

distillation, the bottom liquid layer solidified to an unidentified brown solid lump.

Registry No. N≡CNH₂, 420-04-2; Me₃SiCN, 7677-24-9; Me₃SiN=C=NSiMe₃, 1000-70-0.

Surfactant and Cation Effects on the Electrochemical Reduction of an α,β -Unsaturated Ketone

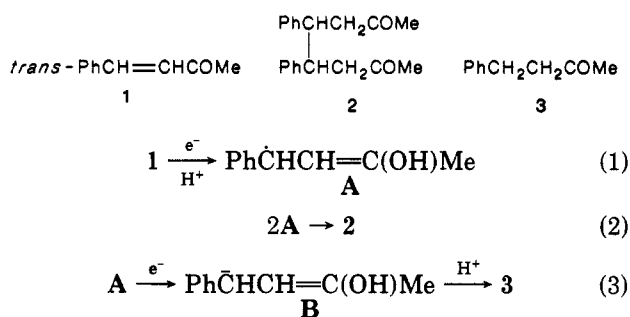
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There have been numerous studies of surfactant effects on electrochemical reactions.¹ However, only a few have addressed synthetic applications.² Herein, we report the effects of surfactants and cations on the electrochemical reduction of α,β -unsaturated ketone 1 at a Hg cathode.

Ketone 1 has been electrochemically reduced previously under various conditions.³ For example, in 1:1 (v/v) EtOH-pH 5.1 NaOCOME-MeCO₂H buffer, its polarography gives two one-electron waves (I and II) with half-wave potentials ($E_{1/2}$) of -1.02 and -1.42 V, respectively,^{3a} and its electrolysis produces *meso*-2 at -1.15 V and 2 and 3 at -1.55 V (vs. SCE).³ The first electron transfer is proton assisted³ and yields radical A (eq 1). Dimerization of A



gives 2 (eq 2), and its further reduction, 3, through carbanion B (eq 3).⁴ Thus, even at potentials more cathodic than $E_{1/2}$ (II), 2 is still formed.⁵ We have investigated the ability of surfactants and several cations to alter the partitioning of A between dimerization and further reduction.

The electrolysis of 0.010 M 1 and differential-pulse polarography of 1.0×10^{-4} M 1 in various media are summarized in Table I. In 1:1 (v/v) EtOH-pH 5.1 0.250 and

Table I. Electrolysis and Differential-Pulse Polarography of 1

entry	medium ^{a,b}	additive, 0.100 M	μ^c	yield, ^d %		$-E_{1/2},^e$ V	
				2	3	I	II
1	1:1 EtOH-H ₂ O (Na)		0.125	12	61	1.07	1.37
2	1:1 EtOH-H ₂ O (Na)		0.225	11	64	1.06	1.36
3	1:1 EtOH-H ₂ O (Na)	NaBr	0.225	12	60	1.06	1.36
4	1:1 EtOH-H ₂ O (Na) ^f	NaBr	0.225	17	60	0.96	g
5 ^h	1:1 EtOH-H ₂ O (Na)		0.125	24	3		
6	1:1 EtOH-H ₂ O (K)	KBr	0.225	4	72	1.06	1.32
7	1:1 EtOH-H ₂ O (K) ⁱ	KBr	0.225	5	76	1.19	1.30
8	1:1 EtOH-H ₂ O (Na)	Me ₄ NBr	0.225	1	95	1.06	1.18
9 ^h	1:1 EtOH-H ₂ O (Na)	Me ₄ NBr	0.225	14	45		
10	1:1 EtOH-H ₂ O (Na)	Bu ₄ NBr	0.225	4	85	1.06	1.22
11	1:1 EtOH-H ₂ O (Na)	HTABr	0.225	3	86	1.06	j
12	1:3 EtOH-H ₂ O (Na)		0.125	2	91	0.96	1.26
13 ^h	1:3 EtOH-H ₂ O (Na)	Me ₄ NBr	0.225	7	63	0.97	1.13
14 ^h	1:3 EtOH-H ₂ O (Na)	HTABr	0.225	1	97	1.01	k
15	H ₂ O (Na)		0.250			0.92	1.21
16	H ₂ O (Na)	NaBr	0.350			0.91	1.18
17	H ₂ O (Na)	Me ₄ NBr	0.350			0.90	1.11
18	H ₂ O (Na)	HTABr	0.350	1	94	0.97	1.09
19	H ₂ O (Na)	HTABr	0.225	1	94		
20	H ₂ O (Na) ^f	HTABr	0.225			0.88	1.11
21 ^h	H ₂ O (Na)	HTABr	0.350	1	91		
22	H ₂ O (Na)	NaDodSO ₄	0.325	3	85	l	1.22
23	H ₂ O (Na)	Brij 35	0.250	3	85	1.01	1.36

