A Metal Free, Selective and Efficient Method for Large Scale Production of Aldehydes, Schiff bases and Oximes by Oxidation of Alcohols Using Peroxidized Soybean Oil (PSO)

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Abstract

A new efficient, cost effective and environmentally friendly method has been developed for the oxidation of alcohols based on emulsion systems formed by peroxidized soybean oil (PSO) under metal free conditions and without external oxidant at room temperature. Peroxidized soybean oil was prepared by reaction of raw soybean oil with formic acid and excess amount of 30 % hydrogen peroxide. Two new developed PSO emulsion systems were conveniently applicable to direct preparation of Schiff base and oximes by oxidation of their corresponding alcohols in the presence of amines. High to excellent yields were obtained for both of Schiff base and oxime materials in little reaction times at room temperature. The method was also investigated for large scale production of the aldehyde, Schiff base and oxime. Similar results in terms of time and reaction conversion were obtained for large scale production of the compounds which demonstrated direct scalability of the process.

Keywords: *Peroxidized Soybean Oil; Emulsion; Alcohol Oxidation; Large Scale; Oxime; Schiff base.*

Introduction

Schiff base compounds have unique properties which attracted a large volume of attention from various fields of research.[1] In medicine, Schiff bases and their transition metal complexes have been shown to have antibacterial,[2] antimicrobial,[3] anti-fungal,[4] anti-tumor[5] and herbicidal activities.[6] In coordination chemistry, they are known as one of the strongest ligand classes that can provide various types of complexes in virtue of the diversity they have in dentate number (two, three, four or more) as well as in the type of donor atoms (N, O and S).[7] In organic synthesis, Schiff bases transition metal complexes found wide application as efficient catalysts for various types of organic reactions.[8]

Oximes (–HC=N-OH) are useful intermediates for the preparation of amides such as ε-caprolactam, a precursor to nylon 6 that can be prepared via Beckmann

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rearrangement.[9] They have been used to protect, purify and characterize carbonyl compounds.[10] Moreover, oximes are considered as important intermediates in the synthesis of nitriles,[11] nitro,[12] nitrones,[13] amines and azaheterocycles.[14] Various catalytic systems have been reported for the efficient preparation of oximes.[15]

Usually, imine compounds are prepared by the condensation of a carbonyl compound with an amine, generally, in the presence of an acid (such as acetic acid) or base as a catalyst, or with heat applied.[16] Although various methods have been reported in recent years for the preparation of the imine bond,[17] the traditional condensation of aldehyde or ketone with amines is still the simplest way to prepare the desired imine. However, alcohol, as a starting material, is much cheaper, greener and more accessible than aldehyde.[18] So, one-pot synthesis of the imine bond through oxidation of alcohol is a potentially more general and useful method. Various catalytic systems including Pd,[19] Ti,[20] Ru,[21] Cu,[22] Mn,[23] Fe,[24] Au[25] have been reported for the direct transformation of alcohols to imines in the presence of amines.

However, most methods in literature for the preparation of imines involve toxic and expensive heavy metal based catalytic systems, boring work up, usually reflux with Dean Stark apparatus using methanol or ethanol as a solvent for long reaction times.[26] In the search of finding a green procedure in chemical synthesis that is solvent and metal free or applicable under aqueous medium conditions, the present work shows the possibility of using peroxidized soybean oil as a novel oxidant for the formation of Schiff bases and oximes in emulsion systems through direct oxidation of alcohols without any surfactant or amphiphilic catalyst. Moreover, the potential of these systems to produce carbonyls, imines and oximes efficiently in large scale is highlighted. As far as we know, it is the first time that the formation of Schiff base compounds has been reported by vegetable oils.

Experimental Section

Material and instrumentals

Soybean oil was purchased from a soybean Co, Golestan, Iran. All chemicals and solvents were purchased from Sigma Aldrich and Merck and were used as received without any further purification. The FT-IR spectra were obtained using a BRUKER EQUINOX 55 FT-IR spectrophotometer using KBr pellet. The ^{1}H-NMR and ^{13}C NMR spectra were recorded in DMSO-d_6 or CDCl$_3$ using a 250 MHz instrument. All chemical shifts are reported in ppm downfield from TMS. Elemental analyses (C, H, N) were performed on a Perkin Elmer-2004 instrument. GC analyses were performed on a Shimadzu-14B gas chromatography equipped with HP-1 capillary column (Dimethyl-polysiloxane 100%, nonpolar, 30 m, 0.25 mm, 0.25 μm) and N$_2$ and anisole as a carrier gas an internal standard, respectively. Microscopic images were acquired using a Nikon Eclipse E200 microscope. The known Schiff base and oxime products were

characterized by their melting points, elemental analysis and FTIR spectra and comparison with literature values.

