ford a crude product. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane, 1/10).

2-Chloro-1-formyloxy-1-phenylethane (Entry 1). ^{1}H NMR ($CDCl_3$) δ 3.77 (m, 2H), 6.07 (dd, *J*=5.05, 7.82 Hz, 1H), 7.35-7.50 (m, 5H), 8.12 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 43, 74, 127, 129, 129.5, 134, 160. IR (cm^{-1}) 1718, 1290, 1240, 1146, 1070. MS m/z (relative intensity) (EI, 70 eV) 184 (8.9, M^+), 183 (33.4), 148 (36.1), 145 (15.5), 107 (86.3), 84 (100), 77 (68).

2-Chloro-1-formyloxy-1-methyl-1-phenylethane (Entry 2). ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 3H), 3.83 (d, *J*= 12.6 Hz, 1H), 3.99 (d, *J*=12.6 Hz, 1H), 7.25-7.57 (m, 5H), 8.08 (s, 1H). IR (cm^{-1}) 1718, 1485, 1440, 1380, 1159, 1055. MS m/z (relative intensity) (EI, 70 eV) 200 (0.7), 198 (2.9, M^+), 162 (1), 153 (17), 152 (25), 149 (25), 121 (73), 117 (26), 115 (30), 103 (32), 77 (28), 43 (100).

1-Chloro-2-formyloxycyclohexane (Entry 3). ^{1}H NMR ($CDCl_3$) δ 1.15-2.45 (m, 8H), 3.80-4.10 (m, 1H), 4.85-5.05 (m, 1H), 8.15 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 22.8, 24.0, 30.4, 34.3, 59.9, 75.3, 159.8. IR (cm^{-1}) 2950, 2895, 1725, 1455, 1177. MS m/z (relative intensity) (EI, 70 eV) 163 (3, M^++1), 134 (2), 86 (87), 84 (100), 81 (100), 80 (100), 57 (100).

1-Chloro-2-formyloxycycloheptane (Entry 4). ^{1}H NMR ($CDCl^3$) δ 1.40-2.35 (m, 10H), 4.00-4.20 (m, 1H), 5.05-5.20 (m, 1H), 8.10 (s, 1H). IR (cm^{-1}) 2850, 1720, 1445, 1161, 965, 873. MS m/z (relative intensity) (EI, 70 eV) 177 (3, M^++1), 147 (1), 95 (100), 86 (100), 84 (100), 68 (65).

1-Chloro-2-formyloxycyclopentane (Entry 5). ^{1}H NMR ($CDCl_3$) δ 1.60-2.40 (m, 6H), 4.15-4.30 (m, 1H), 5.20-5.30 (m, 1H), 8.02 (s, 1H). IR (cm^{-1}) 2980, 1685, 1422, 1309, 1255, 898, 755. MS m/z (relative intensity) (EI, 70 eV) 149 (16, M^++1), 141 (44), 140 (27), 139 (100), 138 (60), 111 (48), 84 (38).

1-Chloro-2-formyloxy-3-phenoxy-propane and 2-chloro-1-formyloxy-3-phenoxy-propane (Entry 6). ^{1}H NMR ($CDCl_3$) δ 3.78 (dd, *J*=5.57, 11.83 Hz, 0.57H), 3.82 (dd, *J*=5.16, 11.82 Hz, 0.57H), 4.13-4.19 (m, 2H), 4.35 (qui, *J*=6.43 Hz, 0.43H), 4.47 (dd, *J*=5.80, 11.83 Hz, 0.43H), 4.56 (dd, *J*=4.70, 11.83 Hz, 0.43H), 5.43 (qui, *J*=5.13 Hz, 0.57H), 6.88-7.33 (m, 5H), 8.05 (s, 0.43 H), 8.08 (s, 0.57 H).