^a H₂O (Na) = NaOCOME-MeCO₂H buffer; H₂O (K) = KO-COME-MeCO₂H buffer in entry 6 and KH₂PO₄-K₂HPO₄ buffer in entry 7. The pH of the buffer before the addition of additive and/or EtOH, if used, was 5.1 unless noted otherwise; the ratio indicates v/v composition. ^b For differential-pulse polarography in entries 15-23, the medium contained 0.5% (v/v) EtOH. ^c For the solution as a whole. ^d From electrolysis of 0.010 M 1 at -1.55 V (vs. SCE) unless noted otherwise. ^e From differential-pulse polarography of 1.0×10^{-4} M 1. ^f pH 3.5. ^g Only an ill-defined shoulder was observed at ca. -1.35 V. ^h Electrolysis at -1.275 V. ⁱ pH 7.0. ^j Only an ill-defined shoulder was observed at ca. -1.14 V. ^k Only an ill-defined shoulder was observed at ca. -1.09 V. ^l The peak was split into components at -0.96 and -0.99 V, presumably due to absorption of NaDodSO₄ on the electrode: Schmid, R. W.; Reilly, C. N. *J. Am. Chem. Soc.* 1958, 80, 2087.

0.450 M NaOCOME-MeCO₂H buffer (entries 1 and 2, respectively), and in the former with added 0.100 M NaBr (entry 3), the yield of 3 was essentially the same. Also, the same $E_{1/2}$ (I) and -II) values were determined in entries 1-3. Thus, in these media with Na⁺ as the cation, the nature of the reduction does not depend on ionic strength over the range of total $\mu = 0.125$ -0.225. However, with the substitution of K⁺ for Na⁺ (entry 6), the yield of 3 increased, and $E_{1/2}$ (II) underwent an anodic shift. Greater changes in the yield of 3 and $E_{1/2}$ (II) were obtained when 0.100 M Me₄NBr, Bu₄NBr, and hexadecyltrimethylammonium bromide (HTABr) were added to the reaction mixture of entry 1 to give those of entries 8, 10, and 11, respectively. But note the invariance of $E_{1/2}$ (I), which is consistent with the proton-assisted character of the first electron transfer³ and indicates that the shifts of $E_{1/2}$ (II) are not due to double-layer effects derived from specific

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(2) For examples, see: (a) Honnorat, A.; Martinet, P. *Electrochim. Acta* 1983 28, 1703. (b) Franklin, T. C.; Honda, T. In *Micellization, Solubilization, and Microemulsions*; Mittal, K. L., Ed.; Plenum: New York, 1977; Vol. II, p 617. (c) Johnston, J. C.; Faulkner, J. D.; Mandell, L.; Day, R. A., Jr. *J. Org. Chem.* 1976, 41, 2611 and references therein.

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(4) For a discussion of the mechanism of electrochemical reduction of α,β -unsaturated carbonyl compounds in aqueous media, see: Baizer, M. M.; Feoktistov, L. G. In *Organic Electrochemistry*, 2nd ed.; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983; p 359.

(5) Electrolysis of 0.01 M 1 at -1.55 V in 1:1 (v/v) EtOH-pH 5.1 NaOCOME-MeCO₂H buffer gave a coulometric n value of 1.58,^{3a} which corresponds to 42% and 58% yields of 2 and 3, respectively, if only these compounds are formed.

