

Reduction of α,β -Unsaturated Ketones Using a Zn/NiCl₂ System in Aqueous Media in the Presence of Anionic and Cationic Surfactants

Hocine Ilikti*, Tayeb Benabdallah, Kamel Bentayeb, Adil A. Othman and Zoubir Derriche

Organic Chemistry and Electrochemistry Laboratory, Department of Chemistry, Faculty of Science, University of Science and Technology, Oran–Mohamed Boudiaf-USTO-MB, BP:1505 El M'Naouar, Oran 31000, Algeria.

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ABSTRACT

The reduction of aromatic and aliphatic α,β -unsaturated ketones, namely acetophenone (1) and (-)-carvone (3) with a Zn/NiCl₂ system in H₂O or H₂O/EtOH media in the absence or presence of anionic and cationic surfactants have been investigated and have shown remarkable results. The anionic sodium dodecyl sulphate (SDS), the cationic cetyltrimethylammonium bromide (CTAB) and the non-micelle-forming didodecyldimethylammonium bromide (DDAB) surfactants were utilized. The reduction of acetophenone in H₂O medium gave only a low yield of 1-phenyl ethanol (2) in comparison with the yields which resulted when a H₂O/EtOH medium was employed. The yields increased relatively in a H₂O medium in the presence of cationic surfactants which showed a gradual increase at low concentrations following different patterns and sharp increases at 60 °C and pH 9. The reduction of (-)-carvone (3) with the same system in H₂O medium gave relatively higher yields than that of acetophenone. In the presence of cationic surfactants CTAB and DDAB in aqueous medium the total reduction yield increased appreciably and sometimes reached 100 % in the presence of DDAB at a concentration of 0.98×10^{-2} mol L⁻¹ at 60 °C. The effects of pH, combined metallic salts and different surfactant concentrations on the reduction of (-)-carvone have been also investigated. This paper focuses on the application of surfactants in the reduction of α,β -enones by metal/metallic chloride/H₂O systems in the absence of organic solvents. This method displays regioselectivity and stereoselectivity. This method may also be considered as a contribution to the antipollution process by means of the elimination of organic solvents from the chemical process.

KEYWORDS

Zinc/nickel chloride/H₂O, reduction, hydrogenation, surfactants, sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB), didodecyldimethylammonium bromide (DDAB).

1. Introduction

Reduction reactions under mild conditions (in terms of pressure and temperature) using metal (M)/NiCl₂ systems (M = Zn, Al, Li, Fe) in aqueous media have been reported in the literature. Examples of those reductions involve saturated and α,β -unsaturated carbonyl compounds, azides, olefins, nitro olefins and alkynes. The carbonyl compounds have been reduced to the corresponding products by Zn/NiCl₂/H₂O,¹⁻³ Al/NiCl₂/H₂O,⁴ Li/NiCl₂/H₂O^{5a} and Li/FeCl₂/H₂O 4,4'-di-tert-butylbiphenyl (DTBB)^{5b} systems. The azides gave the corresponding amines and amides when Fe/NiCl₂/H₂O was used as reducing agent.⁶ Alkenes, mesylates and the alkynes were reduced by the Li/NiCl₂/H₂O system to alkanes^{7a,7b} and alkenes,⁸ respectively. The Al/NiCl₂/H₂O system was also utilized to reduce nitro olefins to carbonyl compounds.^{9a} Another metallic chloride, namely CuCl₂, was also reported to reduce the alkyl and vinyl sulfonates to the corresponding hydrocarbons.^{9b} In all the previously mentioned reduction reactions, additional organic solvents have been used to assist the formation of homogeneous reaction media. Some of these solvents were 2-methoxy ethanol,¹ 1,4-dioxane^{2,3} and THF.⁴⁻⁹ Aqueous ethanol (1:1) media have been used in the electrocatalytic hydrogenation of phenol,¹⁰ derivatives of phenols¹¹ and salicylic acid.¹²

The reduction reactions in heterogeneous or colloidal media are known to give very low yields (see, e.g. refs. 13 and 14). Utili-

zation of surfactants to increase yields in electrocatalytic hydrogenation reactions has already been mentioned.^{10,11} Employing surfactants in catalytic amounts to replace organic solvents to assist the solubility of organic substrates in water in the reduction process has not been reported in the literature. This paper will deal with the effects of anionic and cationic surfactants in the reduction of acetophenone (1) and (-)-carvone (3) in water (as an emulsion medium), water/ethanol (as a homogeneous medium) and water/surfactants (as a homogenous medium) at different pH and temperatures. It also shows the influence of the surfactants on the regio- and stereoselectivity of the reduction system Zn/NiCl₂/H₂O/surfactant, as illustrated by the different yields of the reduction products of (-)-carvone (3) under different conditions.

