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Reduction of Substituted Phenyl 2-Chloroacetates at Silver Cathodes: Electrosynthesis of Coumarins

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To explore the electrosynthesis of coumarins, cyclic voltammetry and controlled-potential (bulk) electrolysis have been employed to investigate the reduction of the carbon–chlorine bond of five substituted phenyl 2-chloroacetates at silver cathodes in dimethylformamide (DMF) containing 0.10 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte; the five substrates are 2-formylphenyl 2-chloroacetate (**1a**), 2-acetylphenyl 2-chloroacetate (**2a**), methyl 2-(2-chloroacetoxy)benzoate (**3a**), 2-formyl-5-methoxyphenyl 2-chloroacetate (**4a**), and 2-formyl-3,5-dimethoxyphenyl 2-chloroacetate (**5a**). We have examined (a) the effects of substituents on the benzene ring of the substrate as well as the nature of the aryl carbonyl moiety on the formation of the coumarin product and (b) the effect of solvent—namely, DMF, acetonitrile (CH₃CN), benzonitrile (PhCN), and propylene carbonate (PC)—and substrate concentration on the yield of the coumarin. It was found that the most unsubstituted substrate (**1a**) afforded the highest yield (41%) of the desired coumarin in a DMF–TBABF₄ medium. A mechanistic scheme is proposed to account for the formation of the coumarin. Furthermore, the only other products seen in these reductions are 2-substituted phenols, which are precursors for synthesis of the various substrates.

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Coumarins have become important in many fields such as biology, medicine, and organic chemistry; for example, coumarins have been employed as polymers for industry.1 Coumarin and its derivatives exhibit biological activity and could possibly be used as anti-coagulant,² antitumor,³ anti-inflammatory,⁴ antibiotic,⁵ anti-HIV-1,⁵ anti-diabetic,⁶ and anti-depressant drugs.⁶ Two of the most well-known coumarin derivatives are (RS)-4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one (Warfarin) and its sodium salt (Coumadin), both of which are prescribed as anti-coagulants. Additionally, optical properties of coumarins allow them to be employed in applications such as laser devices, light-emitting diodes, and fluorescent markers in biomedical imaging.⁷ There are many classic processes for the synthesis of coumarins,⁸⁻¹² including the use of transition-metal catalysts;^{13–19} however, among all of these methods, the most commonly employed is the Pechmann reaction.⁸ Classic approaches allow a large range of derivatives to be prepared, but these methods usually require harsh conditions, such as addition of strong acids, and can afford mixtures of products that are difficult to separate.

Despite the many applications of coumarins mentioned above, very few publications can be found that deal with the electrosynthesis of these compounds. In comparison with traditional methods, electrosynthesis can provide many advantages, such as short reaction times, mild reagents, low energy cost, and easily isolated products; and, in most cases, the reaction can be conducted at room temperature. Batanero and co-workers²⁰⁻²² studied the electrochemical reduction of various substituted phenyl 2,2,2-trichloroacetates at a mercury pool cathode in acetonitrile containing lithium perchlorate as a route to the synthesis of derivatives of 3-chlorocoumarins; product yields were as low as 33% and, in one case, as high as 97%. Earlier work²³ in our laboratory focused on both the direct and cobalt(I)-catalyzed reduction of 2acetylphenyl 2-chloroacetate and 2-acetylphenyl 2,2-dichloroacetate at glassy carbon electrodes in dimethylformamide (DMF) containing 0.10 M tetra-n-butylammonium tetrafluoroborate (TBABF₄); yields of the desired product (4-methylcoumarin) ranged from 20-30% for the direct reduction and 45-50% for the catalytic process.

In the present research, we have utilized silver cathodes in an effort to develop a method for the electrosynthesis of coumarins that requires neither the negative potentials used previously nor the presence of a solution-phase transition-metal catalyst. Previous work has demonstrated that silver has electrocatalytic activity toward the cleavage of carbon-halogen bonds, as seen by a significant positive shift in reduction potentials and by higher current efficiencies; a list of references pertaining to the use of silver cathodes for the reduction of halogenated organic compounds appears in a recent publication.²⁴ In other work,²⁵ our laboratory has investigated the direct and nickel(I) salen-catalyzed reductions of chloroacetamides at carbon and silver electrodes; it was discovered (a) that direct reduction of the carbon–chlorine bond occurs at potentials as much as 600 mV more positive when a silver cathode is used and (b) that direct reduction at silver is 100–200 mV more facile than the nickel(I) salen-promoted reaction.

