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Homogeneous electro-mediated reduction of unsaturated compounds using Ni and Fe as mediators in DMF

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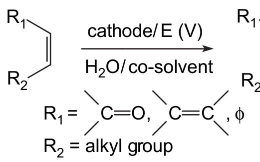
Abstract—The homogeneous electro-mediated reduction (HEMR) of several organic compounds (cyclohexene, cyclohexanone, acetophenone, benzaldehyde, styrene, linalool, 1,3-cyclohexadiene, citral, *trans*-4-phenyl-3-buten-2-one, and piperine) was carried out using Fe^{2+}, Ni^{2+}, and $[Ni^{II}(bpy)]Br_2$ (bpy=2,2′-bipyridine) as electron mediators. An electrochemical system composed of sacrificial anode (Fe, Ni or Zn), nickel cathode, NaI (0.2 M) as supporting electrolyte in DMF and an undivided cell, was used. A constant current $\leq$100 mA was applied with a maximum cell potential of 2.0 V. Non-conjugated olefins are not reactive, but ketones may be easily reduced to the respective alcohol. In the case of conjugated olefins and ketones, $[Ni^{II}(bpy)]Br_2$ or Ni^{2+} mediator presented good reactivity and selectivity in most cases. Fe^{2+} more efficiently mediates the reduction of carbonyl containing systems. Preliminary electroanalytical studies indicate the complexation of the organic substrate by Fe^{2+} and Ni^{2+} ions and $[Ni^{II}(bpy)]Br_2$ complex.

1. Introduction

Over the past several decades, a growing number of new synthetic methods has been forwarded. Most of these methods seek to increase the selectivity, efficiency, and simplicity of synthetic routes to organic molecules. One reaction that has been commonly employed involves the reduction of multiple bonds.[1,2] Catalytic hydrogenation is one among the many reactions available for the reduction of organic compounds, offering advantages of widespread applicability and experimental simplicity. However, the process may become complex when high hydrogen pressure, expensive noble metal catalysts, or specific complexes are involved in the process. Electrochemical methods may be applied as an alternative synthetic route,[3] presenting as principal advantages the simplicity of the system, mild conditions, and the use of electrons as the main reagent.

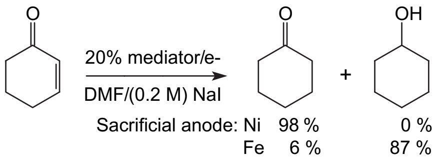
The electrocatalytic hydrogenation (ECH) of organic compounds, for instance, has been intensively studied on heterogeneous surface (Scheme 1), where adsorbed atomic hydrogen is generated in aqueous medium for a posterior catalytic hydrogenation step of the substrate on the cathode surface.[4–6]



Scheme 1. Heterogeneous electrocatalytic hydrogenation of olefins.

Direct electron transfer from the electrode to organic molecules normally occurs at elevated potentials and also produces unstable intermediates including radical anions, radicals, and dianions, often affecting the reaction specificity or selectivity. So the electron transfer by way of stable species (mediators or catalysts) may become a more advantageous route.[3]

Electron transfer mediators have provided the use of electrochemistry as a tool for specific reactions such as: aromatic homo- and hetero-coupling,[7–9] Reformatzky[10] and Barbier[11] type reactions, isoxazoline ring opening,[12] etc. Recently, a new synthetic route for π-bond reduction has been reported (Scheme 2).[13,14] 2-Cyclohexen-1-one was used as a standard



Scheme 2. Homogeneous electro-mediated reduction of 2-cyclohexen-1-one.

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substrate in aprotic solvent (DMF) and several metallic ions and complexes were tested as mediators. Selectivity has been achieved by proper choice of the sacrificial anode.

In this paper we report an extension of the scope of homogeneous electro-mediated reduction (HEMR) to different aliphatic and aromatic olefins and carbonyl compounds, as well as to some more complex conjugated systems. Several organic model compounds were used: cyclohexene, cyclohexanone, acetophenone, benzaldehyde, styrene, linalool, 1,3-cyclohexadiene, citral, and *trans*-4-phenyl-3-buten-2-one. The HEMR method also provided an interesting result for the reduction of a more complex conjugated system like piperine.