Determination of fatty acid composition of soybean oil

The of fatty acid composition in soybean oil including saturated (palmitic acid and stearic acid) and unsaturated acids (oleic, linoleic and linolenic acids) were determined by gas chromatography (GC) and the results come as follows: 10% palmitic acid, 5% stearic acid, 26% oleic acid, 56% linoleic acid and 6% linolenic acid.

Preparation of peroxidized soybean oil (PSO)

Initially, soybean oil (ESO) was epoxidized by a procedure previously described.[27] Briefly, soybean oil (50.0 g) and formic acid (as an active oxygen carrier) were added to a three-necked flask equipped with a mechanical stirrer, a thermometer and a reflux condenser. The flask was placed into a water bath at constant temperature of 50 °C and the reaction mixture was stirred at 1000 rpm for 30 min. Then, a calculated amount of a 30% hydrogen peroxide solution was added dropwise into the mixture during the first 5 hours of reaction. The mole ratio of carbon double bonds to hydrogen peroxide (C=C : H_2O_2) was 1: 1.7. Then, another 40 mL of 30% H_2O_2 was added to the mixture in one shot. The reaction mixture was stirred for 12 h until the epoxide rings are completely opened and peroxide groups are formed (Scheme 1). Afterwards, the reaction mixture was cooled down to room temperature, neutralized and washed with water in order to eliminate excess acid. Diethyl ether was used to enhance the separation of PSO from the water phase. PSO was further dried with anhydrous sodium sulfate and kept in oven at 65 °C overnight.
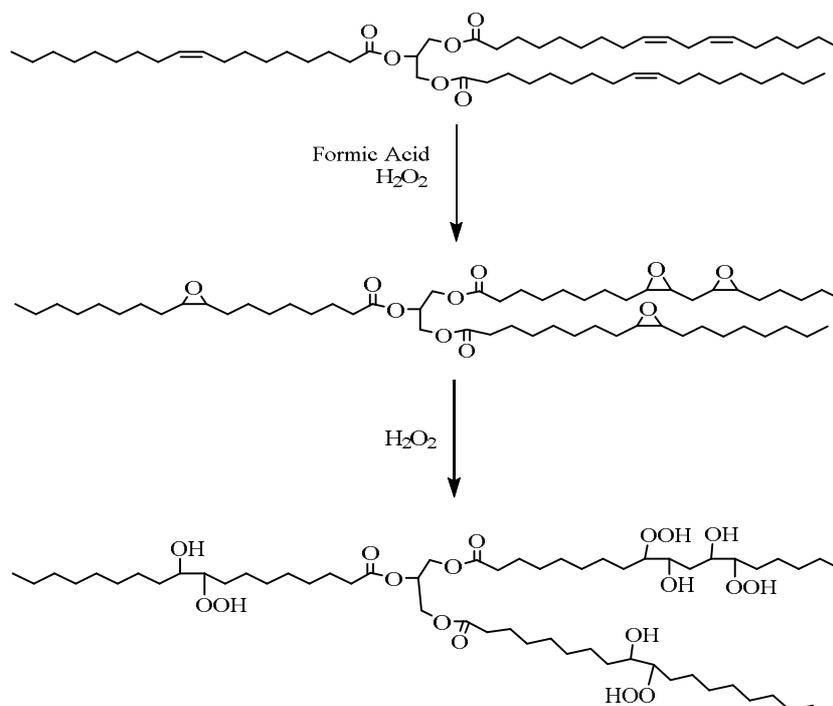
Scheme 1: General reaction scheme for the preparation of PSO.

Preparation of carbonyl compounds in O/W emulsion system using PSO

In a 10 mL round bottom flask, alcohol (5.0 mmol) and 1.2 g of PSO (containing 5.0 mmol peroxide group) were added to 7 mL of water at room temperature. The reaction mixture was vigorously stirred for a sufficient time. Progress of the reaction was screened by TLC. After completion of the reaction, the mixture was centrifuged and the liquid layer was decanted, while PSO stuck around the tube. The product was extracted by DCM (20 mL). The pure product was isolated by evaporation of the solvent without need to any chromatography.

Preparation of Schiff base derivatives in O/W emulsion system by PSO

In a 10 mL round bottom flask, alcohol (5.0 mmol), amine (stoichiometric amount) and 1.2 g PSO (containing 5.0 mmol peroxide group) were added to 3 mL of water in one step at room temperature. The reaction mixture was vigorously stirred for a sufficient time. Progress of the reaction was screened by TLC. After completion of the reaction, the mixture was centrifuged. The PSO and Schiff base product stuck around the tube and the aqueous layer was decanted. Then 10 mL of hot ethanol was added to the remaining mixture in the tube to dissolve the Schiff base product while the PSO remains insoluble. The solution was centrifuged again and the PSO stuck around the tube. The Schiff base product that is now dissolved in ethanol was decanted. The solid pure imine product was obtained after vaporization of ethanol at room temperature overnight. The pure product was isolated by recrystallization in hot ethanol.