As part of an effort to develop a strategy for the electrosynthesis of coumarin and its derivatives, we have explored the direct electrochemical reduction of five different substituted phenyl 2chloroacetates at silver cathodes in DMF as well as several other common organic solvents. Shown below are the compounds used for this study. Cyclic voltammetry and controlled-potential (bulk) electrolysis have been employed to characterize the electrochemistry of these substrates, and gas chromatography (GC) and gas chromatographymass spectrometry (GC–MS) have been utilized for the separation, identification, and quantitation of the electrolysis products.



Experimental

Reagents.— Each of the following chemicals was employed, as received, without further purification: anhydrous diethyl ether (absolute, EMD Chemicals), *n*-hexadecane (99%, Sigma), chloroacetyl chloride (98%, Aldrich), chloroform-*d* (99.8%, Aldrich), coumarin (**1b**, \geq 99%, Sigma), 4-methylcoumarin (**2b**, 98%, Alfa Aesar), 4-methoxycoumarin (**3b**, 98%, Alfa Aesar), 7-methoxycoumarin (**4b**, \geq 98%, SAFC), 5,7-dimethoxycoumarin (**5b**, 98%, Alfa Aesar), 2-hydroxy-4-methoxybenzaldehyde (98%, Sigma Aldrich), 4,6-dimethoxysalicylaldehyde (98%, Sigma-Aldrich), 2'-hydroxyacetophenone (99%, Sigma-Aldrich), and potassium hydroxide (97%, Alfa Aesar). Salicylaldehyde (Fisher Scientific) and methyl

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salicylate (Fisher Scientific) were purified by vacuum distillation prior to use. Dimethylformamide (DMF, 99.9%, EMD Chemicals), acetonitrile (CH₃CN, 99.9%, EMD Chemicals), benzonitrile (PhCN, 99%, Sigma-Aldrich), and propylene carbonate (PC, 99.7%, Sigma-Aldrich) were utilized without further purification as solvents for electrochemical experiments. Tetra-*n*-butylammonium tetrafluoroborate (TBABF₄, >99%, GFS Chemicals), which served as the supporting electrolyte, was recrystallized from water-methanol and stored in a vacuum oven at 70–80°C prior to use. All deaeration procedures were accomplished with zero-grade argon (Air Products).

General procedure for synthesis of substituted phenyl 2chloroacetates (1a-5a).- Preparation and purification of 2formylphenyl 2-chloroacetate (1a), 2-acetylphenyl 2-chloroacetate (**2a**), methyl 2-(2-chloroacetoxy)benzoate (**3a**), 2-formyl-5-methoxyphenyl 2-chloroacetate (**4**a), 2-formyl-3,5and dimethoxyphenyl 2-chloroacetate (5a) were adapted from a procedure outlined by Hennessy and Buchwald.²⁶ This approach involved the reaction of 1 equivalent of salicylaldehyde, 2'-hydroxyacetophenone, methyl salicylate, 2-hydroxy-4-methoxybenzaldehyde, or 4,6dimethoxysalicylaldehyde with 1.5 equivalents of chloroacetyl chloride in a 2:1 ethyl acetate-water mixture and in the presence of 3 equivalents of potassium hydroxide in an ice-water bath. Each reaction mixture was stirred for 1 h at 0°C and then transferred to a separatory funnel; the organic layer was separated, washed twice with brine, dried over anhydrous sodium sulfate, and concentrated with the aid of rotary evaporation. Products 2a-5a were purified by recrystallization from ethanol and water, whereas 1a was obtained as a yellow oil via vacuum distillation. Spectroscopic data were acquired for each compound: (a) for **1a**, ¹H NMR (500 MHz, CDCl₃) δ 4.36 (s, 2H), 7.06 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 9.90 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) & 41.0, 123.1, 127.0, 127.6, 132.2, 135.5, 150.3, 166.0, 189.3; HRMS (ESI) m/z: calcd. for C₉H₇O₃Cl [M]⁺ 198.0078, found 198.0096; (b) for **2a**, ¹H NMR (500 MHz, CDCl₃) δ 2.53 (s, 1H), 4.39 (s, 2H), 7.13 (d, J = 8.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.83 (d, J = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) & 29.0, 41.1, 123.7, 126.7, 129.6, 130.8, 133.9, 148.6, 166.1, 197.2; HRMS (ESI) m/z: calcd. for C₁₀H₉O₃Cl [M]⁺ 212.0235, found 212.0230; (c) for **3a**, ¹H NMR (500 MHz, CDCl₃) δ 3.80 (s, 3H), 4.40 (s, 2H), 7.11 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 8.01 (d, J = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) & 41.1, 52.3, 122.6, 123.5, 126.6, 131.9, 134.2, 150.3, 164.5, 166.2; HRMS (ESI) *m/z*: calcd. for C₁₀H₉O₄Cl [M]⁺ 228.0184, found 228.0186; (d) for 4a, ¹H NMR (500 MHz, CDCl₃) δ 3.86 (s, 3H), 4.43 (s, 2H), 6.71 (d, J = 2.1 Hz, 1H), 6.91–6.89 (m, 1H), 7.80 (d, J = 8.5 Hz, 1H), 9.90 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) & 40.9, 56.0, 108.9, 112.5, 121.2, 134.7, 152.0, 165.3, 165.8, 187.8; HRMS (ESI) m/z: calcd. for C₁₀H₉O₄Cl [M]⁺ 228.0184, found 228.0186; (e) for 5a, ¹H NMR (500 MHz, CDCl₃) δ 3.85 (s, 3H), 3.90 (s, 3H), 4.45 (s, 2H), 6.24 (d, J = 2.25 Hz, 1H), 6.38 (d, J= 8.5 Hz, 1H), 10.21 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 41.2, 55.9, 56.2, 96.5, 101.0, 110.6, 152.0, 164.7, 165.8, 165.9, 186.6; HRMS (ESI) m/z: calcd. for C11H11O5Cl [M]+ 258.0290, found 258.0290.

