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ELECTROREDUCTIVE ACYLATION OF ACTIVATED OLEFINS USING A REACTIVE METAL ANODE

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Abstract: *Electroreductive acylation of 3-aryl substituted α,β-unsaturated esters and nitriles in the presence of aliphatic carboxylic anhydrides using areactive metal anode (Mg, Al, Zn) in an undivided cell afforded the corresponding β-acyl compounds in moderate to good yields. It was found that anionic species formed by electron transfer from a cathode may be stabilized by metal ions freshly formed from an anode and undergo electrophilic attack of carboxylic anhydrides to give the β-acyl products in high yields as compared with the previously reported method using a divided cell.*

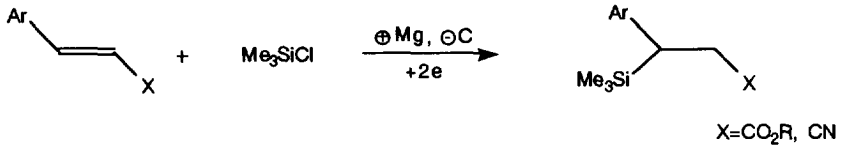
Introduction

Extensive studies[1] have been focused on a variety of synthetic routes for the preparation of 1,4-dicarbonyl compounds as important synthetic intermediates of useful cyclopentenones (e.g. jasmonoids, rethronoids and prostanoids), cyclopentan-1,3-diones, butenolides and furans. Thus, 1,4-addition of an acyl anion or its chemical equivalents[1] to α, β-unsaturated carbonyl compounds may be of importance as one of attractive methods. Though generation and application of an acyl anion are recently extensively investigated,[2] its synthetic utility has been considerably limited because of its instability and difficulties in treatment and generation, and furthermore application of its chemical equivalents generally to organic synthesis requires troublesome and complicated procedure.

On the other hand, it is well known that electroreductive acylation is potentially an extremely useful tool for synthesis of ketones through the formation of a new carbon-carbon bond.[3] Direct electroreduction of activated alkyl halides in the presence of an acid halide (or acetic anhydride) either in a divided cell[3a] or in an undivided cell using a reactive metal anode[3b,c] gives the acylated products in good yields. It was reported that novel acylation of some activated olefins such as α,β-unsaturated esters or nitriles was successfully accomplished by electroreduction in the presence of acid anhydrides in acetonitrile containing tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) using a divided cell equipped with carbon rod electrodes to afford the corresponding γ-ketoesters or nitriles.[4] These products can be regarded as those formed from 1,4-

addition of an acyl anion to these activated olefins, although this electrochemical reaction may not involve the acyl anion itself as the active species. We have also demonstrated electroreductive silylation of activated olefins such as α,β-unsaturated esters, ketones and nitriles in the presence of trialkylsilyl chloride using a reactive metal anode (Mg, Al, Zn) in an undivided cell (Scheme 1).[5]

In the electroreduction system, use of a reactive metal anode (sacrificial anode) in an undivided cell has some remarkable advantages over that of an electrochemically non-sacrificed anode like carbon or platinum in a divided cell.[6] The former reduction system is much more convenient to operate using a much simpler electrolysis cell without any diaphragm and a large amount of expensive supporting electrolyte. Thus, the electrolysis generally proceeds with a lower terminal voltage and higher current efficiency. These facts prompted us to examine the feasibility of electroreductive acylation of α,β-unsaturated esters, ketones and nitriles using a reactive metal anode. Herein, we report the details of the acylation of some activated olefins with respect to high efficiency, convenience and usefulness.