Preparation of oxime derivatives (Water in oil emulsion system, (W/O) by PSO)

Formation of oximes in the W/O emulsion system was typically carried out as follows: hydroxylamine hydrochloride (5.0 mmol) was dissolved in the least amount of water in a 25 mL round bottom flask. Then 2.4 g of PSO and 5.0 mmol of alcohol were added to the mixture and stirred at room temperature. Progress of the reaction was monitored by TLC according to alcohol consumption. Vigorous stirring was applied to the system for a sufficient time. After completion of the reaction, 7 mL of hot ethanol was added to the mixture. PSO was separated by centrifugation and the product was isolated after extraction by 15 mL of ethyl acetate and evaporation of the solvent at reduced pressure.

Results and Discussion

Characterization of PSO

Peroxidation of soybean oil was performed by the addition of formic acid with an excess amount of hydrogen peroxide at 50 °C. PSO was characterized by gas chromatography (GC), ^{1}H NMR, UV-Vis and FTIR techniques.

As shown in Figure 1A, the IR absorption related to the carbonyl group and vinyl bonds appeared at 1735 cm^{-1} and 1658 cm^{-1}, respectively. A single absorption at 725

cm^{-1} was assigned to out-of-plane bending of the =C-H- group. Peroxidation of the double bonds in soybean oil was indicated by the appearnce of two peaks at 1465 cm^{-1} and 1427 cm^{-1} related to peroxide groups.[28] Also, the stretching vibrations for C-O bonds can be seen at 1188 cm^{-1}. Furthermore, the stretching vibrations related to C=C bonds was mostly eliminated from the FTIR spectrum of PSO due to transformation of the double bonds into the hydroperoxide groups. A broad peak about 3500 cm^{-1} corresponding to the stretching vibrations of the hydroxyl groups demonstrates the polar addition of hydroperoxide to the double bonds. The results clearly proved the successful preparation of PSO.

The electronic spectra of soybean oil and PSO are shown in Figure 1B. Soybean oil showed a single absorption band with λ_{max} at 328 nm attributed to $\pi \rightarrow \pi^*$ transitions of the C=C bonds. The disappearance of this band in the UV-Vis spectrum of PSO (Fig. 1A) was another evidence for the transformation of double bonds into peroxide groups.

Figure 1: (A) FTIR spectra of (a) soybean oil and (b) PSO; (B) UV-Vis spectra of soybean oil and PSO; (C) GC analysis of PSO; (D) ^{1}HNMR spectra of (a) soybean oil and (b) PSO.

In accordance with the initial composition of soybean oil, GC analysis of PSO exhibits that the percentage of unsaturated fatty acids have been largely reduced (Figure 1C) after peroxidation of soybean oil. Moreover, the appearnce of three new peaks at lower retention times does clearly confirm the peroxidation process. It is believed that, due to the nonpolar nature of the GC column, the polar peroxidized fatty

acids have lower retention times than the initial corresponding fatty acids. Also, these three new peaks show the absence of any other by-product during the peroxidation reaction.

The formation of peroxide and hydroxyl groups was characterized by ^{1}H NMR (Fig. 1D). The resonance of the α-protons (methylene of glycerol) in the glycerol part of the oil and the methyl protons of the fatty acid chains appear at δ = 1.98-2.04, 3.99, 0.96 and 0.58 ppm, respectively, for both of soybean oil and PSO (Fig. 1D).[29] The appearnce of the peaks at δ = 3.45 and 7.77 ppm for PSO corresponds to the chemical shifts for the hydroxyl and hydroperoxide groups;[30] this provides another evidence for the peroxidation of soybean oil. Moreover, the resonance of the vinyl protons at $\delta \sim$ 5.00 ppm was nearly eliminated after the peroxidation reaction (Fig. 1Da).

The hydroperoxide content in PSO was measured by ^{1}H NMR through the reaction of PSO sample of known weight with excess amount of dimethyl sulfide. The concentration of peroxide groups in PSO was determined by comparing the integrated signal of DMSO *versus* that of dimethyl sulfide. In this way, the peroxide content was found to be 4.5 mmol peroxide groups per 1 gram of PSO.