2. Results and discussion

The HEMR process was performed in an undivided cell as described previously for 2-cyclohexen-1-one reduction (Fig. 1).[14] A sacrificial anode was used to diminish the cell potential and to avoid undesired reactions on this electrode. A porous nickel cathode was employed in order to increase the surface contact and to allow a higher current without an increase of the cell potential (a stainless steel net also can be used). An inert atmosphere (N_2) is desirable to avoid the reduction of atmospheric oxygen. Conductivity was provided by addition of NaI (0.2 M) as the supporting electrolyte. Pre-electrolysis (30 min) in the presence of 1,2-dibromoethane is necessary to reduce the initial solution resistance.[14,15] Then the substrate was added together with 0.2 equiv of the mediator. In general, a constant current of 100 mA was maintained until complete consumption of the substrate was observed. In some cases, reduction of the current was necessary when the cell potential exceeded 2.0 V. The reaction products were identified by GC and GC–MS analysis and yields were determined by comparison with an added internal standard.

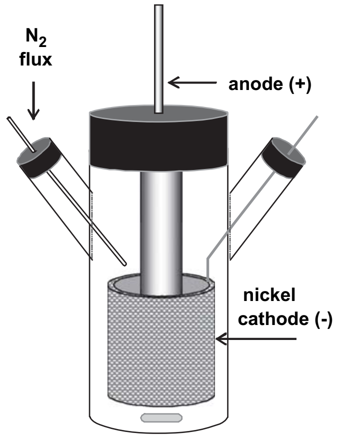


Figure 1. Undivided electrochemical cell used in the HEMR reactions using sacrificial anode. Cathode: Ni^0 foam; and anode: Fe, Zn or Ni.

During the HEMR process, several reactions occur at the same time:[14] (1) oxidation of the (sacrificial) anode, (2) reduction of the mediator on the cathode surface, (3) reduction of the organic substrate by the mediator (reduced form), and (4) protonation of the reduced substrate by residual water in the solvent. If only these reactions occurred, the total electrochemical efficiency (E.E.) of the process ($Q_{\text{theoretical}}/Q_{\text{passed}} \times$total yield) should be 100%, i.e., all electrons transferred to the mediator, on the cathode surface, would be used to reduce the substrate. However, metallic ions generated from the sacrificial anode oxidation and dissolved in the reaction solution can also be reduced on the cathode surface, decreasing the E.E. of the process. In practice, this is not a serious problem since electrons are cheap.

Table 1 summarizes the results obtained from the reduction of a base set of substrates varying the HEMR method. Reduction of cyclohexene was unsuccessful with both mediators (Table 1, entry 1), but conjugation of the double bond with an aromatic ring as in styrene increased considerably the reactivity, especially with the $[Ni^{II}(bpy)]^{2+}/Zn$ system, which gave ethylbenzene in nearly quantitative yield (entry 2). The presence of an allylic hydroxyl group also improved the selectivity of the hydrogenation reaction. In the case of linalool only the double bond between C-2 and C-3 was reduced (entry 3).

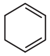
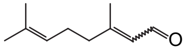
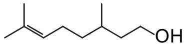
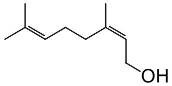
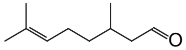
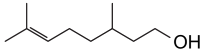
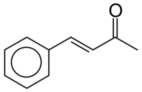
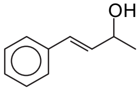
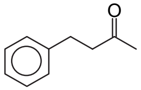
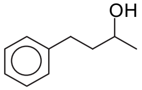
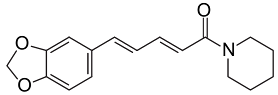
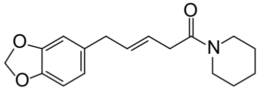
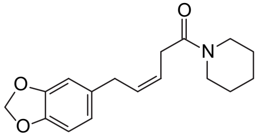
On the other hand, a typical aliphatic ketone such as cyclohexanone was reduced to the alcohol by both the metallic mediator systems (entry 4), but Fe^{2+}/Fe brought higher yield

Table 1. Homogeneous electro-mediated reduction of organic compounds (1.5 mmol), in 20 mL DMF+NaI (0.2 M), nickel cathode, using sacrificial anode (Fe or Zn) and 100 mA as initial constant current