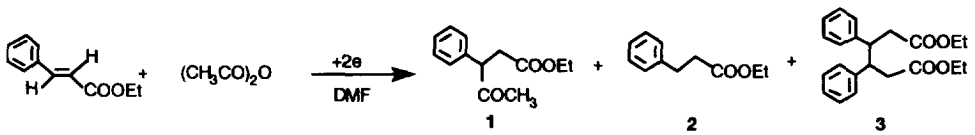
Scheme 1

Results and Discussion

In a typical procedure, the electroreductive acylation of an activated olefin was carried out in N,N-dimethylformamide (DMF) as the solvent containing tetrabutylammonium bromide (Bu_4NBr) as the supporting electrolyte in the presence of an excess mole equivalents of acylating reagent (e.g., acetic anhydride) using a beaker-type undivided cell equipped with a magnesium rod as the anode and a stainless steel plate as the cathode under the constant-current conditions (current density: 19 mA/cm^2) at room temperature until 2 F/mol of electricity passed through the system.[7] Usual work-up including isolation with column chromatography gave the corresponding acylated products in moderate to good yields.

Electroreductive acylation of ethyl cinnamate with acetic anhydride was investigated in detail as a typical example (Scheme 2). Acylated product **1** was obtained as a main product accompanying a small amount of simply reduced product **2** and a radical coupling product **3** as by-products.

Though cathode material in a divided cell generally gives a significant influence on elctroreduction, the yields of the products **1**-**3** were hardly affected by cathode materials and supporting electrolytes used here as



Scheme 2

shown in Table 1 in this reaction (entry 1, 11-18). On the other hand, the reaction was found to be sensitive to current density as well as anode materials. Use of reactive electrodes like Mg, Al and Zn with low current density of 10-11 mA/cm^2 gave γ-ketoester **1** in an excellent yield, while use of platinum or carbon as the anode resulted in some decrease in the conversion of ethyl cinnamate and the yield of the desired product **1** (entry 7-10). These facts represent the importance of reactive metal anodes, and also suggest that intermediates once reduced by a cathode are reoxidized by an anode to the starting materials and/or other products when a platinum or a carbon anode is used in an undivided cell.

Table 1. Electroreductive Acylation of Ethyl Cinnamate

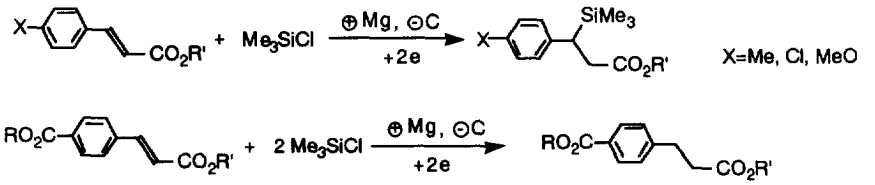
Entry	Anode	Cathode	Current Density (mA/cm^2)	Supporting Electrolye	GC Yield (%)			
					1	2	3	recovery of ethyl cinnamate
1	Mg	SUS	19	Bu_4NBr	74	1	3	1
2	Mg	SUS	10	Bu_4NBr	84	5	3	0
3	Al	SUS	22	Bu_4NBr	36	1	1	35
4	Al	SUS	11	Bu_4NBr	81	7	3	8
5	Zn	SUS	22	Bu_4NBr	45	2	1	32
6	Zn	SUS	11	Bu_4NBr	78	4	2	8
7	Pt	SUS	20	Bu_4NBr	53	3	3	32
8	Pt	SUS	10	Bu_4NBr	49	2	0	23
9	C	C	15	Bu_4NBr	10	0	0	64
10	C	C	7.5	Bu_4NBr	61	2	0	8
11	Mg	Pb	19	Bu_4NBr	82	5	2	0
12	Mg	Mg	19	Bu_4NBr	75	4	4	2
13	Mg	Pt	19	Bu_4NBr	82	6	4	1
14	Mg	C	19	Bu_4NBr	85	4	1	0
15	Mg	C	19	Bu_4NBF_4	87	8	1	4
16	Mg	C	19	Et_4NOTs	87	5	1	8
17	Mg	C	19	Et_4NCl	88	5	1	2
18	Mg	C	19	Me_4NBr	82	14	3	1

Electricity: 2.0 F/mol Solvent: DMF, 25°C.