Investigation of the effect of temperature and PSO amount on the oxidation of benzyl alcohol

The effect of temperature and that of the amount of PSO were studied in the oxidation of benzyl alcohol as a model substrate. We performed the reaction using oil-in-water emulsion system in the presence of PSO at room temperature. The oil-in-water emulsion system was used for the oxidation of benzyl alcohol as well as for direct Schiff base formation. The progress of the reaction was monitored by thin layer chromatography (TLC). Due to the fast reaction kinetics, the experiments were performed at room temperature; benzaldehyde was afforded in quantitative yield in a short reaction time (Table 1, entry 2). We examined then the reaction at a higher temperature where no significant changes in time and efficiency of the reaction were observed (Table 1, entry 4). From an industrial point of view, this is beneficial since processes performed at higher temperatures involve higher consumption of energy. With 1.2 g PSO containing 5.0 mmol peroxide groups the experiments exhibited quantitative yield in 16 min (Table 1, entry 2). Increasing the initial amount of PSO resulted in no significant changes with respect to the time of reaction or yield (Table 1, entry 1). The reaction was found to be independent on the presence of surfactants. This claim was proved by adding some polyvinyl alcohol (PVA) as a surfactant; no improvement could however be observed with respect to the reaction progress (Table 1, entry 3). Moreover, the reaction yield was almost the same as in emulsion system with about twice the amount of soybean oil (Table 1, entry 6). Although the emulsion droplets were instable (It turned into two phases with mild stirring), suitable conditions were provided under vigorous stirring for fast progress of the reaction. The method

exhibited excellent selectivity towards the oxidation of benzyl alcohol (Table 1, entry 2). Benzaldehyde selectivity decreased with increasing PSO amount (or increasing peroxide group), and with 9.0 mmol of PSO the selectivity fell abruptly to 74 % (Table 1, entry 1). The temperature did not affect the selectivity towards aldehyde which remained constant from room temperature upto 60 °C (Table 1, entry 4).

Table 1: Influence of reaction parameters on the oxidation of benzyl alcohol in O/W emulsion system using PSO.[a]

Entry	Solvent	PSO (g)	Time (min)	Yield (%)[b]	Selectivity (%)[c]
1	H_2O	2.0	22	92	74
2	H_2O	1.2	16	98	98
3	H_2O	1.2[d]	16	94	97
4[e]	H_2O	1.2	16	96	97
5	Free solvent[f]	1.2	18	90	84
6	Free solvent[f]	2.0	15	95	88
7	Free solvent[f]	2.5	18	93	62

[a] Reaction conditions: PSO (1.2 g, containing 5.0 mmol peroxide group), benzyl alcohol (5.0 mmol), r.t., H_2O (7 mL) or free solvent.
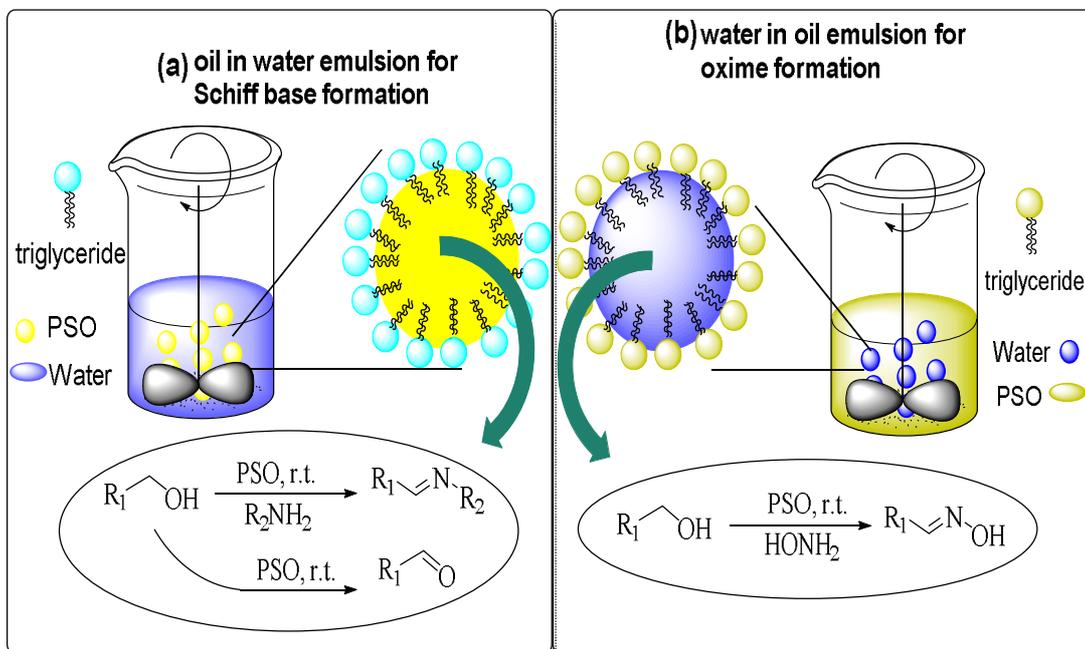[b] Isolated yield.
[c] GC analysis.
[d] 0.1 g of PVA was added to the reaction mixture as a surfactant.
[e] 60 °C.
[f] *Procedure:* after completion of the reaction, 7 mL of EtOH was added to the reaction mixture then centrifuged. The product was separated then purified by flash chromatography.