Entry	Substrate	Mediator[a]/anode	Charge (C)	Product (%)	E.E.[b] (%)
1	Cyclohexene	$FeSO_4/Fe$	900	—	—
		$[Ni^{II}(bpy)]^{2+}/Zn$	900	—	—
2	Styrene	$FeSO_4/Fe$	1500	Ethylbenzene (09)	02
		$[Ni^{II}(bpy)]^{2+}/Zn$	2100	(99)	14
3	Linalool	$FeSO_4/Fe$	3000	3,7-Dimethyl-6-octen-3-ol (08)	01
		$[Ni^{II}(bpy)]^{2+}/Zn$	1500	(46)	09
4	Cyclohexanone	$FeSO_4/Fe$	900	Cyclohexanol (99)	32
		$[Ni^{II}(bpy)]^{2+}/Zn$	3000	(95)	09
5	Acetophenone	$FeSO_4/Fe$	2100	1-Phenyl-ethanol (70)	10
		$[Ni^{II}(bpy)]^{2+}/Zn$	2400	(71)	08
6	Benzaldehyde	$FeSO_4/Fe$	2400	Benzyl alcohol (87)	10
		$[Ni^{II}(bpy)]^{2+}/Zn$	1500	(72)	13

[a] The reactions used 20 mol % of the mediator.
[b] Electrochemical efficiency ($Q_{\text{theoretical}}/Q_{\text{passed}} \times$total yield).

Table 2. Homogeneous electro-mediated reduction of organic compounds (1.5 mmol), in 20 mL DMF+NaI (0.2 M), nickel cathode, using sacrificial anode (Fe or Zn) and 100 mA as initial constant current

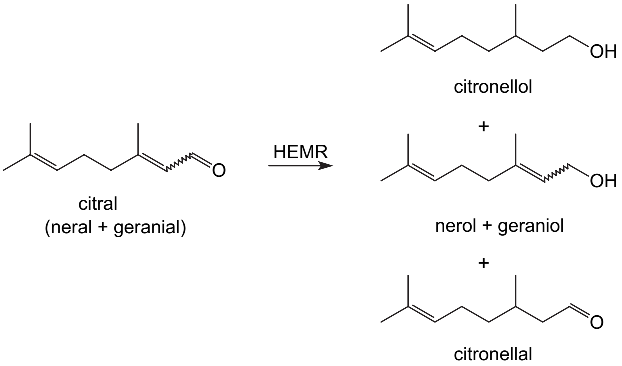
Entry	Substrate	Mediator[a]/anode	Charge (C)	Products (%)				E.E.[b] (%)
1	 1,3-cyclohexadiene	$FeSO_4$/Fe	900		 cyclohexene (38)	 cyclohexane (06)		16
		$[Ni^{II}(bpy)]^{2+}$/Zn	1500		(58)	(02)		12
		$NiBr_2$/Ni	1200		(81)	(18)		28
2	 citral (geranial/neral (6.5:3.5))	$FeSO_4$/Fe	1500	 geraniol (33)	 nerol (18)	 citronellal (02)	 citronellol (48)	27
		$[Ni^{II}(bpy)]^{2+}$/Zn	1200	(29)	(16)	(07)	(10)	17
		$NiBr_2$/Ni	1800	(04)	(04)	(14)	(77)	28
3	 *trans*-4-phenyl-3-buten-2-one	$FeSO_4$/Fe	900	 *trans*-4-phenyl-3-buten-2-ol (10)	 4-phenyl-2-butanone (84)	 4-phenyl-2-butanol (02)		38
		$[Ni^{II}(bpy)]^{2+}$/Zn	1500	(12)	(88)	(—)		20
		$NiBr_2$/Ni	1500	(03)	(57)	(13)		17
4	 piperine	$FeSO_4$/Fe	900	 *trans*-5-benzol[1,3]dioxol-5-yl-1-piperidin-1-yl-pent-3-en-1-one (75)	 *cis*-5-benzol[1,3]dioxol-5-yl-1-piperidin-1-yl-pent-3-en-1-one (25)			38
		$[Ni^{II}(bpy)]^{2+}$/Zn	900	(80)	(20)			38

[a] The reactions used 20 mol % of mediator.