We also chose ethyl cinnamate as a substrate and investigated on the reactivity of various acylating agents (Table 2, entry 1-5). Use of various acid anhydrides gave the corresponding acylated products in high yields (entry 1, 3, 4). Replacement of acid anhydrides by acid chlorides in this electroreduction brought about a considerable decrease in the yield of the acylated product (entry 2). Introduction of an ethoxycarbonyl group to the β-position of ethyl cinnamate was not attained by use of ethyl chloroformate as an acylating reagent instead of acid anhydrides (entry 5).

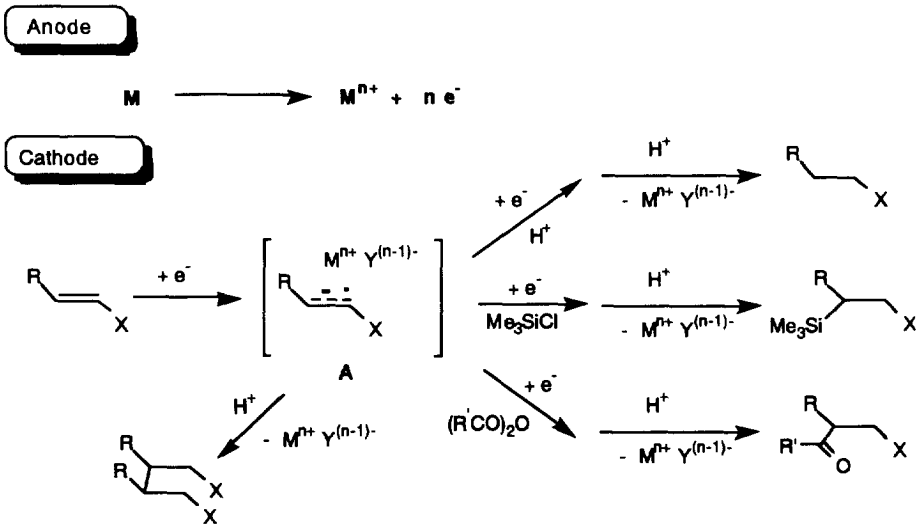
Table 2 (entry 6 - 19) shows the results obtained for several other α,β-unsaturated esters, ketones and nitriles with acetic anhydride. The reaction of aromatic ring-substituted ethyl cinnamates (4-Me, 4-Cl, 4-MeO, 4-MeOOC) with acetic anhydride gave the corresponding acetylated compounds smoothly. It was especially noteworthy that use of ethyl 4-methoxycarbonylphenylacrylate as the substrate also gave the corresponding

acylated product **12** in a good yield although only the simply olefin-reduced product was formed in the case of the electroreductive silylation reported in a previous paper(Scheme 3).[5] It may indicate that in the case of silylation stable anionic species formed from the 4-methoxycarbonyl derivatives undergo O-silylation easily rather than C-silylation, yielding the simply-reduced product after hydrolysis .



Scheme 3

The reactions of ethyl 3-arylacrylates with acetic anhydride gave the corresponding acetylated products in moderate to good yields, comparable to those by the divided cell method.[4] In contrast, the reactions of aliphatic α,β-unsaturated esters led to the low yield of the desired acylated products to give complex mixtures (Table 2, entry 6, 7, 8). These results implies the influence of presence of freshly formed metal salts in this undivided method. Cinnamonitrile as one of α,β-unsaturated nitriles gave the corresponding acylated compound in a good yield (entry 13), though benzalacetone as a typical α,β-unsaturated ketones gave the corresponding acylated product in a low yield accompanying other unknown products (entry 14), because benzalacetone showed two reduction waves at -1.5 and -2.2 V vs. SCE,[8] which may be attributed to the dual generation of a radical anion and a dianion under the condition of the reaction.