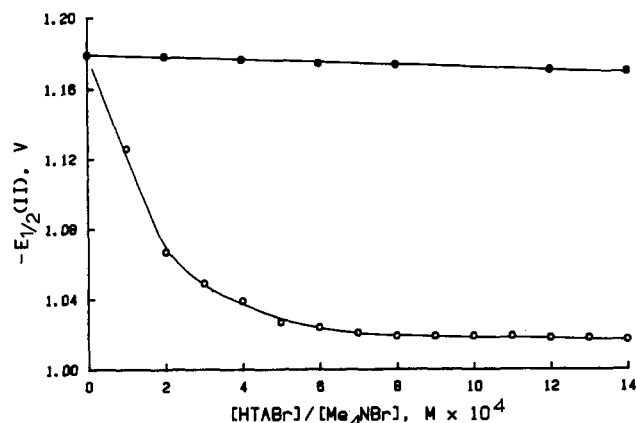


Figure 1. Dependence of $E_{1/2}(\text{II})$ on $[\text{HTABr}]$ (O) and $[\text{Me}_4\text{NBr}]$ (●) for 2.0×10^{-5} M **1** in pH 5.1 0.250 M NaOCOME–MeCO₂H buffer containing 0.2% (v/v) EtOH.

cation absorption on the Hg cathode.⁶ The anodic shifts for the redox couple A,B likely resulted from the preferential stabilization^{1b,c,7} of B by ion pairing, which apparently increased in the order $\text{K}^+ < \text{Bu}_4\text{N}^+ < \text{Me}_4\text{N}^+ < \text{HTA}^+$. The concomitant greater rates of conversion of A to B at -1.55 V led to the higher yields of **3** at the expense of **2**, as would be expected on the basis of eq 2 and 3. Indeed, except for entry 11 with HTABr, the yields of **3** paralleled the anodic shifts of $E_{1/2}(\text{II})$.

The yield of **3** increased, and $E_{1/2}(\text{I})$ and $-(\text{II})$ both became more anodic on going from entry 1 to entry 12 in 1:3 (v/v) EtOH–pH 5.1 0.167 M NaOCOME–MeCO₂H buffer. In entry 13, with the addition of 0.100 M Me₄NBr, $E_{1/2}(\text{I})$ was unaltered, and $E_{1/2}(\text{II})$ shifted anodically, consistent with the trends found on going from entry 1 to entry 8. An analogous addition of 0.100 M HTABr resulted in cathodic and anodic shifts for $E_{1/2}(\text{I})$ and $-(\text{II})$, respectively, in entry 14. The latter reflects increased ion pairing of B, and the former, probably a micellar effect on the protonation of **1**. Due to electrostatic effects, within the micellar pseudophase, **1** will experience a $[\text{H}_3\text{O}^+]$ that is less than that in the aqueous ethanol pseudophase.^{8a} It is known that $E_{1/2}(\text{I})$ is a linear function of pH.^{3a}

Shifts in $E_{1/2}(\text{I})$ and $-(\text{II})$ analogous to those above occurred on going from entries 12–14 to entries 15–18 in aqueous NaOCOME–MeCO₂H buffer. Yield data for **2** and **3** are unavailable for entries 15–17 because 0.010 M **1** is not attainable in these media.

The addition of micellar HTABr (entries 18 and 19), sodium dodecyl sulfate (NaDodSO₄, entry 22), or polyoxyethylene(23) dodecyl ether (Brij 35, entry 23) to the aqueous buffer allowed its use as a reaction medium on a synthetic scale without the need for EtOH as a cosolvent. For 2.0×10^{-5} M **1** in pH 5.1 0.250 M NaOCOME–MeCO₂H buffer containing 0.2% (v/v) EtOH, Figure 1 gives the dependence of $E_{1/2}(\text{II})$ on $[\text{Me}_4\text{NBr}]$ and $[\text{HTABr}]$. A comparison of the two curves suggests a micellar effect by HTABr, whose cmc is 6.0×10^{-5} M in the buffer. As $[\text{Me}_4\text{NBr}]$ increased, $E_{1/2}(\text{II})$ underwent small, linear, anodic shifts. In contrast, as $[\text{HTABr}]$ increased, $E_{1/2}(\text{II})$ experienced larger anodic shifts and became essentially constant above the cmc. A micellar effect is also indicated by the results with Brij 35 in entry 23; the relatively high

yield of **3** was unexpected on the basis of the large value of $E_{1/2}(\text{II})$. In all of the other entries, the yield of **3** roughly correlated with $E_{1/2}(\text{II})$. Perhaps the dimerization of radical A was suppressed within the Brij 35 micellar pseudophase.