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Selective Reduction of Ketones in the Presence of Aldehydes

Ji Hwan An, Tae Bo Sim, Jaesung Choi, and Nung Min Yoon*

Department of Chemistry, Sogang University, Seoul 121-742, Korea
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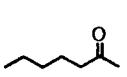
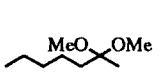
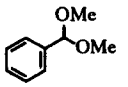
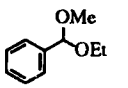
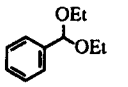
Selective reduction of ketones in the presence of aldehydes have been carried out successfully with sodium borohydride and catalytic amounts of lanthanide chlorides such as $CeCl_3$ or $ErCl_3$ in alcoholic solvents,[1-3] and with lithium tri-*t*-butoxyaluminohydride in ether solvents after preferential transformation of aldehydes into aldimines with *t*-butylamine.[4] When lanthanide salts are present, cyclohexanone was reduced in the presence of hexanal with excellent selectivity (100:2). However, the selectivity between other common aldehydes and ketones were generally not good. For example, 5-nonanone was reduced in the presence of benzaldehyde with only fair selectivity (84:17).[1] Recently we observed that 4-nitrobenzaldehyde readily forms acetal in methanol, in contrast to the sluggish formation of ketals from ketones. This prompted us to explore the possibility of selective reduction of ketones in the presence of aldehydes by preferential formation of acetals from aldehydes in the presence of ketones. First we studied the acetal and ketal formation of an equimolar mixture of benzaldehyde and 2-heptanone in the presence of catalytic amounts of HCl in methanol and methanol-ethanol mixtures. The results are summarized in Table 1. As shown in Table 1, the results in methanol-ethanol (6:1) were very promising for the selective reduction of ketones in the presence of aldehydes. We first attempted to use sodium borohydride for the ketone reduction, however sodium borohydride decomposed rapidly in the presence of catalytic amounts of HCl, and thus the reduction of ketone was not completed. Since borohydride exchange resin (BER) decomposes slowly in weakly acidic condition,[5] and has the advantage of simple work up,[5,6] BER was believed to be suitable for the selective reduction. We report here the selective reduction

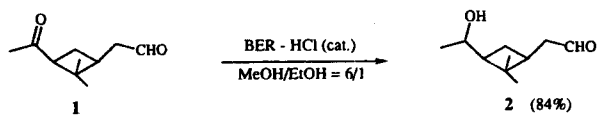
Table 1. Acetalization of Benzaldehyde and Ketalization of 2-Heptanone Catalyzed by HCl in Methanol-Ethanol Mixed Solvents[a]

ratio of MeOH/EtOH	time (min)						
only MeOH	5	89	11	2	98		
1:1	5	100		34	36	23	5
	30	100		34	36	23	5
3:1	5	100		18	70	12	
	60	99	1	13	70	16	1
6:1	5	99	1	10	80	8	1
	30	98	2	1	87	11	1
10:1	5	97	3	5	85	10	

[a] One mmol each of benzaldehyde and 2-heptanone was stirred in the presence of 1 drop of *conc* HCl in 20 mL of mixed solvent at room temperature.

of ketones in the presence of aldehydes with BER in methanol-ethanol (6 : 1) in the presence of catalytic amounts of HCl.