Scheme 4

Table 2. Electroreductive Acylation of α, β-Unsaturated Esters and Nitriles

Entry	Olefin	Acylating Agent	Product	Isolated Yield (%)
1	$PhCH=CHCO_2Et$	$(CH_3CO)_2O$	$PhCH(COCH_3)CH_2CO_2Et$ **1**	85 (58)*
2	$PhCH=CHCO_2Et$	CH_3COCl	$PhCH(COCH_3)CH_2CO_2Et$ **1**	30
3	$PhCH=CHCO_2Et$	$(C_2H_5CO)_2O$	$PhCH(COC_2H_5)CH_2CO_2Et$ **4**	82
4	$PhCH=CHCO_2Et$	$(n\text{-}C_3H_7CO)_2O$	$PhCH(COC_3H_7\text{-}n)CH_2CO_2Et$ **5**	60
5	$PhCH=CHCO_2Et$	$ClCO_2Et$	—	—
6	$CH_2=CHCO_2Me$	$(CH_3CO)_2O$	$CH_3CO(CH_2)_2CO_2Me$ **6**	10 (62)*
7	$CH_3CH=CHCO_2Me$	$(CH_3CO)_2O$	$CH_3CH(COCH_3)CH_2CO_2Me$ **7**	24 (75)*
8		$(CH_3CO)_2O$	 **8**	0 (74)*
9	$4\text{-}CH_3C_6H_4CH=CHCO_2Et$	$(CH_3CO)_2O$	$4\text{-}CH_3C_6H_4CH(COCH_3)CH_2CO_2Et$ **9**	79
10	$4\text{-}ClC_6H_4CH=CHCO_2Et$	$(CH_3CO)_2O$	$4\text{-}ClC_6H_4CH(COCH_3)CH_2CO_2Et$ **10**	65
11	$4\text{-}CH_3OC_6H_4CH=CHCO_2Et$	$(CH_3CO)_2O$	$4\text{-}CH_3OC_6H_4CH(COCH_3)CH_2CO_2Et$ **11**	65
12	$4\text{-}CH_3OOCC_6H_4CH=CHCO_2Et$	$(CH_3CO)_2O$	$4\text{-}CH_3OOCC_6H_4CH(COCH_3)CH_2CO_2Et$ **12**	67
13	$PhCH=CHCN$	$(CH_3CO)_2O$	$PhCH(COCH_3)CH_2CN$ **13**	77 (74)*
14	$PhCH=CHCOMe$	$(CH_3CO)_2O$	$PhCH(COCH_3)CH_2COMe$ **14**	7
15		$(CH_3CO)_2O$	 **15**	58
16		$(CH_3CO)_2O$	 **16**	73
17		$(CH_3CO)_2O$	 **17**	64
18		$(CH_3CO)_2O$	 **18**	58
19		$(CH_3CO)_2O$	 **19**	45

* Ref. 4a

As already proposed for other reactions using reactive metal anodes,[6] the mechanism of our silylation and acylation may be postulated as shown in Scheme 4. The initiation step involves one electron transfer from a cathode to an activated olefin to yield an anionic species **A**, which subsequently does nucleophilic attack to a carboxylic anhydride (or trimethylsilyl chloride) and further one-electron reduction to yield an acylated product (or a silylated product). Protonation to **A** followed by one-electron reduction gave a simply reduced product as by-products. Dimerization of **A** followed by protonation gave a radical-coupling product as by-products. At anode, most part of electricity is used for dissolving anode metal to generate the corresponding metal ion (M^{n+}).

However, the role of the metal ions (M^{n+}) through corrosion of the anode is not clearly elucidated in this mechanism. Nedelec et al. reported that electrochemically generated Zn^{2+} stabilizes anionic intermediates

(CCl_3^- or $RCCl_2^-$) leading to cross-coupling with benzyl bromide in good yields.[9] Therefore, electroreductive acylations of ethyl cinnamate in a divided cell were performed in the absence or the presence of M^{n+}, employing commercially available and soluble magnesium bromide etherate ($MgBr_2(Et_2O)$), or electrochemically generated salts from electroreduction of dibromoethane using a metal anode (Mg, Zn, Al) and a carbon cathode.[10] The results were shown in Table 3. It clearly indicates that the presence of M^{n+} increases the yield of acylated product **1** and the effect of addition of electrochemically generated M^{n+} like Mg*, Zn* were more effective than that of commercially available metal salts like $MgBr_2(Et_2O)$. Notably, the metal salts works more efficiently under the conditions using a reactive metal anode in an undivided cell, presumably because fresh metal ions are continuously produced as the reaction proceeds under these conditions.