2. Results and Discussion

2.1. The Reduction of Acetophenone (1)

The reduction of acetophenone (1) using different Zn/metal (II) chlorides of Ni, Fe, Cu and Co in a homogeneous medium (1:1 H₂O/EtOH), under different pH (2, 7, 9) and at temperatures of 30 °C and 60 °C gave only one product, namely 1-phenyl ethanol (2, Scheme 1) which was separated by gas chromatography and characterized as stated in the experimental section.

Among the other chlorides used, the Zn/NiCl₂ system gave the highest yield at 30 °C and 60 °C, following the sequence Ni >

* To whom correspondence should be addressed. E-mail: ilikti@yahoo.fr

Table 1 The reduction of acetophenone (1) with different Zn/MCl₂ systems in a homogeneous medium (1:1 H₂O/EtOH) at different pH and temperatures (30 °C and 60 °C).

pH	Yield of 1-phenylethanol (2)/%							
	M=Ni		M=Fe		M=Cu		M=Co	
	30 °C	60 °C	30 °C	60 °C	30 °C	60 °C	30 °C	60 °C
2	15	31	0.5	2	2.5	3.5	1.0	2.0
7	04	71.5	1.0	2	0.5	4.0	0.5	1.0
9	11	92	2	9	3.0	5.0	0.5	3.0

Fe > Cu > Co as shown in Table 1. This sequence is in accord with the results reported in the literature.¹⁵

Carrying out the reduction in H₂O medium only gave much lower yields than those observed in H₂O/EtOH medium, even at elevated temperature (60 °C) and for similar reaction times. The increment of yield after 6 h seemed to be negligible in water medium, as shown in Table 2.

The low yields in H₂O medium may be related to phase separation of acetophenone in water, while the presence of ethanol assisted the solubility of the substrate in water.^{13,14} Also ethanol is known to be a source of hydrogen. Surfactants can also be used selectively in catalytic amounts to assist solubility of the substrate in water, thus when the reduction of acetophenone was effected by the Zn/NiCl₂/H₂O system in presence of anionic (SDS) and cationic (CTAB, DDAB) surfactants in various concentrations and temperatures, the yields of 1-phenylethanol were considerably improved after 6 h (see Tables 2 and 3).

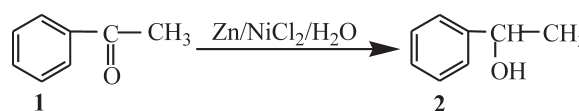
Table 3 and Fig. 1 show that each surfactant is unique in effecting the reduction of acetophenone at various concentrations and at different temperatures. At 30 °C, DDAB showed maximum conversion of acetophenone to 2 (66 %) at concentration 6.2×10^{-2} mol L⁻¹. When CTAB was used at concentration 1.55×10^{-2} mol L⁻¹ an optimum yield of 29 % resulted, while SDS showed its maximum yield (27 %) at a higher concentration of 3.1×10^{-2} mol L⁻¹.

At 60 °C, the conversion of 1 into 2 was quantitative when DDAB was used at a concentration of 3.1×10^{-2} mol L⁻¹, but when CTAB was utilized at a concentration 3.1×10^{-2} mol L⁻¹ a maximum yield of 80 % resulted, and when SDS was used at a concentration of 3.1×10^{-2} mol L⁻¹ a maximum yield of 70 % was obtained.

2.2. The Reduction of (-)-Carvone (3)

The reduction of (-)-carvone (3) using Zn/MCl₂ as reductive systems in aqueous medium and at different pH (2, 7, 9) and at 60 °C gave the *cis*- and *trans*-dihydrocarvones (DHC, 4), *cis*- and *trans*-tetrahydrocarvones (THC, 5) and four diastereoisomers of carvomenthols (CMOH, 6a–d) in different ratios as shown in Scheme 2 and Table 4.