Cells, electrodes, procedures, and instrumentation.— A description of the cell used for cyclic voltammetry can be found in a previous publication.²⁷ We constructed planar, circular glassy carbon and silver working cathodes (each with a geometric area of 0.071 cm²) by press-fitting a short piece of either a glassy carbon rod (Grade GC-20, 3.0-mm-diameter, Tokai Electrode Manufacturing Company, Tokyo, Japan) or a silver rod (3.0-mm-diameter, 99.9% purity, Alfa Aesar) into the end of a machined Teflon tube. Electrical connection to each of these working electrodes was made via a 3.0-mm-diameter stainless-steel pole that contacted the cathode material and extended upward through the tube. A coil of platinum wire served as the auxiliary (counter) electrode for cyclic voltammetry. Prior to each scan, the glassy carbon and silver working electrodes were cleaned with an

aqueous suspension of 0.05- μ m alumina on a polishing pad, followed by a rinse with distilled water in an ultrasonic bath. All potentials are reported with respect to a reference electrode that consisted of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride;^{28–30} this electrode has a potential of -0.76 V versus an aqueous saturated calomel electrode (SCE) at 25°C. Cyclic voltammetry experiments were performed as described in a previous paper.³¹

Information about the cell, instrumentation, and procedures used for controlled-potential (bulk) electrolysis is provided elsewhere.^{32,33} Silver gauze working electrodes (approximate surface area of 20 cm²) were constructed from commercially available material (Alfa Aesar, 99.9%, 20 mesh woven from 0.356-mm diameter wire). For bulk electrolyses, the aforementioned cadmium-saturated mercury amalgam reference electrode was utilized, and the auxiliary anode was a graphite rod immersed in a DMF–0.10 M TBABF₄ solution separated from the cathode compartment by a sintered-glass disk backed by a methyl cellulose–DMF–0.10 M TBABF₄ plug.

Separation, identification, and quantitation of electrolysis products.— At the end of each controlled-potential (bulk) electrolysis, the catholyte was partitioned three times between diethyl ether and brine. Then the ether phase was dried over anhydrous sodium sulfate and concentrated with the aid of rotary evaporation. Products were separated and identified by means of gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Each chromatograph (Agilent 7890A) was equipped with a 30 m \times 0.25 mm capillary column (J & W Scientific) with a DB-5 stationary phase; the GC system utilized a flame-ionization detector, whereas the GC-MS system included an inert mass-selective detector operating in electron ionization mode (70 eV). Gas chromatographic retention times and mass spectral data for the electrolysis products were compared with those for commercially available or chemically synthesized authentic samples. Identities of all synthesized materials were confirmed by means of both ¹H and ¹³C NMR spectrometry (500 MHz, Varian Inova) and high-resolution GC-MS (Thermo Electron Corporation) coupled to a MAT-95XP magnetic-sector mass spectrometer. Procedures used for the quantitation of electrolysis products have been described in an earlier paper.³⁴ Peak areas for the various products were determined with respect to an internal standard (n-hexadecane) added in known amount to the electrolysis cell prior to the start of each controlledpotential reduction. All yields are reported as the absolute percentage of starting material incorporated in the desired product (1b-5b).