Scheme 2: (a) Schiff base/ carbonyl formation using O/W emulsion system and (b) oxime formation.

Water in oil emulsion system (W/O) was also used for direct oxime preparation from alcohol and hydroxylamine hydrochloride; excellent yields were achieved with this

system at room temperature. On the other hand, O/W systems did not show suitable results for the preparation of oximes. A possible explanation for this behavior is that peroxidation reaction of the C=C double bonds in soybean oil leads to the formation of hydrophilic sites in the fatty acid chains and thus to H-bonding with water molecules. Peroxidized fatty acid chains become thus directed inside water molecules whereas the glycerol parts directed to PSO providing a W/O emulsion system as drawn in Scheme 2b. In such a case, the oximes are prepared inside the water droplets (Scheme 2). Progress of the reaction was monitored by TLC according to degree of consumption of benzyl alcohol. The highest yield in such systems was obtained with 2.4 g of soybean oil (Table 2, entry 2). Table 3 demonstrates also the absence of PVA influence just as has been observed with the oxidation of benzyl alcohol (Table 2, entry 4). Again, the reaction was independent of temperature (96% at 60 °C). The reaction did not show any progress in the absence of water which exhibits the effect of water for this emulsion system as discussed above.

Table 2: Effect of solvent and peroxide amount on direct preparation of oxime: The reaction of benzyl alcohol and hydroxyl amine salt with PSO through O/W system.[a]

Entry	Solvent	PSO (g)	Time (min)	Yield (%)[b]
1	PSO	1.2	22	76
2	PSO	2.4	16	96
3	PSO	2.6	15	96
4	PSO	2.4[c]	15	39
5	PSO[d]	2.4	30	N.R.

[a] Reaction conditions: PSO, benzyl alcohol (5.0 mmol), $NH_2OH.HCl$ (5.0 mmol), r.t., H_2O (least amount for complete dissolution of $NH_2OH.HCl$).
[b] Isolated yield.
[c] 0.1 g PVA was used as surfactant and added to the reaction mixture.
[d] Without water.

Figure 2 represents the optical micrographs of prepared emulsions showing clearly the formation of emulsion droplets. The images were taken immediately after vigorously stirring of oil in water emulsion (Fig. 2a) and water in oil emulsion (Fig. 2b) at room temperature.
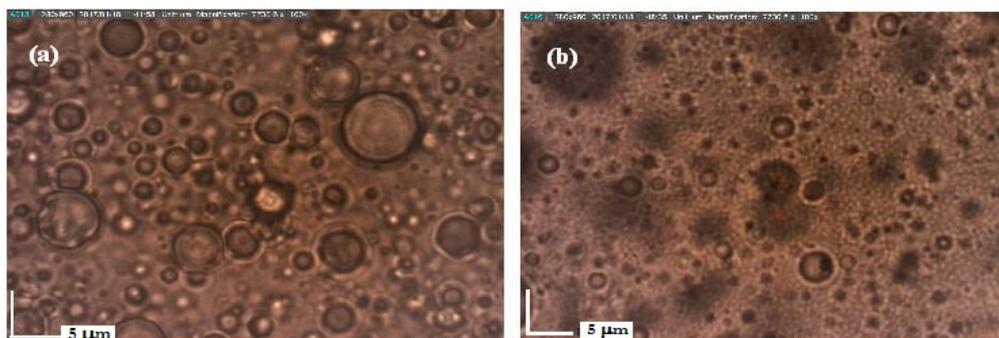

Figure 2: (a) Optical micrograph of the reaction mixture of O/W emulsion system using PSO for oxidation of benzyl alcohol; (b) optical micrograph of the reaction mixture of W/O emulsion system for direct preparation of benzaldehyde oxime

Discussion

With optimized conditions in hand, various alcohols were selectively oxidized to the corresponding aldehydes or ketone and the results are tabulated in Table 3. For all of substrates, no considerable over-oxidation to carboxylic acid was found. As shown in Table 3, substituents on the aromatic ring had little influence on the reactivity of the alcohol. All tested alcohols afforded the aldehyde in high to excellent yields (Table 3). Secondary alcohol afforded ketones in lower efficiency and longer reaction times than observed with primary alcohols (Table 4, entry 2k). As shown in optimization tests, the method was completely inert with respect to the oxidation of aldehydes as noticed when benzaldehyde and 2-anisaldehyde were used as substrates (not shown at Table 4).