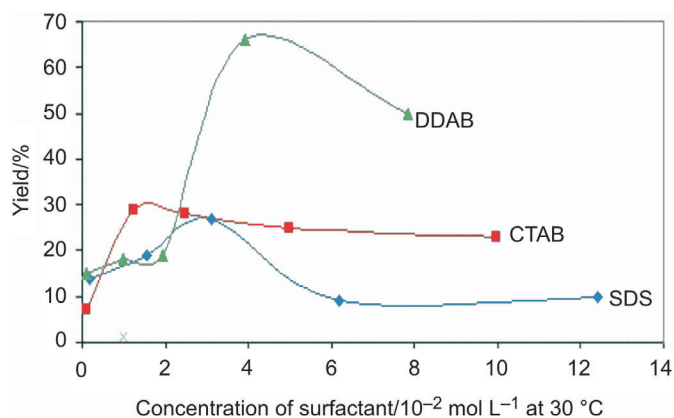
The IR spectra and the GC chromatograms did not show any trace of the anticipated products carvotanacetone (7) or 2,3-dihydrocarveol (8) which suggested that this reduction

**Scheme 1****Table 2** The reduction of acetophenone (1) with the Zn/NiCl₂ system in 1:1H₂O/EtOH and in H₂O at different temperatures, times and reaction medium pH.

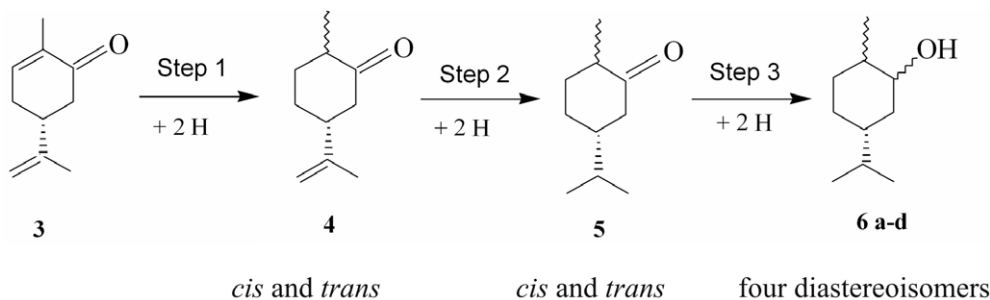
Medium	Temperature/°C	Time/h	Yield/%
H ₂ O/EtOH (1:1)	30	6	46
	60	6	77
	60	8	86
H ₂ O	30	6	10
	60	6	40
	60	8	46

method is regioselective, as evidenced by reducing the conjugated olefinic double bond prior to the reduction of the isolated olefinic bond and the carbonyl group.

Among the many metal chlorides examined in the reduction of (-)-carvone (3) in the homogeneous medium, NiCl₂ had a better

**Figure 1** Yields of 1-phenylethanol (2) formed by reduction of acetophenone with Zn/NiCl₂/H₂O at different concentrations of surfactants at 30 °C.**Table 3** The reduction of acetophenone (1) in the Zn/NiCl₂/H₂O system with different concentrations of surfactants at pH 9 and at 30 °C and 60 °C for 6 h.

Surfactant	Yield of 2/%									
	[C] = 0.16×10^{-2} mol L ⁻¹		[C] = 1.55×10^{-2} mol L ⁻¹		[C] = 3.1×10^{-2} mol L ⁻¹		[C] = 6.2×10^{-2} mol L ⁻¹		[C] = 12.4×10^{-2} mol L ⁻¹	
	30 °C	60 °C	30 °C	60 °C	30 °C	60 °C	30 °C	60 °C	30 °C	60 °C
SDS	14	–	19	39.5	27	70	9	–	10	–
CTAB	7	–	29	25	28	80	25	–	23	–
DDAB	15	–	18	19	19	100	66	–	50	–



Scheme 2

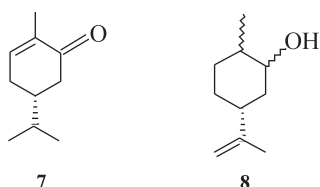


Figure 2 Some of the theoretical products not observed in the reduction of (-)-carvone (3).

reductive power and regioselectivity when compared with the chlorides of Fe, Cu and Co, as shown in Table 5. This result suggests that the reduction preferentially occurs at the conjugated double bond to give DHC (4, 30 %), then at the isolated double bond to give THC (5, 30 %) and lastly at the carbonyl double bond to give CMOH (6a–d, 15 %).

