The X-ray crystal structure of compound 8 (Figure 1) clearly illustrates the features which oppose the formation of 2. The bonds formed in the Diels–Alder cycloaddition, C(15)–C(16) and C(18)–C(19), are quite long: 1.586 (3) and 1.571 (3) Å, respectively. While these bonds are not quite the longest ever observed in a Diels–Alder adduct,[6] compound 8 nevertheless teeters on the edge of a retro-Diels–Alder process, and the alternative reaction, the desired decarbonylation, would only force the already crowded phenyl groups closer together. It is more difficult to understand why the attempted dehydrogenation of 8 fails; however, such reactions generally require somewhat elevated temperatures, and the carbonyl and the bridgehead phenyl groups provide some steric hindrance to the approach of dehydrogenating agents to C(15) and C(19).

Experimental Section

3-Aminoacenaphthene (4) was prepared by catalytic hydrogenation of 3-nitroacenaphthene according to Friedman et al.,[7] except that 10% palladium on activated carbon was used in place of Adams' catalyst. 3-Nitroacenaphthene was prepared according to Morgan and Harrison.[8]

3-[(1-Methyl-3-oxobut-1-enyl)amino]acenaphthene (5). 3-Aminoacenaphthene (8.68 g, 51.3 mmol) and 2,4-pentanedione (13 mL, 127 mmol) were mixed and heated for 16 h at 100 °C. The mixture was cooled, and the product was recrystallized from benzene–hexanes to give compound 5 as light brown crystals (10.0 g, 39.8 mmol, 78%): mp 150–152 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.02 (s, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 3.40 and 3.43 (AA'BB' system, 4 H, CH_2's), 5.26 (s, 1 H, vinyl H), 7.31 (m, 2 H, aryl H), 7.46 (t, 1 H, J = 8 Hz, aryl H), 7.61 (d, 1 H, J = 8 Hz, aryl H), 7.62 (d, 1 H, J = 8 Hz, aryl H), 12.54 (br s, 1 H, NH); MS m/z 251 (M^+, 100), 236 ($M - CH_3$, 50), 208 ($M - COCH_3$, 78); exact mass 251.1317, calcd for $C_{17}H_{17}NO$ 251.1310.

7,9-Dimethyl-10-azaaceanthrene (6). The enamine 5 (0.45 g, 1.79 mmol) was mixed in a Pyrex tube with polyphosphoric acid (10 g). The mixture was heated gradually to 160–170 °C with stirring. After all of the solid had dissolved (~2 h), the tube was cooled, water was added, and the reaction mixture was quenched with excess aqueous NaOH. The resulting mixture was extracted with ether (200 mL), and the extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave the pure yellow-orange product (0.42 g, 100% yield): mp 164–166 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.75 (s, 3 H, CH_3), 2.78 (s, 3 H, CH_3), 3.56 and 3.94 (AA'BB' system, 4 H, CH_2's), 7.11 (s, 1 H, aryl H), 7.27 (d, 1 H, J = 6 Hz, aryl H), 7.47 (dd, 1 H, J = 8, 6 Hz, aryl H), 7.75 (d, 1 H, J = 8 Hz, aryl H), 8.25 (s, 1 H, aryl H); MS m/z 233 (M^+, 83), 232 ($M - H$, 100), 231 ($M - H_2$, 18), 217 (13), 189 (13); exact mass 233.1174, calcd for $C_{17}H_{15}N$ 233.1205.