[b] Electrochemical efficiency ($Q_{\text{theoretical}}/Q_{\text{passed}}\times$total yield).

and electrochemical efficiency. Comparable preparative yields with both systems were also obtained in the case of the aromatic carbonyl compounds acetophenone and benzaldehyde (entries 5 and 6).

In the following experiments some conjugated compounds were examined (Table 2). 1,3-Cyclohexadiene produced mixtures resulting from simple and double hydrogenation (entry 1); the best yield, selectivity, and electrochemical efficiency were observed in the Ni^{2+}/Ni system. The same mediator combination was also able to reduce selectively citral (Scheme 3), a commercial mixture of geranial (trans) and neral (cis) (6.5:3.5); in contrast to the behavior of 2-cyclohexen-1-one,[14] the main product with Ni^{2+}/Ni was citronellol, a result of double hydrogenation of the conjugated carbonyl system (entry 2). Using the $[Ni^{II}(bpy)]^{2+}$ complex, a weak preference for the reduction of only the carbonyl bond to geraniol/nerol was observed, whereas Fe^{2+}/Fe produced comparable amounts of both types of product. It can be observed for Fe^{2+} and $[Ni^{II}(bpy)]^{2+}$ mediated reactions that the geraniol/nerol proportion remains the same as citral, while in the presence of Ni^{2+} as mediator an equal (1:1) trans/cis product was observed. In addition, minor amounts of citronellal, as a result of hydrogenation of the conjugated C═C bond, were also detected with all three mediator systems, but the isolated C═C bond was not reduced at all.



Scheme 3. Homogeneous electro-mediated reduction of the citral.

In the case of *trans*-4-phenyl-3-buten-2-one (an example of conjugation of an aromatic ring, a C═C double bond and a carbonyl group) the predominant reaction was the selective reduction of the central C═C bond (entry 3). Fe^{2+}/Fe and $[Ni^{II}(bpy)]^{2+}/Zn$ gave similar yields, but the first mediator system was superior in electrochemical efficiency. Ni^{2+}/Ni proved to be less efficient and selective.

Finally, piperine, a natural diene conjugated to an aromatic ring and an amide moiety, was submitted to HEMR. Simple hydrogenation occurred selectively in a 1,4 manner to produce a mixture of trans and cis isomers (3:1 and 4:1, using Fe^{2+} and $[Ni^{II}(bpy)]^{2+}$ as mediators, respectively) of the mono-unsaturated compound dihydropiperine (entry 4). Preparative yields and good E.E. were obtained with both the mediator systems, comparable to the chemical reduction (Zn/HOAc) of the piperine.[16]

Analyzing the results described above, one can conclude that both metallic mediators are highly efficient for the hydrogenation of conjugated olefins. Non-conjugated olefins are only affected in the case of allylic alcohols. Unsaturated carbonyl compounds are selectively reduced at the C═C double bond in the case of ketones and amides. Unsaturated aldehydes like citral are more reactive and give double hydrogenation, especially when Ni^{2+}/Ni is used.

It is interesting to compare the results obtained from citral hydrogenation by ECH[4,6] and HEMR, described in Table 2. Although electrochemical efficiency obtained in the HEMR method is lower than those obtained in the ECH at variable current density (84%)[4] and static current density (38%),[6] the total hydrogenation product (citronellol) obtained from the HEMR method (77%) was superior to two other ECH methods (70%[4] and 60%,[6] respectively). Other substrates, described in Tables 1 and 2, corroborate the superiority of HEMR.

Similarly, the ECH reaction of *trans*-4-phenyl-3-buten-2-one was carried out using the same reaction conditions as described in the literature[6] (Q=222 C), producing 4-phenyl-2-butanone (45%) and 4-phenyl-2-butanol (15%), and E.E. of 75%. Also in this case, yield and selectivity of the HEMR method (Table 2, entry 3) showed better results.