It was also found that by adding small amounts of other metallic chlorides to the reduction system Zn/NiCl₂, such as chlorides of Co, Fe or Cu, the combined metallic chloride systems Zn/NiCl₂/MCl₂/H₂O (see Table 6) showed a higher conversion of (-)-carvone (3) to its corresponding reduction products, particularly when CoCl₂ and FeCl₂ were used, compared with the products obtained when Zn/NiCl₂ only was used (see Table 5). The order of reducing ability followed the sequence NiCl₂ [Co > Fe > Cu], as shown in Table 6.

The combination of Ni/Co chlorides was found to be the most powerful as can be seen from its ability to reduce the two olefinic bonds completely under normal experimental conditions.

The reduction of (-)-carvone (3) with the Zn/NiCl₂/H₂O system in the presence of the surfactants SDS, CTAB and DDAB gave similar products 4, 5 and 6a–d in relatively different ratios as summarized in Table 7.

The anionic surfactant SDS had a negative effect on the hydrogenation when it was added to the Zn/NiCl₂/H₂O system; it showed an even lower yield than when water was used by itself, while the cationic surfactants CTAB and DDAB showed higher yields in aqueous medium (82 % and 91 %) at pH 2 and 9, respectively.

The regioselectivity of this reduction is demonstrated by the optimum yields obtained with a specific surfactant and pH values as shown in Table 7. For the best yield of DHC (4) the reduction of (-)-carvone (3) should be performed in presence of

Table 7 The reduction of (-)-carvone (3) under Zn/NiCl₂/H₂O/surfactant systems at different pH at 60 °C.

Medium	Yield/%									Total conversion/%		
	DHC (4)			THC (5)			CMOH (6a–d)			DHC (4)	THC (5)	CMOH (6a–d)
	pH=2	pH=7	pH=9	pH=2	pH=7	pH=9	pH=2	pH=7	pH=9			
H ₂ O	18	40	21	12	8	12	17	–	17	47	48	50
SDS/H ₂ O 3.15 mmol	17	30	7	–	–	–	–	–	–	17	30	7
CTAB/H ₂ O 2.5 mmol	51	28	42	22	18	22	9	75	15	82	53.5	79
DDAB/H ₂ O 1.97 mmol	30	30	15	30	13	60	15	15	23	75	55	91

Table 4. The reduction of (-)-carvone (3) with Zn/NiCl₂/H₂O at different pH at 60 °C for 6 h.

Product	Yield/%		
	pH = 2	pH = 7	pH = 9
DHC (4)	18	40	21
THC (5)	12	8	12
CMOH (6a–d)	17	–	17
Total conversion/%	47	48	50

Table 5. The reduction of (-)-carvone (3) with Zn/MCl₂/H₂O/EtOH systems at pH 9 for 6 h at 60 °C.

Product	Yield/%			
	M = Ni	M = Fe	M = Cu	M = Co
DHC (4)	30	6	5	3
THC (5)	30	7	7	4
CMOH (6a–d)	15	7	3	3
Total conversion/%	75	20	15	10

Table 6. The reduction of (-)-carvone (3) by combined metallic salt Zn[NiCl₂/MCl₂]/H₂O systems at pH 9 at 60 °C for 6 h.

MCl ₂ system/%	Yield/%			Total conversion/%
	DHC (4)	THC (5)	CMOH (6)	
Ni/Co (95/5)	–	20	79	99
Ni/Co (85/15)	5	8	73	86
Ni/Fe (95/5)	7	14	59	80
Ni/Fe (85/15)	10.5	22	53.5	86
Ni/Cu (95/5)	7	5	18	30
Ni/Cu (85/15)	5	7	23	35

CTAB at pH 2, while the best result for THC (5) can be achieved by using DDAB at pH 9 and the best yield for CMOH (6a–d) may be obtained when CTAB is utilized at pH 7. The optimum conditions for each surfactant are presented in Table 8.