Comparisons of entry 3 with 4, 6 with 7, and 18 with 20 illustrate the expected pH dependence of $E_{1/2}(\text{I})$ and independence of $E_{1/2}(\text{II})$.^{3a} Furthermore, these entries indicate that the enhanced yields of **3** with HTABr and NaDodSO₄ in pH 5.1 NaOCOME–MeCO₂H buffer do not result simply from the lower and higher $[\text{H}_3\text{O}^+]$, respectively, within the Stern layer of the micellar pseudophase.⁸ In entry 18, $E_{1/2}(\text{I})$ shifted cathodically relative to entry 15 without micellar HTABr. This shift is consistent with solubilization of **1** within the Stern layer of the micellar pseudophase and the pH dependence of $E_{1/2}(\text{I})$.

Entries 5, 9, 13, 14, and 21 were performed at -1.275 V instead of -1.55 V. They demonstrate that HTABr, and to a lesser degree Me₄NBr, allows the use of more anodic voltages in the synthesis of **3** without sacrificing yield.

No attempt was made to determine the influence of the micellar media on the regiochemistry of the dimerization of radical A; of the possible dimers, only **2** was quantitated (see the Experimental Section). In a study of the electrochemical reduction of several α,β -unsaturated aldehydes, Mandell and co-workers^{2c} found no regiochemical control of dimerization by micellar HTABr.

Honnorat and Martinet^{2a} have reported micellar effects on the electrochemical reduction of acetophenone in H₂O that are similar, in part, to those obtained above with **1**. With HTABr in acidic media, $E_{1/2}(\text{I})$ and $-(\text{II})$ underwent anodic shifts, and with Brij 35 in neutral and basic media, cathodic shifts. With NaDodSO₄, regardless of the pH, they were essentially unchanged. Micellar HTABr in acidic media facilitated the formation of 2-phenylethanol at the expense of 2,3-diphenyl-2,3-butanediol, and there was no effect of ionic strength on the product composition. Interactions of reaction intermediates with HTA⁺ were proposed. Brij 35 at pH 7 decreased, and NaDodSO₄ at pH 9.4 increased the yield of 2-phenylethanol.

In summary, by micellar and/or ion-pairing effects, surfactants and various cations altered the partitioning of radical A between dimerization to **2** and further reduction to **3** through carbanion B. The latter effects also permitted the use of more anodic potentials in the synthesis of **3** from **1** than otherwise possible. Additionally, micellar surfactants allowed the use of aqueous media without a cosolvent.

Experimental Section

General Procedures. All melting and boiling points are uncorrected. High-performance liquid chromatography (HPLC) analyses were performed on a Beckman Model 344 chromatograph equipped with a column inlet filter (2 μm) and a precolumn [3 cm \times 4.6 mm i.d.; 10- μm LiChrosorb RP-18 (Brownlee)] between the sample injector and column [25 cm \times 4.0 mm i.d.; 10- μm LiChrosorb RP-18 (EM)]. HPLC-grade H₂O and MeCN (J. T. Baker) were employed for elution. For detection and quantitation, a Beckman Model 165 UV–vis variable-wavelength detector was used with a Hewlett-Packard Model 3390A reporting integrator. Values of cmc were measured as before.⁹ The cmc of HTABr in 1:3 (v/v) EtOH–pH 5.1 0.167 M NaOCOME–MeCO₂H buffer is 3.1×10^{-4} M. No association of HTABr up to 0.20 M was detected in 1:1 (v/v) EtOH–pH 5.1 0.250 M NaOCOME–MeCO₂H buffer. The cmc values of NaDodSO₄ and Brij 35 in H₂O are 8.1×10^{-3} and $(6.0\text{--}9.1) \times 10^{-5}$ M, respectively.¹⁰

(6) For a discussion of such effects, see: Bard, A. J.; Faulkner, L. J. *Electrochemical Methods*; Wiley: New York, 1980; Chapters 1 and 12.

