 MHz frequency). The aliquots were irradiated at different currents (internal temperature ranging from 45 to 60 °C) for different time periods. The reaction mixture was cooled at room temperature, treated with water, and extracted with dichloromethane. The organic solvent layer was washed with sodium thiosulfate and then with water and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification (distillation/chromatography on silica gel) produced the corresponding carbonyl compounds (Scheme 3).

Scheme 3. Regeneration of Carbonyl Compounds from Oxime

4. MATERIALS AND METHODS

4.1. Isolation of Saponin from S. laurifolia. Dry fruit of S. laurifolia (10 g) was taken, and the pericarp of the fruit was removed, dried, and powdered. This powder was suspended in the desired volume (100 mL) of water. The aliquot was subjected to agitation for a time duration of 3 h by a magnetic stirrer. Then, the supernatant solution obtained was centrifuged and filtrated to extract out the active component as saponin into the corresponding aqueous medium. This extract was utilized as solvent for the regeneration of carbonyl compound.

4.2. Surface Activity of the Aqueous Extract of S. laurifolia. The surface tension of the aqueous extract was measured by a surface tensiometer (Kyowa-350, Japan). The surface tension of pure water is 72 mN/m, and it gets saturated until a minimum value of 40 mN/m when the concentration of the surfactant reaches 0.017 g/cm³ (1.7 wt %). It is reported that the minimum surface tension is achieved at 0.017 g/cm³, which may be the CMC of the dispersant. This is because, above this concentration, there is no further reduction in the surface tension value.

4.3. Preparation of Oxime and Carbonyl Compound. The chemicals are from Aldrich and purified by the standard procedure whenever necessary. Triple-distilled water is used throughout the experiment. Oxime derivatives are prepared from the corresponding carbonyl compounds. The products were characterized by elemental analyses; determination of melting point, boiling point, etc.; and direct comparison of the spectral data with those of the authentic samples. Infrared (IR) spectra and ¹H NMR (in deuterio solvent chloroform) spectra were recorded on a JASCO FT/IR/S-300 spectrophotometer and JFAL FX-90 instrument, respectively.

4.4. Method of Regeneration of Carbonyl Compound. In a typical procedure, oxime derivatives (1 mmol) iodine (1.5 mmol) and S. laurifolia extract (5 mL) were taken in an Erlenmeyer flask and placed inside a microwave oven (2450 MHz frequency). The aliquots were irradiated at different currents (internal temperature ranging from 45 to 60 °C) for different time periods. The reaction mixture was cooled at room temperature, treated with water, and extracted with dichloromethane. The organic solvent layer was washed with sodium thiosulfate and then with water and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification (distillation/chromatography on silica gel) produced the corresponding carbonyl compounds (Scheme 3).

ACS Omega 2020, 5, 7716−7721
expedient synthesis of bis(indolyl)methanes and 3-substituted indolyl ketones. Green Chem. Lett. Rev. 2012, 5, 73–81.

(43) Rao, K. J.; Paria, S. Solubilization of Naphthalene in the Presence of Plant-Synthetic Mixed Surfactant Systems. J. Phys. Chem. B 2009, 113, 474–481.

(44) Rao, K. J.; Chaudhuri, R. G.; Paria, S. Naphthalene degradation in the presence of natural-synthetic surfactants mixture by mixed bacterial cultures. J. Environ. Chem. Eng. 2014, 2, 826–831.