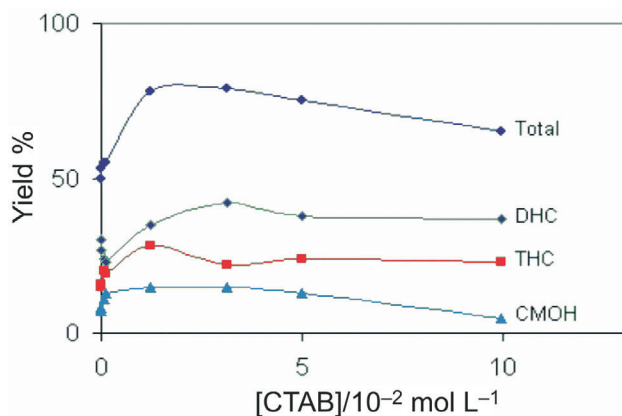


Figure 3 Yields of products formed by reduction of (-)-carvone (**3**) with Zn/NiCl₂/H₂O at different concentrations of CTAB.

CTAB showed its maximum effect (total yield of 79 %) when the concentration was $3.15 \times 10^{-2} \text{ mol L}^{-1}$ and DDAB showed its maximum yield (100 %) when its concentration was $0.98 \times 10^{-2} \text{ mol L}^{-1}$ (see Figs 3 and 4).

Table 8 shows that the regioselectivity in CTAB favoured DHC (**4**) at all concentrations, while for DDAB, the preference went to DHC (**4**), then shifted towards THC (**5**) after the concentration reached $0.196 \times 10^{-2} \text{ mol L}^{-1}$.

2.3. The Interpretation of Reduction by the Zn/NiCl₂/H₂O System

The reduction of unsaturated bonds by the above catalyst has been documented in the literature^{1–9} and comprises three major steps.

Step 1: Since zinc has a low reduction potential, Ni²⁺ is reduced on the surface of metallic zinc, leaving zinc particles that are coated with metallic nickel.²

Step 2: Atomic hydrogen is generated from water in two ways and adsorbed by metal (M = Ni) as follows:

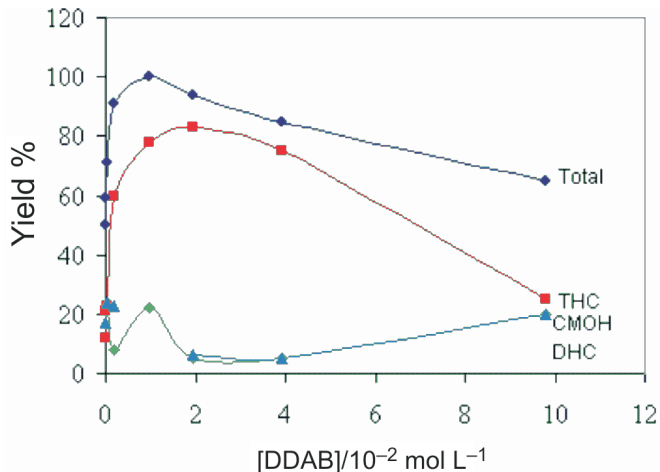
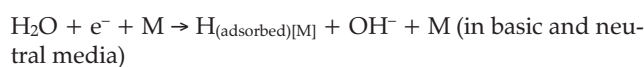


Figure 4 Yields of products formed by reduction of (-)-carvone (**3**) with Zn/NiCl₂/H₂O at different concentrations of DDAB.



or



Step 3: Hydrogen adsorbed on the surface of metallic Ni (H_[M]) adds to the unsaturated bonds (Y=Z) of the substrate which is adsorbed on the metallic surface of the catalyst Y=Z_[M] in two steps:



2.4. The Effect of pH

Zinc does not release hydrogen rapidly at neutral pH (see Table 1) despite its electronegative potential,¹⁶ while acid

Table 8 The reduction of (-)-carvone (**3**) in Zn/NiCl₂/H₂O/surfactant systems at pH 9 and at 60 °C for 6 h.