The use of metallic ions as the catalyst has already been described in the reduction of organic substrates. The $Zn/NiCl_2$ system was used as a selective route for the reduction of α,β-unsaturated carbonyls.[17,18] Also, the reduction of alkenes and alkynes was tested with $LiAlH_4$ in the presence of several metallic ions ($TiCl_3$, VCl_3, $CrCl_3$, $FeCl_2$, $FeCl_3$, $CoCl_2$, and $NiCl_2$).[19] $NaBH_4/CoCl_2$ was applied in the reduction of disubstituted olefins[20] and benzonitrile.[21] The principal advantages of the HEMR over the above related processes is the ability to control the number of moles of electrons by following the charge passed, cell potential, and current density. The use of mild conditions and a clean source of electrons is another advantage.

2.1. Mechanism proposal

In the electro-mediated reduction of the 2-cyclohexen-1-one, described previously,[14] a reduction mechanism involving homogeneous electron transfer was proposed. A more detailed study of the electrochemical system by cyclic voltammetry revealed that Fe^{2+} (Fig. 2) and Ni^{2+} (Fig. 3) ions are reduced at more elevated potentials, than in aqueous medium, −1.74 and −1.28 V, respectively, and the corresponding oxidation peaks are observed at −0.38 and 0.24 V, respectively. The addition of small amount of substrate (2-cyclohexen-1-one) causes the displacement of the reduction peaks to more negative potentials and the disappearance of the oxidation peak, showing that the intermediation of the electron transfer process occurred, which may be explained by an intermediate complex formation before the reduction step (Scheme 4).

The cyclic voltamogram of the $[Ni^{II}(bpy)]Br_2$ complex shows a cathodic (Epc=−1.09 V) and anodic peak (Epa=−0.92 V) corresponding to a reversible reduction system $[Ni^{II}(bpy)]^{2+}/[Ni^{0}(bpy)]$[8] (Fig. 4). Differently to Fe^{2+} and Ni^{2+}, the intermediate complex is more evident when $[Ni^{II}(bpy)]Br_2$ complex is used as mediator. A second reversible system can be observed with addition of 2-cyclohexen-1-one

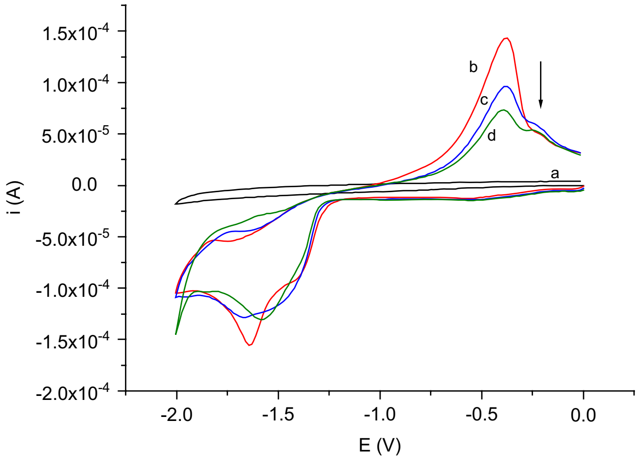


Figure 2. Cyclic voltamogram of: (a) DMF (0.1 M $TBABF_4$) with posterior addition of (b) $FeCl_2$ (0.01 M), and successive additions of (c) 10 μL and (d) 30 μL of 2-cyclohexen-1-one, using vitreous carbon as working electrode, Ag/AgCl (3.0 M KCl) as reference electrode, $v=0.1\ V\ s^{-1}$.

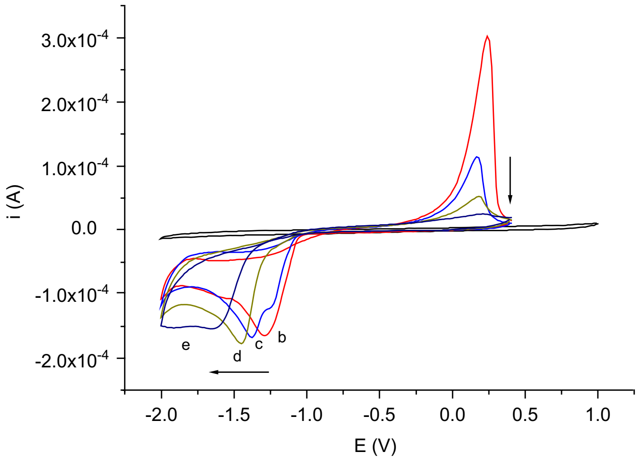


Figure 3. Cyclic voltamogram of: (a) DMF (0.1 M $TBABF_4$) with posterior addition of (b) $NiBr_2$ (0.01 M), and successive additions of (c, d, e) 10 μL of 2-cyclohexen-1-one, using vitreous carbon as working electrode, Ag/AgCl (3.0 M KCl) as reference electrode, $v=0.1\ V\ s^{-1}$.