Table 3: Oxidation of alcohols in O/W emulsion system using PSO.[a]
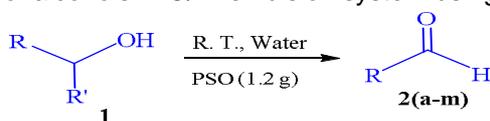
Entry	R	P [b]	Time (min)	Yield (%)[c]
a	C_6H_5	H	16	98
b	$4\text{-}ClC_6H_5$	H	20	96
c	$4\text{-}MeOC_6H_5$	H	10	98
d	$3\text{-}NO_2C_6H_5$	H	30	88
e	$2\text{-}ClC_6H_5$	H	30	93
f	$4\text{-}NO_2C_6H_5$	H	44	95
g	$2\text{-}OHC_6H_5$	H	15	98
h	Cyclohexyl	H	27	98
i	C_6H_5	$CH(OH)C_6H_5$	45	98[d]
j	$CHCHC_6H_5$	H	40	98[e]
k	C_6H_5	CH_3	120	77

[a] Reaction conditions: PSO (1.2 g, containing 5.0 mmol peroxide group), benzyl alcohol (5.0 mmol), r.t., H_2O (7 mL).
[b] Unless otherwise noted, selectivity was > 98%.
[c] GC yield.
[d] Selectivity 54%.
[e] Selectivity 77%.

Schiff base compounds as well as oxime derivatives were prepared in emulsion conditions in quantitative yields (Table 4). Both, electron rich and electron deficient aromatic rings operated well with this method. It seems that the high effective concentration of the substrates inside the emulsion droplets brings the materials molecules close to each other and is thus responsible for the low influence of substitutes on the benzene ring. Furthermore, water that forms during the imine bond formation quickly leaves the oil droplet and acts as a driving force.

Table 4: Schiff base formation in O/W emulsion system using PSO.[a]
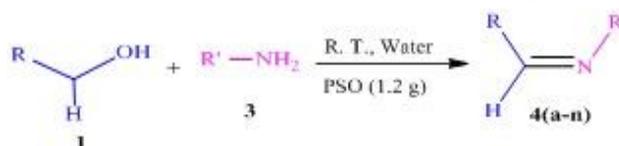
Entry	R	3	Time (min)	Yield (%)[b]	M.p. (°C)[Ref.]
a	C_6H_5	aniline	30	90	55[31]
b	$(Me)_2NC_6H_4$	3-aminophenol	22	94	138-141
c	Furyl	o-Phenylenediamine	35	97	165[32]
d	$2\text{-}OHC_6H_5$	o-Phenylenediamine	17	98	95[33]
e	$2\text{-}OHC_6H_5$	1,3-propylenediamine	25	96	52[34]
f	$2\text{-}OHC_6H_5$	2-aminophenol	19	98	85[35]
g	C_6H_5	2-aminophenol	35	97	87[26]
h	$CHCHC_6H_5$	aniline	240	70	53[36]
i	$C_5H_4CH_2OH$	2-aminophenol	33	95	214[37]
j[c]	$2\text{-}OHC_6H_5$	Allylamine	60	92	-
k[d]	$2\text{-}OHC_6H_5$	3,4-diaminobenzoic acid	35	90	75
l	$3,4\text{-}(OH)_2C_6H_3$	3,3'-diaminobenzidine	120	92	400
m	$4\text{-}OHC_6H_5$	3,3'-diaminobenzidine	75	89	93-97
n	$4\text{-}OHC_6H_5$	4-(4-Aminobenzyl) benzenamine	24	95	218-220

[a] Reaction conditions: Unless otherwise noted, the reaction was carried out with the addition of 5.0 mmol alcohol, stoichiometric amount of amine, 1.2 g PSO, 3 mL of water, r.t.
[b] Isolated yield.
[c] Purification of the product was performed according to Khorshidifard *et al.* work.[38]
[d] Under nitrogen streaming.

As shown in Table 4, 2-((allylimino)methyl)phenol **2j**, which in traditional methods needs a large volume of solvent or reflux conditions for preparation,[38] was successfully synthesized in high yield with the present emulsion method. Even the bulky Schiff bases **2l** and **2m** resulting from the condensation of 3,3'-diaminobenzidine with alcohol derivatives gave excellent yields of the corresponding imine. Complete results of the preparation of a series of Schiff base compounds are summarized in Table 4.

The water-in-oil emulsion system (W/O) was found to be an efficient system for the formation of the oxime derivatives. Table 5 demonstrated a variety of oxime compounds formed in the W/O emulsion system. Similiarly to Schiff base compounds, the direct preparation of oximes using PSO in W/O emulsion conditions gives high to excellent yield for most of the investigated substrates. Benzophenoxime has the least conversion with 77% yield in 130 min.