Thirteen representative equimolar mixtures of aldehyde and ketone, and two equimolar mixtures of cyclohexanone and other common ketone were treated with catalytic amounts of HCl in methanol-ethanol (6 : 1) and then reduced with 3-5 equiv of BER at room temperature. As shown in Table 2, the selectivities are excellent in all cases. In the cases of sterically hindered ketones, an increased amount of BER (5 equiv) was required (entries 2, 6, 7, 9, and 14). In the selective reductions of *trans*-4-hexen-3-one and 4-methyl-3-penten-2-one in the presence of benzaldehyde, the ketones were selectively reduced to the corresponding allylic alcohols in both cases (entries 6 and 7) however *trans*-4-hexen-3-ol was accompanied by a considerable amount of saturated alcohol (17%) due to 1,4-reduction (entry 6). The selectivity of cyclohexanone and hexanal was poor (entry 13): only 14% of cyclohexanol was obtained together with 86% of cyclohexanone ketal and 100% of hexanal acetal. Since cyclohexanone readily forms ketal, 4-heptanone and acetophenone can be reduced in the presence of cyclohexanone with good selectivities (entries 14 and 15). Finally we applied this method to the selective reduction of ketoaldehyde, **1** and the corresponding hydroxyaldehyde, **2** was obtained in 84% isolated yield. It is interesting to note that opposite selectivity resulted when the mixture was reduced with BER in methanol without prior acetalization. For instance, acetophenone was reduced preferentially in the presence of hexanal with perfect selectivity (100 : 0) (entry 3), whereas opposite selectivity (4.7 : 99.5) was found previously with BER alone.[6] In conclusion, the present method is a good alternative to the existing methods for the selective reduction of common ketones in the presence of aldehydes and cyclohexanone.



1 2 (84%)

Table 2. Selective Reduction of Ketones in the Presence of Aldehydes with BER[a]

Entry	Substrate	Product	Yield[b]
1	hexanal		0
	2-heptanone	2-heptanol	96
2[c]	hexanal		0
	4-heptanone	4-heptanol	98
3	hexanal		0
	acetophenone	*sec*-phenethyl alcohol	100
4	benzaldehyde	benzyl alcohol	2
	2-heptanone	2-heptanol	96
5	benzaldehyde	benzyl alcohol	2
	acetophenone	*sec*-phenethyl alcohol	99
6[c]	benzaldehyde	benzyl alcohol	2
	trans-4-hexen-3-one	*trans*-4-hexen-3-ol	83
		3-hexanol	17
7[c,d]	benzaldehyde	benzyl alcohol	3
	4-methyl-3-penten-2-one	4-methyl-3-penten-2-ol	98
8	2-methoxybenzaldehyde	2-methoxybenzyl alcohol	1
	2-heptanone	2-heptanol	95
9[c]	2-methoxybenzaldehyde	2-methoxybenzyl alcohol	1
	4-heptanone	4-heptanol	99
10	4-chlorobenzaldehyde	4-chlorobenzyl alcohol	2
	2-heptanone	2-heptanol	98
11	4-nitrobenzaldehyde	4-nitrobenzyl alcohol	1
	2-heptanone	2-heptanol	97
12	cinnamaldehyde		0
	2-heptanone	2-heptanol	95
13	hexanal		0
	cyclohexanone	cyclohexanol	14
14[c]	cyclohexanone	cyclohexanol	9
	4-heptanone	4-heptanol	100
15	cyclohexanone	cyclohexanol	8
	acetophenone	*sec*-phenethyl alcohol	99

[a] Reduction was carried out for 3 h with 3 equiv of BER in methanol-ethanol (6 : 1) after stirring equimolar mixture of aldehyde and ketone for 30 min in the presence of 1 drop of *conc* HCl at room temperature. [b] Yields were estimated by GLPC using appropriate internal standards, and the remainder was acetal and ketal. [c] 5 equiv of BER was used. [d] In 9 h.

Experimental

General Procedure for Competitive Reduction. Competitive reduction of hexanal and 2-heptanone is described as a representative: one mmol each of hexanal, 2-heptanone, and mesitylene (internal standard) was dissolved in 20 mL of methanol and ethanol (6 : 1 in volume) followed by the addition of 1 drop (*ca.* 0.15 mmol) of *conc* HCl. The mixture was stirred for 30 min at room temperature, and BER (0.94 g, 3 mmol) was added. After 3 h, the GLPC analysis of the mixture on column FFAP showed 96% of 2-heptanol, 2% of 2-heptanone ketal, and 100% of hexanal acetal.