Table 3. Electrororeductive Acylation of Ethyl Cinnamate in a Divided Cell in the Presence of Electrochemically Generated Metal Ions[a)]

Entry	Additive Salts	GC Yield (%)			
		1	2	3	recovery of ethyl cinnamate
1	none	65 (58)[b)]	0	0	3
2	$MgBr_2(Et_2O)$ [c)]	68	6	2	8
3	Mg* [d)]	73	16	1	8
4	Zn* [d)]	78	7	1	11
5	Al* [d)]	67	2	1	15

a) Anode: carbon, Cathode: carbon, 2 F/mol; Ethyl Cinnamate: 5 mmol, Bu_4NBr: 0.75 mmol, Acetic anhydride: 79 mmol. b) Ref. 4. c) $MgBr_2(Et_2O)$: 5 mmol. d) Preformed salts from electroreduction of dibromoethane with a metal anode and carbon cathode.

From these observation, anionic species formed by electron transfer from a cathode are considered to be stabilized by freshly formed metal ions generated from an anode (Scheme 4, **A**), and attack carboxylic acid anhydrides to give desired acylated products in higher yield compared with the previously reported method using a divided cell in the case of 3-aryl substituted α, β-unsaturated esters and nitriles.[4]

On this electroreductive acylation, easily available various acid anhydrides can be used as an acylating reagent. Furthermore, the use of reactive metal anode enable us to eliminate a diaphragm between a catholyte and an anolyte and to reduce a large amount of expensive supporting electrolytes so that high current efficiency and simple procedure was attained. Though the presence of metal ions formed from corrosion of an anode metal influenced the reactivity and stability of an anionic species intermediate formed at a cathode, it provided the great improvement in the yield of β-aryacrylates and nitriles. Thus, the present electrochemical reaction offers a simple, versatile, and chemoselective approach for the introduction of an acyl group into the β-position of activated olefins.

Experimental Section

General. ^{1}H-NMR spectra were recorded on a JEOL EX-90Q and EX-270 (90 and 270 MHz, respectively) spectrometer in $CDCl_3$ with Me_4Si as an internal standard. Infrared spectra were measured on a JASCO A-3 or Shimadzu IR-435 spectrometer. Mass spectra were obtained on a JEOL JMS-DX303HF spectrometer connected with a HP 5890 gas chromatograph with a 30 m TC-1 capillary column and a JMA-DA5000 data processing system. Electron impact (EI) mass spectra were obtained at 70 eV; only selected ions are reported here. Vapor-phase chromatography (VPC) was performed on a Shimadzu GC-4BM gas chromatograph equipped with a 2 m x 3 mm column packed with Silicon OV-17 on Chromsorb. The flow rate was usually 80 ml/min. The apparatus of cyclic voltammetric studies consisted of a potentiostat (Hokuto Denko Co. Ltd., HA-104), a function generator (Hokuto Denko Co., Ltd., HB-104), an TYPE 3086 X-Y recorder (Yokogawa Electric Works Ltd.), and a beaker-type cell. Platinum wires were used as a working electrode and an auxiliary electrode, and the reference electrode was SCE. DMF was distilled over CaH_2 before use. Other reagents were used as received. Magnesium used as anode was purchased from Rare Metallic Co., Ltd., the purity being 99.9 %. Zn and Al plates were from Nacalai Tesque, Inc. and the purity was 99.9 % and 99 %, respectively.

Electrochemical Acylation of Activated Olefins (Typical Procedure).