Results and Discussion

Cyclic voltammetric behavior of substituted phenyl 2chloroacetates.— Shown in Figure 1 is a representative pair of cyclic voltammograms recorded at a scan rate of 100 mV s⁻¹ with glassy carbon (solid curve) and silver (dot-dashed curve) disk electrodes for a 3.0 mM solution of 2-formylphenyl 2-chloroacetate (1a) in oxygen-free DMF containing 0.10 M TBABF₄. For both electrodes, we observed three irreversible cathodic peaks. We propose that the first peak is due to reductive cleavage of the carbon-chlorine bond; note that the potential for the first peak for a silver cathode is shifted positively by 280 mV in comparison with the glassy carbon electrode. Reduction of coumarin or salicylaldehyde is responsible for the second cathodic peak; both products are observed for controlled-potential (bulk) electrolyses conducted at a potential corresponding to the first cathodic peak (as will be discussed later), and their reduction potentials were determined from cyclic voltammetric studies with authentic samples of each product under the same conditions. We suggest that the third peak is attributable to reduction of the conjugate base of salicylaldehyde, which is formed at potentials corresponding to the first cathodic peak, as will be discussed later in the mechanistic section of this paper.

Because the main objective of this work was focused on the reductive electrochemical cyclization of substituted phenyl 2-chloroacetates (**1a–5a**) at silver cathodes, we measured the cathodic peak potentials for reduction of all five substrates. As shown in Table I, only two



Figure 1. Cyclic voltammograms for a 3.0 mM solution of 1a recorded with a glassy carbon (solid curve) and silver (dot-dashed curve) disk electrode at 100 mV s⁻¹ in oxygen-free DMF containing 0.10 M TBABF₄. Potentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus SCE at 25°C. For the cyclic voltammogram recorded with glassy carbon, the potential was scanned from 0 to -2.0 to 0 V; for the cyclic voltammogram recorded with silver, the potential was scanned from 0 to -1.8 to 0 V.

cathodic peaks are observed when silver is employed as an electrode for compounds 2a-5a; we believe that these two peaks correspond to the first two stages for the reduction of **1a**. For the first and second cathodic peaks for **1a-5a**, the tabulated results are similar; the notable exception is that the second cathodic peak potential for reduction of **3a** is at least 360 mV more negative than that for any of the other compounds. Interestingly, on the basis of the controlled–potential (bulk) electrolyses discussed below, we know that **3a** behaves differently.

Controlled-potential (bulk) electrolyses of 1a-5a at silver gauze electrodes in DMF.— A series of controlled-potential electrolyses of compounds 1a-5a at a silver gauze cathode was carried out in DMF containing 0.10 M TBABF₄. Coulometric *n* values and yields of the desired coumarins (1b-5b) are compiled in Table II; each entry corresponds to the average of at least duplicate experiments. Tabulated *n* values (the number of electrons transferred per molecule of substrate) were accurate to ± 0.10 . For all substrates, the coulometric *n* value was slightly higher than 1, supporting a mechanism where the carbon–chlorine bond is mainly cleaved in a one-electron process to give a radical intermediate that cyclizes intramolecularly to form a coumarin. It is interesting that the nature of the carbonyl moiety influences the yield of the coumarin; for substrates 1a, 2a, and 3a,

Table I. Cathodic peak potentials (E_{pc}) for reduction of 3.0 mM solutions of 1a–5a obtained from cyclic voltammograms recorded with a silver cathode at 100 mV s⁻¹ in oxygen-free DMF containing 0.10 M TBABF₄.

Substrate	$(E_{\rm pc})_1 ({\rm V})^{\rm a}$	$(E_{\rm pc})_2 ({\rm V})^{\rm a}$	$(E_{\rm pc})_3 ({\rm V})^a$
1a	-0.52	-0.97	-1.67
2a	-0.62	-1.07	_b
3a	-0.59	-1.44	_b
4a	-0.53	-1.08	_b
5a	-0.57	-1.05	_b

^aPotentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus SCE at 25°C.