Selective Reduction of Ketoaldehyde 1 to Hydroxyaldehyde 2. Ketoaldehyde[7] **1** (0.50 g, 3 mmol), prepared by ozonolysis of α-pinene in 72% yield[8], was dissolved in 30 mL of methanol and ethanol (6: 1 in volume) followed by the addition of 3 drops of *conc* HCl. The mixture was stirred for 10 min at room temperature, and BER (4.69 g, 15 mmol) was added. After 1 h, BER was removed by filtration. The filtrate was concentrated, and the crude oil (acetal) was dissolved in 20 mL of methylene chloride and hydrolyzed with 2 N HCl. The methylene chloride solution was dried over anhydrous $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica gel (eluted with hexane-EtOAc, 6 : 4) to afford 0.43 g (84%) of hydroxyaldehyde **2** as a yellowish oil: ^{1}H NMR ($CDCl_3$): δ 1.01-1.26 (m, 1H), 1.01 (s, 3H), 1.05 (d, 3H, *J*=6.4 Hz), 1.15 (s, 3H), 1.73-1.87 (m, 1H), 1.94-2.07 (m, 1H), 2.20-2.46 (m, 3H), 3.67-3.75 (m, 1 H), 9.72 (t, 1H, *J*=1.7 Hz); IR (NaCl, neat) 3407, 2871, 2721, 1721, 1462 cm^{-1}; MS m/z (relative intensity) (EI, 70 eV) 155 (1), 137 (1), 100 (38), 98 (14), 85 (100), 69 (55), 43 (16); Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.28; H, 10.57.

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7. Spectral data of ketoaldehyde: ^{1}H NMR ($CDCl_3$): δ 0.84 (s, 3H), 1.33 (s, 3H), 1.89-2.05 (m, 2H), 2.03 (s, 3H), 2.35-2.49 (m, 3H), 2.91 (dd, 1H, *J*=9.4, 8.2 Hz), 9.73 (t, 1H, *J*=1.5 Hz); MS m/z (relative intensity) (EI, 70 eV) 168 (M^+, 1), 153 (2), 140 (2), 98 (58), 97 (41), 83 (100), 69 (57), 43 (19).
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Electrochemical Behavior of Iron(II) Chelates-Sodium Dodecyl Sulfate in H_2SO_4 Aqueous Solution

Young Chun Ko, Jongbaik Ree†, and Keun Ho Chung†

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea
†Department of Chemistry Education, Chonnam National University, Kwangju 500-757, Korea
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Surfactants which possess both a polar or ionic head group and a hydrocarbon chain have been used in a variety of biochemical applications.[1-3] The hydrocarbon chain (hydrophobic part) of surfactants in aqueous solution is directed inward, and the polar head group (hydrophilic part) is directed outward into the bulk polar solvent.[4-6] Thus, micellar assemblies have been extensively utilized in order to apply models for biological membranes[7] and redox processes in biological systems.[8] In the vicinity of a critical micelle concentration (CMC), however the study of ions and organic molecules has received little attention.[9,10]

In this note, the investigation of electrochemical behaviors of two iron(II)chelates, tris(2,2'-bipyridine)iron(II)- and tris(1,10-phenanthroline)iron(II)-sodium dodecyl sulfate (SDS) in H_2SO_4 aqueous solution using cyclic voltammetry (CV) is reported. The behaviors in the vicinity of a CMC is especially addressed. The structure of the double layer around a glassy carbon electrode (GC) resulting from iron chelate-SDS interactions is rationalized using the model proposed by Jaramillo *et al.*[11] Information on iron(II) chelates-SDS interactions comes from considering changes in peak currents and potentials determined by CV. The hydrophobic and electrostatic contribution to micelle association is estimated semi-quantitatively, and the effect of added SDS on iron(II) chelates with varying ligand is compared.

Experiments

Tris(2,2'-bipyridine)iron(II), $Fe(bpy)_3^{2+}$, and tris(1,10-phenanthroline)iron(II), $Fe(ph)_3^{2+}$, were prepared according