In a 50 ml of beaker-type undivided glass cell equipped with a Mg rod (20 x 115 x 7 mm) as the anode and three carbon rods (8ϕ x 100 mm) or a stainless steel plate (20 x 20 x 1 mm) as the cathode were introduced 25 ml of anhydrous DMF as a solvent, Bu_4NBr (0.5 g, 1.55 mmol) as a supporting electrolyte, acetic anhydride (7.5 ml, 79 mmol), and ethyl cinnamate (0.88 g, 5 mmol) as an activated olefin. The electrolysis was carried out under N_2 at a constant current (current density; 19 mA/dm^2) with magnetic stirring until 2 F/mol of electricity was passed (about 0.52 g of Mg anode was consumed.) by using a Takasago GP-050-2 DC power supply. The reaction mixture was then poured into a cold saturated aqueous NaCl solution. Organic materials were extracted with ether and dried over anhydrous $MgSO_4$. After removal of the solvent, the isolation by column chromatography gave an acylated compound **1** in a good yield, with a small amount of simply reduced product **2** and a radical coupling product **3** as the by-products. After isolation and identification of the products, working curves were used with a diethyl phthalate as an internal standard for analysis of the reaction of ethyl cinnamate as shown in Table 3.

Electrochemical Acylation in the Presence of Electrogenerated Metal Salts (Typical Procedure).

The reactions were conducted in two steps using a divided cell equipped with a ceramic diaphragm in a modified way of the literature.[9] Solutions of 7 g (21.7 mmol) of Bu_4NBr in 50 ml and 20 ml of anhydrous DMF, were placed in the two chambers of the divided cell equipped with a ceramic diaphragm (25ϕ x 70 mm). For the first step, the bigger chamber was fitted with a Mg rod (20 x 115 x 7 mm) and three carbon rods (8 ϕ x 100 mm) as the anode and the cathode, respectively. In this chamber were then introduced 0.94 g (5 mmol) of dibromoethane to prepare $MgBr_2$ and then 2 F/mol of electricity was passed. For the second step, the Mg rod in the bigger chamber was removed and the smaller chamber was equipped with two carbon rods (8ϕ x 100 mm). Ethyl cinnamate (0.88 g, mol) and acetic anhydride (7.5 ml, 79 mmol) were introduced into the bigger chamber (the cathodic chamber) and the electrolysis was carried out in the divided cell under N_2 at a constant

current (current density; 19 mA/dm^2) with magnetic stirring until 2 F/mol of electricity was passed. Work-up and analysis were performed as described above.

Ethyl 3-phenyl-4-oxopentanoate (1)[4a,b, 11]
IR (neat)1720, 1735 cm^{-1}; ^{1}H NMR($CDCl_3$) δ1.21 (t, 3H), 2.17 (s, 3H), 2.52 (dd, 1H, J=16.8 Hz, J=5.0 Hz), 3.20 (dd, 1H, J=16.8 Hz, J=9.9 Hz), 4.10 (dq, 2H), 4.18 (dd, 1H, J=9.9 Hz, 5.0 Hz), 7.14-7.37 (m, 5H); EIMS: m/e 220 (M^+); Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.10; H, 7.28.

Ethyl 3-phenyl-4-oxohexanoate (4)
IR (neat)1720, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ0.98 (t, 3H), 1.18 (t, 3H), 2.46 (q, 2H), 2.53(dd, 1H, J=16.8 Hz, 5.0 Hz), 3.22 (dd, 1H, J=16.8 Hz, 9.9 Hz), 4.09 (q, 2H), 4.18 (dd, 1H, J=9.9 Hz, 5.0 Hz), 7.19-7.32 (m, 5H); EIMS: m/e 234 (M^+); Anal Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.81; H, 7.69.

Ethyl 3-phenyl-4-oxoheptanoate (5)
IR (neat) 1718, 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ0.78 (t, 3H), 1.20 (t, 3H), 1.53 (m, 2H), 2.38 (q, 2H), 2.51 (dd, 1H, J=16.8 Hz, 5.0 Hz), 3.21 (dd, 1H, 16.8 Hz, 9.9 Hz), 4.09 (q, 2H), 4.16 (dd, 1H, J=9.9 Hz, 5.0 Hz), 7.18-7.34 (m, 5H); EIMS: m/e 248 (M^+); Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.61; H, 8.10.