$$S + M^{2+} \longrightarrow [M\,S]^{2+} \tag{1}$$

$$[M\,S]^{2+} + 2\,e^- \longrightarrow [M\,S]^0 \tag{2}$$

$$[M\,S]^0 \longrightarrow [M^{2+}\,S^{2-}] \tag{3}$$

$$[M^{2+}\,S^{2-}] + 2\,H^+ \longrightarrow M^{2+} + SH_2 \tag{4}$$

S = conjugated olefin or ketone
M = Metallic ion

Scheme 4. HEMR of organic substrates by Fe^{2+} or Ni^{2+}.

(Epc=−1.58 V/Epa=−1.46 V) with a simultaneous displacement of the first oxidation peak (Epa=−0.69 V). Therefore, it is possible in this case that the electron transfer occurs before the interaction with the substrate (Scheme 5).

The results observed in electrosynthesis and electroanalytical experiments indicate a homogeneous electro-mediated mechanism for reduction of the organic substrates studied here. Additional work is necessary for a detailed mechanistic proposal.

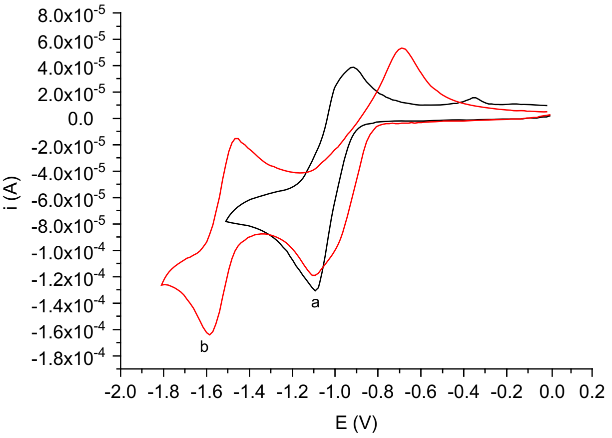


Figure 4. Cyclic voltamogram of: (a) $[Ni^{II}(bpy)]Br_2$ (1.0 mmol) in DMF (0.1 M $TBABF_4$) with posterior addition of (b) 2-cyclohexen-1-one (0.5 mmol), using vitreous carbon as working electrode, Ag/AgCl (3.0 M KCl) as reference electrode, $v=0.1\ V\ s^{-1}$.

$$[Ni^{II}(bpy)]^{2+} + 2\,e^- \longrightarrow Ni^0(bpy) \tag{1}$$

$$Ni^0(bpy) + S \longrightarrow [Ni^0(bpy)S] \tag{2}$$

$$[Ni^0(bpy)S] \longrightarrow [Ni^{II}(bpy)S^{2-}] \tag{3}$$

$$[Ni^{II}(bpy)S^{2-}] + 2\,H^+ \longrightarrow [Ni^{II}(bpy)]^{2+} + SH_2 \tag{4}$$

S = conjugated olefin or ketone

Scheme 5. HEMR of organic substrates by $[Ni^{II}(bpy)]Br_2$.

3. Conclusion

In conclusion, our results demonstrate that reduction of olefins and carbonyl compounds is possible using the HEMR approach. Non-conjugated olefins are unreactive, except allylic alcohols, which are partially reduced by the $NiBr_2$/Ni system. The same mediator showed good reactivity and selectivity for conjugated dienes. Carbonyl compounds can be reduced using both the metallic mediators; in the case of α,β-unsaturated aldehydes, ketones, and amides selective mono- or dihydrogenation is possible depending on the reactivity of the carbonyl group.

4. Experimental

All organic substrates and products, used as GC standards, were purchased from Aldrich or Acros. DMF, ethyl acetate, *n*-hexane, and toluene were used as received. NaI, $FeSO_4$, $FeCl_2\cdot 6H_2O$, and $NiBr_2\cdot xH_2O$ were purchased from Acros. All metal rods were purchased from Nitech and Ni foam cathode from Goodfellow.