Medium	Concentration /10 ⁻² mol L ⁻¹	Yield/%			Total conversion/%
		DHC(4)	THC(5)	CMOH(6a-d)	
SDS/H ₂ O	0	30	15	3	48
	0.0124	28	16	3	47
	0.062	25	12	5	42
	0.124	18	7	–	25
	1.24	10	2	–	12
	3.15	7	–	–	7
	4.98	8	–	–	8
	9.96	13	–	–	13
CTAB/H ₂ O	0	27	16	7	50
	0.0124	30	15	8	53
	0.062	24	20	11	55
	0.124	23	19	13	55
	1.24	35	28	15	78
	3.15	42	22	15	79
	4.98	38	24	13	75
	9.96	37	23	5	65
DDAB/H ₂ O	0	21	12	17	50
	0.0098	21	21	17	59
	0.049	24	23	24	71
	0.196	8	60	23	91
	0.98	22	78	–	100
	1.96	5	83	6	94
	3.92	5	75	5	85
	9.80	20	25	20	65

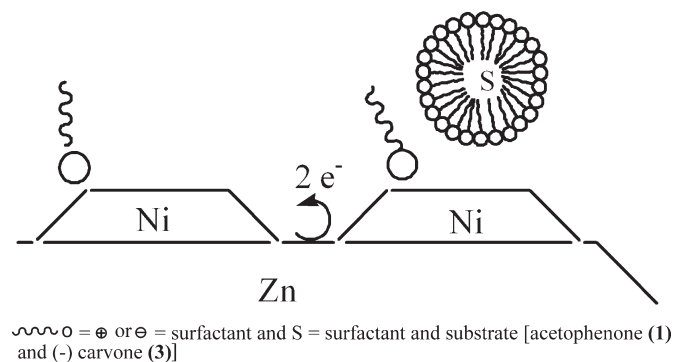


Figure 5 Proposed action of cationic micelles at optimum concentration.

enhances the formation of atomic hydrogen (see step 2 above) which increases the evolution of H_2 gas and reduces the reduction yield (see Tables 1, 4 and 7).

2.5. The Roles of Nickel and Other Metals

Freshly-deposited nickel acts as an electrochemical cell which facilitates the transformation of the electrons released from zinc and enhances the evolution of atomic hydrogen from water.² Nickel also plays an important catalytic role in adsorbing the evolved hydrogen and the organic substrates and thus the reduction process takes place on its surface.

2.6. The Effect of the Surfactant

It is well known that the presence of an assistant solvent and elevated temperature in heterogeneous catalytic reduction processes in general and in the Zn/NiCl₂ system in particular are essential for the solubility of the substrate and to increase its contact with the catalyst. Surfactants are known to have a similar role in assisting solubility of organic substrates in water through the formation of micelles.^{10–14} The kind of surfactant and its concentration in the reaction medium were found to be effective (see Tables 3 and 8 and Figs. 3 and 4). The anionic surfactant SDS had very low or even no effect on the reduction of 1 and 3 by the Zn/NiCl₂ system in aqueous solution due to the fact that the SDS micelles are crowded on Ni²⁺ ions and thus inhibit their reduction to metallic Ni. While in the presence of the cationic surfactants CTAB and DDAB the Ni²⁺ ions naturally do not associate with the cationic surfactants and therefore they are easily reduced to metallic Ni which deposits on the zinc dust surface and acts as a catalyst² as shown in Fig. 5. When the amount of the cationic surfactant increases it will be adsorbed heavily on the Ni¹¹ and Zn surfaces and hinder the solvated substrates [acetophenone (1) and (-)-carvone (3)] by surfactants in reaching the Ni surface and inhibit the reduction process (see Table 8 and Figs 5 and 6).

3. Conclusions

Reduction reactions of α,β -unsaturated ketones under mild conditions of pressure and temperature using Zn/metallic chlorides in aqueous medium and organic solvents are known in the literature.^{1–9} Similar reductions, utilizing surfactants to replace organic solvents, which are considered as one cause of environmental pollution, have not been reported. Among the Zn/metallic chloride systems, NiCl₂ was found to be the most effective. When acetophenone (1) and (-)-carvone (3) were reduced using the Zn/NiCl₂/H₂O system without organic solvent, the yields were very low. The yields of reduction increased when (i) ethanol was added to Zn/NiCl₂/H₂O; (ii) a small amount of CoCl₂, FeCl₂ or CuCl₂ was added to the NiCl₂; (iii) catalytic amounts of cationic surfactants CTAB or DDAB at pH 2 and pH 9