Methyl 4-oxopentanoate (6)
IR (neat) 1720, 1740 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 2.15(s, 3H), 2.50 (t, 2H, J=5.5Hz), 2.67 (t, 2H, J=5.5 Hz), EIMS: m/e 130(M^+) ; Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.59, H, 7.69.

Methyl 3-methyl-4-oxopentanoate (7)
IR (neat) 1712, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13 (d, 3H, J=7.3 Hz), 2.19 (s, 3H), 2.27 (dd, 1H, J=16.5 Hz, 5.3 Hz), 2.74 (dd, J=16.5 Hz, 8.6 Hz), 3.63 (s, 3H). EIMS m/e 144 (M^+), Anal. Calcd for $C_7H_{12}O_3$, C, 58.31; H, 8.39. Found: C, 58.59; H, 8.29.

Ethyl (4-methylphenyl)-4-oxopentanoate (9)
IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ1.21(t, 3H), 2.10 (s, 3H), 2.32(s, 3H), 2.50(dd, 1H, J=16.7 Hz, 5.1 Hz), 3.18 (dd, 1H, J=16.7 Hz, 9.5 Hz), 4.16 (dd, 1H, J=9.5 Hz, 5.1 Hz), 4.10 (q, 2H), 7.11 (s, 4H); EIMS: m/e 234 (M^+); Anal. Calcd for $C_{14}H_{18}O_3$; C, 71.77; H, 7.74, Found: C, 71.65; H, 7.68.

Ethyl 3-(4-chlorophenyl)-4-oxopentanoate (10)
IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ1.20 (t, 3H), 2.10 (s, 3H), 2.50 (dd, ^{1}H, J=16.7 Hz, 6.4 Hz), 3.80 (dd, 1H, J=16.7 Hz, 9.8 Hz), 4.20 (dd, 1H, J=9.8 Hz, 6.4 Hz), 4.10 (q, 2H), 7.22 (q, 4H); EIMS: m/e 254 (M^+); Anal. Calcd for $C_{13}H_{15}O_3Cl$; C, 61.30; H, 5.94. Found: C; 61.58, H, 6.01.

Ethyl 3-(4-metoxyphenyl)-4-oxopentanoate (11)
IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ1.18 (s, 3H), 2.07 (s, 3H), 2.45 (dd, 1H, J=16.7 Hz, 5.1 Hz), 3.55(dd, 1H, J=16.7 Hz, 9.5 Hz), 3.75 (s, 3H), 4.05 (q, 2H), 4.10(dd, 1H, J=9.5 Hz, 5.1 Hz), 6.62-

7.22(ABq, 4H); EIMS: m/e 250 (M^+); Anal. Calcd for $C_{14}H_{18}O_4$; C, 67.18; H, 7.25. Found: C, 67.15; H, 7.18.

Ethyl 3-(4-carbomethoxyphenyl)-4-oxopentanoate (12)
IR(neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ1.22 (t, 3H), 2.13 (s, 3H), 2.60 (dd, 1H, J=16.7 Hz, J=5.1 Hz), 3.24 (dd, 1H, J=16.7 Hz, J=9.8 Hz), 3.93 (s, 3H), 4.07 (q, 2H), 4.30 (dd, 2H, J=5.1 Hz, 9.8 Hz), 7.20-8.15 (ABq, 4H); EIMS: m/e 278 (M^+); Anal. Calcd for $C_{15}H_{18}O_5$; C, 64.74; H, 6.52. Found: C, 64.89; H, 6.26.

4-Cyano-3-phenyl-2-butanone (13)[4, 12]
IR (neat) 2200, 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ2.09 (s, 3H), 2.68 (dd, 1H, J=16.7 Hz, 9.0 Hz), 3.00 (dd, 1H, 16.7 Hz, 6.4 Hz), 4.04 (dd, 1H, J=9.0 Hz, 6.4 Hz), 7.0-7.44 (m, 4H); EIMS: m/e 173 (M^+); Anal. Calcd for $C_{11}H_{11}ON$; C, 76.28; H, 6.40; N, 8.09. Found: C, 76.39; H, 6.31; N, 8.08.