^bA third cathodic peak was not observed for this substrate.

Table II. Coulometric data and product yields for direct reduction	ns
of 1a–5a at silver gauze cathodes.	

Solvent ^a	Potential (V) ^b	n ^c	Coumarin; yield (%) ^d
DMF	-0.72	1.3	1b ; 41
CH ₃ CN	-0.63	1.3	1b : 37
PhCN	-0.69	1.2	1b; trace
PC	-0.63	1.1	1b: trace
DMF	-0.80	1.1	2b ; 21
DMF	-0.80	1.2	2b : 28
DMF	-0.80	1.2	2b : 36
DMF	-0.80	1.1	2b : 31
DMF	-0.72	1.3	3b; trace
DMF	-0.73	1.3	4b ; 34
DMF	-0.79	1.2	5b : 35
	Solvent ^a DMF CH ₃ CN PhCN PC DMF DMF DMF DMF DMF DMF DMF	Solvent ^a Potential (V) ^b DMF -0.72 CH ₃ CN -0.63 PhCN -0.69 PC -0.63 DMF -0.80 DMF -0.80 DMF -0.80 DMF -0.72 DMF -0.73 DMF -0.72	Solvent ^a Potential (V) ^b n ^c DMF -0.72 1.3 CH ₃ CN -0.63 1.3 PhCN -0.69 1.2 PC -0.63 1.1 DMF -0.80 1.1 DMF -0.80 1.2 DMF -0.80 1.2 DMF -0.80 1.2 DMF -0.80 1.2 DMF -0.73 1.3 DMF -0.72 1.3 DMF -0.73 1.3 DMF -0.79 1.2

^aAll solutions contained 0.10 M TBABF₄ as the supporting electrolyte. ^bPotentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus SCE at 25°C.

^cAverage number of electrons per molecule of substrate.

 $^{\rm d}{\rm Yield}$ expressed as the percentage of substrate converted into the coumarin.

we observed a decrease in the amount of coumarin as the carbonyl functionality changed from an aldehyde (41% of 1b) to a ketone (21% of 2b) to a methyl ester (trace of 3b), respectively. It is unclear how stereochemical and electronic effects dictate this phenomenon, but it is clear that the identity of the carbonyl group plays an important role in the cyclization to form the coumarin. Substrates 1a, 4a, and 5a, all of which are aldehydes, led to the production of coumarins in comparable yields (34-41%), which demonstrates the tolerance of the electrochemical process to substituents on the benzene ring. For the electrolysis of 2a at a silver cathode, the observed yield of 2b is reasonably close to that found in earlier work²³ dealing with either direct reduction of 2a at reticulated vitreous carbon or cobalt(I) salen-catalyzed reduction of 2a. However the use of silver as a cathode permits a more positive electrolysis potential (compared to a bare carbon electrode) and eliminates the need for an expensive and nonreusable procatalyst.

For all of the electrolyses, the only other product observed is a substituted phenol: (a) for **1a**, **4a**, and **5a**, this product is salicylaldehyde, 2-hydroxy-4-methoxybenzaldehyde, and 4,6dimethoxysalicylaldehyde, respectively; (b) for **2a**, this product is 2'-hydroxyacetophenone; and (c) for **3a**, this product is methyl salicylate. Each of these additional products could be formed via a one- or two-electron process, as discussed below; however, these compounds are not of interest and were not quantitated. It should be noted that these side products need not necessarily be wasted, as they are building blocks (which can be recovered and reused) to synthesize the starting materials (**1a–5a**) employed in this work.

A reviewer expressed concern about the stability of the various starting materials (1a-5a) before and during an electrolysis, arguing that the substrates might undergo hydrolysis, perhaps due to the presence of residual water in the solvent–electrolyte. To test this point, we prepared a 10.0 mM solution of 2a in DMF–0.10 M TBABF₄. A small aliquot of this solution was immediately subjected to GC and GC–MS analysis, and only 2a was seen. After a waiting period of 60 min, the solution was reexamined, and no evidence for decomposition of 2a was found. We conclude that, under the conditions of our experiments, there was no hydrolytic loss of the starting material (which would have led to a diminution in the yield of the desired coumarin). Moreover, reductive consumption of 1a-5a occurs to the greatest extent at the beginning of an electrolysis, which is another argument against loss of starting material via hydrolysis.