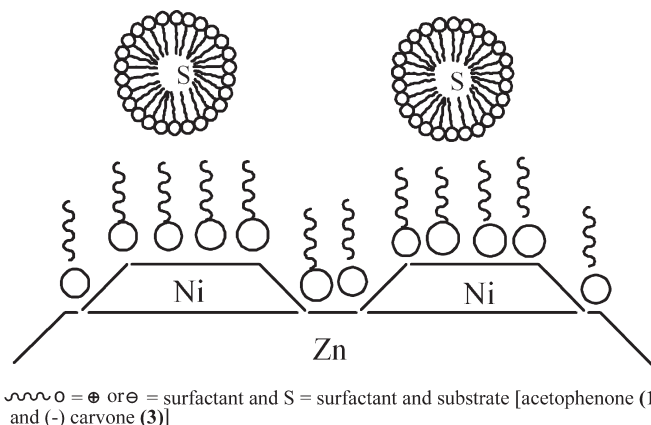


Figure 6 Proposed action of anionic micelles at high concentrations.

respectively were utilized; (iv) each surfactant exhibited optimum conditions and quantitative conversion could be achieved by utilizing DDAB in a catalytic amount ($1.96 \times 10^{-2} \text{ mol L}^{-1}$) at 60 °C. The reduction of (-)-carvone (3) with Zn/NiCl₂/H₂O/(CTAB or DDAB) showed regio- and stereoselectivity, exhibited by the best yields obtained under optimum conditions. For the best yield of DHC (4), the reduction should be performed in the presence of CTAB at pH 2, while the best results for THC (5) could be obtained by using CTAB at pH 4 and the best yield of CMOH (6a–d) may be achieved when DDAB is used at pH 9.

Regioselectivity is represented by the similar ratios of CMOH (6a–d) under different reaction conditions. The yield of reduction of (-)-carvone (3) decreased when an anionic surfactant, SDS, was used.

4. Experimental

4.1. General

The chemicals were commercially available: acetophenone (98 %) from Aldrich, (-)-carvone (98 %), dihydrocarvone (98 %), zinc dust (97 %), NiCl₂·6H₂O (97 %), sodium dodecyl sulphate (SDS, 98 %), cetyltrimethylammonium bromide (CTAB, 98 %), didodecyltrimethylammonium bromide (DDAB, 99 %) from Janssen Chemicals, phosphoric acid (99 %), CoCl₂ and FeCl₂ from Acros. The aqueous and aqueous-ethanol buffers were prepared according to Lide.¹⁷ Thin layer chromatography (TLC) was carried out on DC-Aluofolien-Kiesel-gel 60 (Merck). FT-IR spectra were recorded on KBr discs using a Genesis II FT-IR spectrophotometer. NMR spectra were recorded on a Bruker AM 300 spectrometer (300 MHz for ¹H and 75 MHz for ¹³C) using CDCl₃ as solvent and TMS as internal standard; chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. The separation and identification of products were done by a Varian 3300 gas liquid chromatograph (using H₂, He and N₂ gases) equipped with a flame ionization detector (FID), using a DB-wax fused silica capillary column (30 m \times 0.25 μm , J & W Scientific), coupled with a Shimadzu GR6A integrator. The products were identified by comparing their retention times with those of authentic samples [temperature programme: RT \rightarrow 100 °C (2 min); 100 °C \rightarrow 220 °C (at 20 °C min⁻¹)]. The yields and the mass balances were determined by the internal standard method using n-decane (99 %, Janssen Chemicals).

4.2. General Procedure for Reduction of Carbonyl Compounds using Metal/Metallic Chloride/Medium

In a three-necked round-bottomed flask (50 mL) fitted with a condenser and magnetic stirrer, water (11 mL) or [ethanol

(5.5 mL) + water (5.5 mL)] and surfactant (see Tables 2–8 for the quantities used) and substrate (5 mmol) were added. Zinc dust (1.9 g, 0.029 mmol) and the metal chloride (2.9 mmol) were added with stirring. Evolution of gas started immediately. The reaction mixture was heated under reflux at the temperature reported (see Tables 2–8) in an appropriate bath. The progress of the reaction was monitored by TLC, eluted with 1:1 ethanol-petroleum ether (40–60) until no change in the size(s) of the product spot(s) was observed. The reaction mixture was cooled to room temperature, saturated with NaCl solution (1 mL), filtered and washed with ether. The filtrate was extracted four times with ether (50 mL). The combined filtrates were dried over anhydrous $MgSO_4$, filtered, and the solvent evaporated. The crude product was weighed and the resulting mixture was separated by gas chromatography and identified by comparison of retention times with authentic samples. Physical and spectroscopic data for the known compounds were as follows:

Acetophenone (1): $R_t = 8.4$ min; IR: 1680 (CO), 1600 cm^{-1} (C=C aromatic); 1H NMR: δ 2.5 (3H, s, CH_3), 5–8.5 ppm (5H, m, H-aromatic).