7,9-Dimethyl-10-azaaceanthrylene (7). Compound 6 (0.42 g, 1.8 mmol) and DDQ (0.45 g, 2.0 mmol) were refluxed in benzene (140 mL) for 2 h. After cooling the solution was washed with 1 N NaOH followed by water. The orange organic phase was dried and concentrated to give 0.23 g of an orange solid. This material was a mixture of unreacted compound 6 (36%) and product 7 (64%), and it was used without further purification: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.78 (s, 3 H, CH_3), 2.80 (s, 3 H, CH_3), 7.10 (d, 1 H, J = 5 Hz, vinyl H), 7.11 (s, 1 H, aryl H), 7.57 (dd, 1 H, J = 8, 6 Hz, aryl H), 7.79 (d, 1 H, J = 6 Hz, aryl H), 7.85 (d, 1 H, J = 5 Hz, vinyl H), 7.95 (d, 1 H, J = 8 Hz, aryl H), 8.51 (s, 1 H, aryl H). Various runs gave product purities of 40–70% with starting material 6 as the sole contaminant; however, the use of excess DDQ gave significantly lower yields.

5,7-Dimethyl-13-oxo-1,2,3,4-tetraphenyl-4a,12c-dihydro-1,4-methanofluoreno[1,9-*gh*]quinoline (8). Compound 7 (0.44 g, 45% pure, 0.86 mmol of 7), tetracyclone (0.80 g, 2.1 mmol, recrystallized from a 1:1 mixture of 95% ethanol and toluene), and benzene (5 mL) were placed in a Pyrex tube and heated to 100 °C for 84 h. After cooling, the solution was chromatographed on a silica gel column (benzene). The first major component to elute after unreacted tetracyclone was pure Diels–Alder adduct 8 (0.43 g, 0.70 mmol, 81% based on 7), a light yellow solid. Single crystals for X-ray analysis were obtained from CH_2Cl_2–methanol: mp 191–193 °C (purple liquid); ^{1}H NMR ($CDCl_3$), 270 MHz) δ 2.55 (s, 3 H, CH_3), 2.71 (s, 3 H, CH_3), 5.02 (d, 1 H, J = 7 Hz, benzylic methine), 5.70 (d, 1 H, J = 7 Hz, benzylic methine), 5.81 (dd, 2 H, J = 7, 1 Hz, aryl H), 6.03 (dd, 2 H, J = 7, 1 Hz, aryl H), 6.29 (t, 2 H, J = 8 Hz, aryl H), 6.53 (t, 1 H, J = 7 Hz, aryl H), 6.64 (t, 2 H, J = 8 Hz, aryl H), 6.82 (t, 1 H, J = 7 Hz, aryl H), 7.02 (s, 1 H, aryl H), 7.15–7.42 (m, 6 H, aryl H), 7.50 (t, 2 H, J = 7 Hz, aryl H), 7.74 (m, 3 H, aryl H), 7.90 (dd, 2 H, J = 8, 2 Hz, aryl H), 8.26 (s, 1 H, aryl H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 19.5, 24.5, 49.0, 50.4, 67.7, 68.3, 119.9, 121.4, 121.9, 123.8, 125.9, 126.3, 126.4, 126.5, 126.6, 127.0, 127.2, 127.5, 127.8, 128.1, 128.8, 130.4, 130.5, 131.0, 131.9, 133.6, 134.5, 134.6, 135.7, 140.4, 141.6, 141.7, 142.0, 143.3, 143.7, 144.3, 158.3, 202.2; MS m/z 615 (M^+, 0.2), 587 ($M - CO$, 6), 384 (tetracyclone, 82), 231 (7,9-dimethyl-10-azaaceanthrylene, 100), 178 (diphenylacetylene, 83); exact mass 615.2554, calcd for $C_{46}H_{33}NO$ 615.2564.