Table 5: Oximes formation in W/O emulsion system using PSO.[a, b]
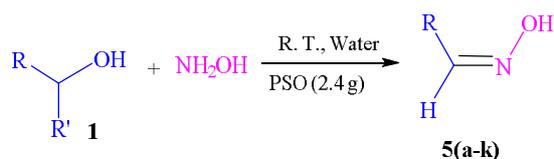
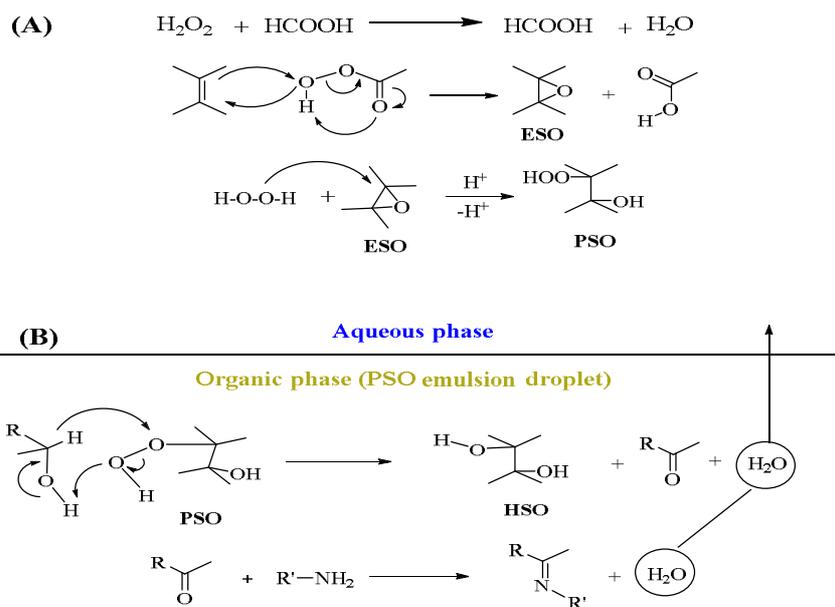| Entry	R	P	Time (min)	Yield (%)[c]	M.p. (°C)[Ref.]
a	C_6H_5	H	22	96	31[39]
b	$4\text{-}ClC_6H_4$	H	25	92	106[39]
c	$4\text{-}MeOC_6H_4$	H	17	98	118[39]
d	$3\text{-}NO_2C_6H_4$	H	45	82	122[39]
e	$2\text{-}ClC_6H_4$	H	40	88	76[39]
f	$2\text{-}NO_2C_6H_4$	H	60	89	133[39]
g	$2\text{-}OHC_6H_4$	H	30	90	120[39]
h	Cyclohexyl	H	37	94	87[39]
i	C_6H_5	$CH(OH)C_6H_5$	55	93	154[39]
j	$CHCHC_6H_5$	H	66	91	120-123[39]
k	C_6H_5	CH_3	180	77	59[15]

[a] Reaction conditions: PSO (2.4 g), alcohol (0.5 mmol), $NH_2OH.HCl$ (0.5 mmol), H_2O (At least amount for complete dissolution of $NH_2OH.HCl$), r.t.
[b] Unless otherwise noted, selectivity was 96-98%.
[c] Isolated yield.

The emulsions formed by PSO in water provide suitable medium for imine bond formation due to: i) raising the effective concentration and thus the interaction between alcohol and amine molecules which gather into the emulsion droplets due to hydrophilic/hydrophobic interactions and ii) water formed during the Schiff base bond formation leaves quickly the emulsion and causes the reaction to go forward and act thus as a driving force (Scheme 3B). The poor solubility of the Schiff base/oxime compound in water[8] helps the separation of the products as powder in the aqueous media.

A proposed reaction mechanism for the imine formation in O/W emulsion system using PSO is shown in Scheme 3. At first, the epoxidation of soybean oil takes place by the peroxide species resulting from the reaction of formic acid and hydrogen peroxide. Excess hydrogen peroxide causes the epoxide ring to open forming thus PSO (Scheme 3A). Alcohol oxidation takes place inside the PSO droplets in one step, producing hydroxylated soybean oil (HAS) and the corresponding carbonyl compound. Further reaction of the carbonyl compound with the amine present in the emulsion droplet affords the imine in the next step (Scheme 3B).
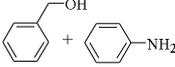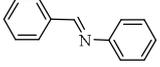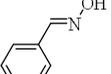
(A)

$$H_2O_2 + HCOOH \longrightarrow HCOOH + H_2O$$

ESO

PSO

(B)

Aqueous phase

Organic phase (PSO emulsion droplet)

PSO   **HSO**

Scheme 3: Proposed mechanism for the direct preparation of Schiff bases from alcohols and amine in O/W emulsion system using PSO.