Electrochemical behavior of 1a in different solvents.— Acetonitrile (CH₃CN), benzonitrile (PhCN), and propylene carbonate (PC) were employed to study their effects as solvents on the yield of coumarin formed by reduction of 1a at a silver cathode. As shown above, reduction of 1a, the least-substituted substrate, was found to produce coumarin in the highest yield (41%) in DMF; therefore, it was chosen for the study of solvent effects. Figure 2 is a set of cyclic voltammograms recorded at 100 mV s⁻¹ for reduction of a 3.0 mM solution of 1a at a silver cathode in DMF, CH₃CN, PhCN, and PC containing 0.10 M TBABF₄. Two key differences are seen in these cyclic voltammograms. First, the peak potential for the first electrontransfer process is essentially the same for DMF, CH₃CN, and PhCN, whereas that for PC is shifted to a more positive value. Second, the current for the first peak is more than twice as large in CH₃CN (in comparison with the other solvents), which is most likely due to its much lower viscosity.35-

Compound **1a** was subjected to controlled–potential (bulk) electrolyses at a silver cathode in CH₃CN, PhCN, and PC containing 0.10 M TBABF₄ at a potential approximately 200 mV more negative than each of its respective first-peak potentials; the coulometric *n* values and the yields of **1b** are included in Table II. Electrolyses in PhCN and PC led only to the desired product (**1b**) in trace quantities. On the other hand, CH₃CN proved to be a suitable alternative solvent for the formation of coumarin (**1b**) in 37% yield, which is similar to the results found with DMF (41%).

Effect of concentration of **2a** on controlled-potential (bulk) electrolyses in DMF.— To explore the effect of changing the concentration of substrate on the yield of the coumarin, a series of electroly-



0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 -0.5 0.0 Potential (V)

Figure 2. Cyclic voltammograms for a 3.0 mM solution of **1a** recorded with a silver disk electrode at 100 mV s⁻¹ in oxygen-free DMF (solid curve), PC (dashed curve), PhCN (dotted curve), and CH₃CN (dot–dash curve) containing 0.10 M TBABF₄. Potentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus SCE at 25°C. For each solvent, the potential scan was as follows: (a) DMF: 0 to -1.8 to 0 V; (b) PC: 0 to -1.4 to 0 V; (c) PhCN: 0 to -1.0 to 0 V; (d) CH₃CN: 0 to -1.5 to 0 V.

Scheme 1. Mechanism for reduction of substituted phenyl 2chloroacetates.

ses of 2a was conducted. Presented in Table II are the yields of 4methylcoumarin (2b) produced from the reduction of concentrations of 2a ranging from 5.0 to 50.0 mM. As we increased the concentration of 2a, the yield of 2b reached a plateau between approximately 30-35%, which is commensurate with the results seen when 5.0 mM 1a, 4a, and 5a were electrolyzed. In comparison with previously reported results,²³ we find that silver performs as well as a bare carbon electrode for a concentration of 2a of 10 mM.

Proposed mechanism for electrochemical reduction of substituted phenyl 2-chloroacetates.— Scheme 1 represents a plausible sequence of mechanistic steps for the reduction of substituted phenyl 2-chloroacetates. Reduction of the chloroacetate (a) occurs via oneelectron reductive cleavage of the carbon-chlorine bond to form a radical intermediate (i_1) and a chloride ion (Reaction 1). Cyclization takes place when radical i_1 attacks the carbonyl carbon, a process followed by hydrogen atom abstraction from the solvent to form i_2 (Reaction 2). Rapid loss of a water molecule then takes place to afford the coumarin (**b**) (Reaction 3). A substituted phenol (**c**) can arise via two possible routes. After the first electron-transfer event to form i_1 , the latter radical can expel a ketene, leaving behind the oxy-radical i₃, which can abstract a hydrogen atom from solvent to yield c (Reaction 4). On the other hand, as seen in Reaction 5, further one-electron reduction of radical i_1 could take place at potentials corresponding to the first cathodic peak to give carbanion i_4 , which loses ketene to produce phenolate i5, and the latter species is protonated (probably from residual water in the solvent) to produce the final product (c). This last electrochemical process might account for the somewhat elevated coulometric *n* values, which range from 1.1–1.3 (Table II).

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