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Solvents and Materials. Absolute EtOH (U.S. Industrial Chemicals), HPLC-grade water, and Hg (Alfa, electronic grade) were used as received to prepare electrolysis reaction mixtures. *meso*-2 [mp 159–160 °C (lit.¹¹ mp 163.5–164 °C)] and (*E*)-4-phenyl-3-buten-2-ol [mp 36–38 °C (lit.¹² mp 35–36 °C)] were prepared by literature procedures.^{3a,13} The materials below were obtained from Aldrich, except for NaDodSO₄ (BDH, specially pure). HTABr, NaDodSO₄, and Brij 35 were purified by literature procedures.¹⁴ Me₄NBr (mp >300 °C) and Bu₄NBr (mp 115–117 °C) were recrystallized from MeOH (5 °C). 1 was recrystallized from hexane (–5 °C) with Norit treatment (mp 39.5–40 °C). 3 [bp 116–118 °C (ca. 20 mmHg)] and PhCOMe (bp 191–192 °C) were distilled. 4-Phenyl-2-butanol and *n*-butylbenzene were used as received.

Electrolysis Apparatus. A Princeton Applied Research Model 173 potentiostat/galvanostat was used for controlled-potential electrolyses, which were performed in a jacketed, cylindrical 90-mL glass cell (4.7-cm diameter) fitted with a Teflon lid containing a central opening (5 mm diameter) and five peripheral openings (8 mm diameter). A glass stirrer was inserted through the former, and the latter provided access for the anode (Ag/AgBr) and reference electrode (SCE) compartments, a N₂ tube, and an electrical connection to the Hg cathode at the bottom of the cell. Before introduction into the reaction mixture, purified N₂ was passed through a gas-washing bottle containing the same solvent used in a given electrolysis.

Electrolysis Procedure and Analysis. For entry 3, 20 mL each of EtOH and pH 5.1 0.250 M NaOCOMe–MeCO₂H buffer was mixed, followed by the addition of 412 mg (4.00 mmol) of NaBr, to give a solution containing 0.100 M NaBr and total $\mu = 0.225$. The reaction media for the other entries were prepared similarly. To the above cell thermostated at 25.0 ± 0.1 °C was added ca. 10 mL of Hg and 40 mL of the reaction solvent. Stirring and the N₂ flow were begun and continued throughout the experiment. After 15 min, the solvent was preelectrolyzed at –1.60 V (vs. SCE) for 1 h. After 58.5 mg (0.400 mmol) of powdered 1 was added and dissolved (taking up to 15 min in micellar media), the reaction mixture was electrolyzed for 2 h. Then, 51.0 mg (0.425 mmol) of PhCOMe was added as internal standard, and a sample of the mixture was filtered (Millipore HV, 0.45 μ m) and analyzed by calibrated HPLC at 220 nm. The results are summarized in Table I; the yields are averages of at least duplicate runs. In general, little or no 1 remained at the end of an electrolysis. A different sample of Hg was used for each medium, and after every electrolysis, it was washed successively with three 25-mL portions each of EtOH, H₂O, and EtOH and filtered through a filter paper funnel containing a pin hole.

Polarography. Differential-pulse polarography was performed with a Princeton Applied Research Model 174A polarographic analyzer. A dropping Hg electrode, a Pt wire anode, and a SCE reference electrode with a 0.2 M Na₂SO₄ bridge were used. The scan range was –0.80 to –1.60 V, the scan rate was 2 mV/s, and the drop rate was 0.5 s. The sample was degassed with Ar.

Acknowledgment is made to Professor Daniel A. Buttry for helpful discussions and to the U.S. Army Research Office and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1, 1896-62-4; 2, 7028-44-6; 3, 2550-26-7; HTABr, 57-09-0; NaDodSO₄, 151-21-3; Brij, 9002-92-0; Na⁺, 17341-25-2; K⁺, 24203-36-9; Me₄N⁺, 51-92-3; Bu₄N⁺, 10549-76-5.