Insight into the scalability of the process

The application scope of the process was evaluated by preparing the compounds in large scale. PSO demonstrated its potential as an efficient oxidant for industrial aspects. An overall analysis of the scale-up results presented in this study demonstrates the direct scalability of alcohol oxidation optimized under small scale conditions to a larger scale (Table 6). By keeping the previously optimized reaction parameters (time, temperature, oxidant, solvent, …), similar results in terms of reaction conversion and isolated product yield have been obtained for the oxidation of benzyl alcohol, the direct preparation of imine from the reaction of benzyl alcohol and aniline and the preparation of benzaldoxime from the oxidation of benzyl alcohol in the presence of hydroxyl amine salt. In all cases, it was possible to achieve similar isolated product yields on going from a small scale (5.0 mmol starting alcohol) to a larger scale (500.0 mmol) without changing the previously optimized reaction conditions (direct scalability).

Furthermore, the efficiency of the present methodology is displayed by comparing the direct preparation of *N*-benzylidenebenzylamine described in this work from the reaction of benzyl alcohol and benzyl amine in presence of PSO with the results reported in literature (Table 7). In comparison with other catalysts reported in literature, we observe that the PSO method which uses water as a solvent gives a comparable yield in a shorter reaction time (Table 7). In fact, most of the various previously reported methods suffer from so long reaction times needed to achieve convenient yields as well as from the use of expensive and toxic transition metal catalysts in addition to tedious work-up procedures

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Table 6: Large scale production of benzaldehyde, *N*-benzylidenebenzylamine and benzaldoxime using PSO.[a]

Entry	Substrate	Product	Time (min)	Yield (%)[b]	Selectivity (%)
1[c]			20	79	98
2[d]			45	84	95
3[e]			32	88	99

[a] The reactions were performed in a 1 L round-bottom flask with mechanical stirring.
[b] Isolated yield.
[c] Reaction conditions: 500.0 mmol benzyl alcohol, 112 g PSO, 1500 mL of water, r.t.
[d] Reaction conditions: 500.0 mmol benzyl alcohol, 500.0 mmol aniline, 112 g PSO, 1500 mL of water, r.t.
[e] Reaction conditions: 500.0 mmol benzyl alcohol, 500.0 mmol hydroxylamine hydrochloride, 240 g PSO, 1500 mL of water, r.t.

Table 7: Comparison with literature reports for one-pot preparation of *N*-benzylidenebenzylamine.

Entry	Catalyst	Solvent/ T (°C)	Time (h)	Yield (%)[a]	[Ref]
1	PSA-Schiff base Mn(III) complex	Ethanol/R.T.	2.4	92	[18]
2	PNP-type Ru pincer complex (0.02 mol), air	Toluene/ Ref.	56	79	[21]
3	$Cu(ClO_4)_2 \cdot 6H_2O$ (5 mol %), KOH, O_2	Toluene/ 70	19	90	[22]
4	CuI (1 mol%), Bipy (1 mol%), TEMPO (2 mol%), air	CH_3CN/R.T.	6	>99	[22]
5	MnO_2, 4A mol sieves	DMF/Ref.	24	>95	[23]
6	$Fe(NO_3)_3$/TEMPO	Toluene/ 80	24	97	[24]
7	Au/TiO_2, $KOCH_3$ (10 mol%), O_2	-/R.T.	24	-[c]	[25]
8	$Pd(OAc)_2$ (1 mol%), air	-[b]/ R.T.	72	99	[40]
9	PSO (1.2 g)	Water/R.T.	30 min	94	Present Work

[a] GC yield.　　[b] Neat.　　[c] Conversion = 23%.

Conclusions

As a novel, green and efficient protocol we have successfully developed two emulsion systems for the formation of carbonyl compounds, Schiff bases and oximes using PSO. The oxidation proceeds at room temperature inside the emulsion droplets in absence of any external oxidant or emulsifier. The amount of peroxide group in PSO was found to be 4.5 mmol.g^{-1}. The process was demonstrated to have a great potential for the large scale production of carbonyl, Schiff base and oxime compounds as well as at laboratory scale through the oxidation of their corresponding alcohols. Ease of work up, mild and safe conditions, green media, cost effectiveness, fast reaction rates and high to excellent yield were some of the advantages of this work which make it

suitable for facile preparation of the mentioned materials. Finally, we are trying to utilize the hydroxylated soybean oil (HSO), a waste material that forms in the oxidation reactions, as a formaldehyde scavenger.

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