Ethyl 3-(2-naphtyl)-4-oxopentanoate (15)
IR (neat) 1730 cm-1; ^1H NMR($CDCl_3$) δ1.21 (t, 3H), 2.17 (s, 3H), 2.62 (dd, 1H, J=17.2 Hz, 5.3 Hz), 3.31(dd, 1H, J=17.2 Hz, J=9.6 Hz), 4.12 (dq, 2H), 4.36 (dd, 1H, J=9.6 Hz, 5.3 Hz), 7.26-7.85 (m, 7H); EIMS: m/e 270 (M+); Anal. Calcd for $C_{17}H_{18}O_3$; C, 75.53; H, 6.71. Found: C, 75.71; H, 6.74.

Ethyl 3-(2-furyl)-4-oxopentanoate (16)
IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ1.23 (t, 3H), 2.17 (s, 3H), 2.60 (dd, 1H, J=16.8 Hz, J=5.2 Hz), 3.15 (dd, 1H, J=16.8 Hz, J=9.2 Hz), 4.12 (dq, 2H), 4.28 (dd, 1H, J=9.2 Hz, 5.2 Hz), 6.17 (d, 1H), 6.32 (dd, 1H), 7.35 (dd, 1H); EIMS: m/e 210 (M+); Anal. Calcd for $C_{11}H_{14}O_4$; C, 62.85; H, 6.71. Found: C, 62.63; H, 6.65.

Ethyl 3-(2-thienyl)-4-oxopentanoate (17)
IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ1.22 (t, 3H), 2.19 (s, 3H), 2.60 (dd, 1H, J=16.8 Hz, J=5.0 Hz), 3.20 (dd, 1H, J=16.8 Hz, J=9.9 Hz), 4.10 (q, 2H), 4.44 (dd, 1H, J=9.9 Hz, 5.0 Hz), 6.89 (d, 1H), 6.95 (dd, 1H), 7.21 (dd, 1H); EIMS: m/e 226 (M^+); Anal. Calcd for $C_{11}H_{14}O_3S$; C, 58.39; H, 6.24. Found: C, 58.50; H, 6.31.

Ethyl 3-(3-thienyl)-4-oxopentanoate (18)
IR (neat) 1730 cm^{-1}; ^1H NMR($CDCl_3$) δ1.11 (t, 3H), 2.04 (s, 3H), 2.43 (dd, 1H, J=16.8 Hz, J=5.0 Hz), 3.06(dd, 1H, J=16.8 Hz, J=9.6 Hz), 4.00 (q, 2H), 4.23(dd, 1H, J=9.6 Hz, 5.0 Hz), 6.83 (dd, 1H), 7.02 (dd, 1H), 7.20 (dd, 1H); m/e 226 (M^+); Anal. Calcd for $C_{11}H_{14}O_3S$; C, 58.39; H, 6.24. Found: C, 58.25; H, 6.03.

Ethyl 3-(3,4-methylenedioxyphenyl)-4-oxopentanoate (19)
IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ1.17 (t, 3H), 2.06 (s, 3H), 2.43 (dd, 1H, J=16.8 Hz, J=5.3 Hz), 3.08 (dd, 1H, J=16.8 Hz, J=9.6 Hz), 4.05 (q, 2H), 4.04 (m, 3H), 5.89 (s, 2H), 6.62-6.73 (m, 3H); m/e 264 (M^+); Anal. Calcd for $C_{14}H_{16}O_5$; C, 63.63; H, 6.10. Found: C, 63.58; H, 6.02.

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10. In the case of using a Zn anode,

anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

cathode: $BrCH_2CH_2Br + 2e^- \longrightarrow H_2C{=}CH_2 + 2Br^-$

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