Supplementary Material Available: Detailed descriptions of the electrolysis cell and the HPLC analyses, including retention times and calibration factors (1 page). Ordering information is given on any current masthead page.

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A Facile Access to (*R*)-Malic Acid

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Of the two enantiomeric malic acids, the (*R*) isomer has been considered to be the more difficultly accessible, hence its higher cost. As a result of this situation, several syntheses of (*R*)-malic acid or its immediate derivatives have been published within the last few years. Thus, Seebach and co-workers¹ have transformed (*R,R*)-dimethyl tartrate into (*R*)-dimethyl malate in four steps and 44% overall yield. Wynberg and Staring² produced the optically pure acid in 79% overall yield by application of a remarkable asymmetric cycloaddition catalyzed by quinidine. A very recent report³ describes the synthesis of enantiomerically pure (*R*)-malic acid from (*R*)-aspartic acid in three steps and 68% overall yield.

We describe herein a simple and expedient synthesis of (*R*)-dimethyl malate (3) from (*R,R*)-dimethyl tartrate (1) in two steps and 67% overall yield (Scheme I). Thus, 1 was transformed into the corresponding crystalline thionocarbonate derivative 2 in 76% yield. Treatment of 2 with tri-*n*-butyltin hydride⁴ gave (*R*)-dimethyl malate (3) in 88% yield after purification by flash chromatography. The optical purity of 3 was ascertained by comparison of its chiroptical properties with reported constants for pure material.^{1,3,5} The transformation of 3 into optically pure (*R*)-malic acid has already been reported.²

Experimental Section

(4*R*,5*R*)-2-Thioxo-4,5-bis(methoxycarbonyl)-1,3-dioxolane (2). To a stirred solution of (*2R,3R*)-dimethyl tartrate (1)⁶ [$[\alpha]_D^{25}$ –8° (c 5.83, CHCl₃); 3.56 g, 20 mmol] in THF (80 mL) was added a solution of thiocarbonyldiimidazole⁷ (3.56 g, 20 mmol) in THF (80 mL) dropwise over 15 min under argon, and the resulting yellow solution was stirred for 2 h at room temperature. The solution was concentrated under reduced pressure to one-third its initial volume, ether (300 mL) was added, and the resulting solution was washed consecutively with HCl (100 mL), water (100 mL), saturated bicarbonate (50 mL), and water again. Processing the organic phase in the usual manner and removal of the solvent gave the thionocarbonate derivative 2 as a light yellow oil that crystallized on standing; yield 3.35 g (76%). A sample was purified by flash chromatography⁸ for analytical purposes (hexane–ethyl acetate, 2:1): mp 59–60 °C; [$\alpha]_D^{25}$ –45° (c 11.5, CHCl₃); MS, *m/e* 221 (M + 1); ¹H NMR (400 MHz, CDCl₃) δ 3.92 (3 H, s), 5.38 (1 H, s); IR (KBr) 1750, 1435, 1375 cm^{–1}. Anal. Calcd for C₇H₈O₆S: C, 38.18; H, 3.66; S, 14.56. Found: C, 38.11; H, 3.64; S, 14.42.

(*R*)-Dimethyl Malate (3). A solution containing 2 (2 g, 9.08 mmol) and tri-*n*-butyltin hydride (2.69 mL, 10 mmol) was refluxed under argon for 20 min. After the mixture was allowed to cool to room temperature, 50 mL of methanol and 6 g of silica were added. The mixture was stirred for 2 h, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (*n*-hexane, then hexane–ethyl acetate gradient, 1:1). The desired fractions were evaporated, and the residue was partitioned between acetonitrile and *n*-hexane. The lower layer was processed as usual to give the title product as a colorless oil: yield 1.3 g (88%); [$\alpha]_D^{25}$ 6.2° (neat) [lit.¹ [$\alpha]_D$ 6.4°]; [$\alpha]_D^{25}$ 9.5°

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