The controlled current preparative electrolyses and cyclic voltammetry experiments were carried out with AUTOLAB/PGSTAT 30 potentiostat/galvanostat, using undivided cells of 20.0 mL capacity. A metal rod (Fe, Ni or Zn) of 0.8 cm diameter and nickel foam (10.0×4.0 cm, Nitech) were used as sacrificial anode (immersed >1 cm in solution) and working electrode, respectively, (Ni foil or bar can also be used as cathode). The Ni foam electrode can be reused about 20 times, after cleaning with a 6.0 M HCl solution after each application. The anode should be polished before electrolysis. For experiments involving Ni^0bpy as mediator, the precursor $[Ni^{II}(bpy)]Br_2$ was prepared separately according to the literature.[22] The electrolytic cell was charged under nitrogen with 15.0 mL DMF containing NaI (4.0 mmol) and 1,2-dibromoethane (1.4 mmol). A pre-electrolysis was initiated under 150 mA constant current, during 30 min. The substrate (1.5 mmol) was mixed with mediator (0.3 mmol) ($FeSO_4$, $NiBr_2$, and $[Ni^{II}(bpy)]Br_2$) in 5.0 mL of solvent and then added to the cell. A 100 mA constant current was applied until full consumption of the starting reagent. The product yield was determined on a 0.5 mL aliquot of the reaction solution. Water (2.0 mL) was added to the aliquot and the products were extracted with 2.0 mL of ethyl acetate (hexane for cyclohexene and 1,3-cyclohexadiene substrates) containing 0.067 mmol of toluene, used as internal standard. The product yields were determined by GC analysis. Toluene was used as internal standard to quantify products and reagents. GC–MS analysis were obtained with a Varian 3380 GC or Finnigan MAT-GCQ instrument, fitted with a 30 m capillary CP-SPL5CB Chrompack column, using 60–200 °C temperature range (20 °C min^{-1}). Comparisons with authentic sample were performed to identify hydrogenation products and reagents and confirmed by GC–MS. Electrochemical efficiency of the process can be calculated by equations relating current (I), time (t), charge (Q), electrons (e^-) involved and mole number of hydrogen (n) promoted in the process: $Q=I$ (A)$\times t$ (s)$=e^-\times n\times F$, where $F=96{,}487$ C mol^{-1}.

The reaction product from HEMR of piperine was isolated from the reaction medium by using the same extraction procedure as described above; using 20.0 mL of distilled water and 3×10.0 mL of diethyl ether. It was identified by ^1H NMR and MS as a cis/trans isomers mixture. The crude product was purified by silica gel column chromatography.

4.1. *trans*-5-Benzol[1,3]dioxol-5-yl-1-piperidin-1-yl-pent-3-en-1-one [23512-55-2]

^1H NMR (300 MHz, $CDCl_3$): δ 1.55 (m, J=6.6 Hz, 4H), 1.62 (m, J=4.5 Hz, 2H), 3.20 (d, J=5.1 Hz, 2H), 3.35 (d, J=5.4 Hz, 2H), 3.30–3.60 (4H), 5.64 (m, 1H), 5.91 (s, 2H), 6.64 (m, 1H), 6.67–6.74 (m, 3H). *m*/*e* 287 (53), 204 (35), 174 (35), 152 (44), 135 (30), 112 (73), 84 (53), 69 (100).

4.2. *cis*-5-Benzol[1,3]dioxol-5-yl-1-piperidin-1-yl-pent-3-en-1-one

^1H NMR (300 MHz, $CDCl_3$): δ 1.55 (m, J=6.6 Hz, 4H), 1.62 (m, J=4.5 Hz, 2H), 3.12 (d, J=6.3 Hz, 2H), 3.29 (d, J=3.9 Hz, 2H), 3.30–3.60 (4H), 5.63 (m, 1H), 5.91 (s, 2H), 6.64 (m, 1H), 6.66–6.74 (m, 3H). *m*/*e* 287 (53), 204 (35), 174 (35), 152 (44), 135 (30), 112 (73), 84 (53), 69 (100).

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