2-Phenylethanol (2): $R_t = 7.51$ min; IR: 3400 (OH), 1600 cm^{-1} (C=C aromatic); 1H NMR: δ 1.5 (3H, d, CH_3), 2.1 (1H, s, OH), 4.9 (1H, q, H_1), 7.4–8 ppm (5H, m, H-aromatic).

(-)-*Carvone* (3): $R_t = 13.89$ min; IR: 1670 (CO), 1645 cm^{-1} (C=C aromatic); 1H NMR: δ 1.6 (6H, s, $3H_7, 3H_9$), 4.88 (2H, m, $2H_{10}$), 6.75 (1H, dd, H_6), 6.9 (2H, m, $2H_3$), 7.3 ppm (2H, dd, $2H_5$).

Dihydrocarvones (DHC, 4): $R_t = 9.03, 9.62$ min; IR: 1700 cm^{-1} (CO); 1H NMR: δ 1.2 (3H, d, H_1), 1.7 (3H, s, H_{10}), 3.5 (3H, m, $H_{2\text{and}6}$), 4.8 ppm (2H, s, H_9).

Tetrahydrocarvones (THC, 5): $R_t = 7.37, 8.6$ min; IR: 1700 cm^{-1} (CO); 1H NMR: δ 0.9 (6H, dd, $3H_9$ and $3H_{10}$), 1.02 (3H, d, H_7), 1.2–1.63 (6H, m, $2H_3, 2H_4, H_5, H_8$), 2.31 ppm (3H, m, $H_2, 2H_6$).

Neocarvomenthol (NCM, 6a): $R_t = 10.36$ min; IR: 3500 cm^{-1} (OH); 1H NMR: δ 0.83 (3H, d, $H_{9\text{ or }10}$, $J = 6.5$ Hz), 0.84 (3H, d, $H_{10\text{ or }9}$, $J = 6.5$ Hz), 0.96 (3H, d, H_7 , $J = 6.5$ Hz), 1.15–1.55 (6H, m, $2H_3, 2H_4, H_5, H_8$), 1.7 (3H, d-quint, $H_2, 2H_6$), 3.85 ppm (1H, m, H_1).

Neoisocarvomenthol (NICM, 6b): $R_t = 14.33$ min; IR: 3500 cm^{-1} (OH); 1H NMR: δ 0.88 (6H, d, $6H_{9\text{and}10}$, $J = 6.7$ Hz), 0.92 (3H, d, $3H_7$, $J = 7.1$ Hz), 1.02–1.7 (6H, m, $2H_3, 2H_4, H_5, H_8$), 2.07 (3H, m, $H_{2\text{and}6}$), 3.73 ppm (1H, m, H_1).

Isoicarvomenthol (ICM, 6c): $R_t = 12.47$ min; IR 3500 cm^{-1} (OH); 1H NMR: δ 0.90 (6H, d, $6H_{9\text{and}10}$), 0.97 (3H, d, H_7 , $J = 6.8$ Hz), 1.35–1.8 (9H, m, $H_2, 2H_3, 2H_4, H_5, 2H_6, H_8$), 3.56 ppm (1H, m, H_1).

Carvomenthol (CM, 6d): $R_t = 11.45, 11.67$ min; IR: 3500 cm^{-1} (OH); 1H NMR: δ 0.87 (6H, d, $H_{9\text{and}10}$, $J = 6.8$ Hz), 1.01 (3H, d, H_7 , $J = 6.3$ Hz), 1.2 (5H, m, $H_{3,4\text{and}5}$), 1.46 (1H, sept, H_8 , $J = 6.5$ Hz), 1.57 (1H, s, OH), 1.63 (1H, m, H_1), 1.73 (1H, m, H_6), 1.95 (1H, m, H_2), 3.13 ppm (1H, td, $H_{1,2}$, $J_{1,2} = 10.2$ Hz, $J_{1-6a} = 10.2$ Hz, $J_{1-6e} = 4.2$ Hz).

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