X-ray Crystallographic Analysis of Compound 8. A single crystal of $8 \cdot CH_2Cl_2$ measuring 0.04 mm × 0.29 mm × 0.70 mm was used for X-ray measurements. Crystal data: $C_{46}H_{33}NO \cdot CH_2Cl_2$; triclinic, space group $P\bar{1}$; a = 10.778 (3) Å, b = 11.751 (3) Å, c = 15.034 (5) Å, α = 90.54 (2)°, β = 106.45 (2)°, γ = 95.83 (2)°, V = 1815.2 (9) Å^3, Z = 2, D_{calc} = 1.28 g/cm^3. Intensity measurements were made with $3° \le 2\theta \le 114°$ by using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at room temperature on a Nicolet R3m diffractometer. Of a total of 4556 unique reflections, 3929 were considered to be observed [$|F_o| > 3\sigma(F_o)$]. The structure was solved by direct methods and refined by using the SHELXTL software. In the final stages of refinement, all non-hydrogen atoms were refined with anisotropic temperature factors, and a riding model with idealized geometry was used for the hydrogens. Refinement converged at R = 0.054, R_w = 0.064. Full details are provided in the supplementary material.

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Registry No. 2, 137718-26-4; 4, 55939-13-4; 5, 137695-60-4; 6, 137695-61-5; 7, 137695-62-6; 8, 137718-28-6; $CHCOCH_2COCH_3$, 123-54-6; tetracyclone, 479-33-4; 7-methyl-9-[(1,2,3,4-tetraphenyl-5-oxocyclopent-3-enyl)methyl]-10-azaaceanthrylene, 137695-63-7.

Supplementary Material Available: NMR spectra of 5, 6, and 8 and single-crystal structure reports for compound 8 and 7-methyl-9-[(1,2,3,4-tetraphenyl-5-oxocyclopent-3-enyl)methyl]-10-azaaceanthrylene (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(6) To the best of our knowledge, the current "record" is held by the Diels–Alder adduct of tetrakis(trifluoromethyl)-5-thiabicyclo[2.1.0]pent-2-ene and tetramethylfuran, where the bond lengths of interest are 1.64 (2) and 1.63 (2) Å: Kikutani, N.; Iitaka, Y.; Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y. *Acta Crystallogr., Sect. B* **1975**, *31*, 1478–1480.

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Production of Aldehydes via Electrochemical Reduction of Acyl Halides at Mercury and Carbon Cathodes in Acetonitrile

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There have been few publications[1-4] concerning the electrochemistry of acyl halides in nonaqueous media.

Barba and co-workers[1] reported that reduction of benzoyl chloride at mercury in acetone containing lithium perchlorate occurs by one-electron cleavage of the carbon–chlorine bond to form the benzoyl radical; it was proposed that the benzoyl radical dimerizes to give benzil, which is immediately reduced and acylated to afford almost quantitatively a one-to-two mixture of *cis*- and *trans*-stilbenediol dibenzoate. In related work, Guirado, Barba, and Martin obtained *trans*-biphthalyl from phthaloyl dichloride[2] and prepared 2,4-dibenzyl-1,3-cyclobutanedione from cinnamoyl chloride;[3] both processes were postulated to involve an electrogenerated acyl radical intermediate.

Cheek and Horine[4] investigated the electrolytic reduction of benzoyl chloride at both carbon and platinum in acetonitrile containing tetraethylammonium perchlorate. These workers confirmed the production of *cis*- and *trans*-stilbenediol dibenzoate from benzoyl chloride, and they discovered that the stilbenediol dibenzoates are reducible to diphenylacetylene. By electrolyzing benzoyl chloride in the presence of *p*-anisoyl chloride and at a potential where the latter is not reducible, and by failing to detect any cross-coupling product derived from attack of a benzoyl anion on *p*-anisoyl chloride, Cheek and Horine concluded that benzoyl chloride undergoes one-electron reduction to the benzoyl radical.

In the present work concerning the electrochemical reductions of heptanoyl chloride and benzoyl chloride at carbon and mercury in acetonitrile containing tetraalkylammonium salts, we have found that aldehydes, not previously observed among products formed from the electrolysis of acyl halides, can be obtained. From experiments with deuterated acetonitrile and deuterium oxide, we have established that heptaldehyde arises solely from the heptanoyl radical, whereas benzaldehyde is produced from both acyl radicals and anions.

Experimental Section

Reagents. Acetonitrile, purchased from American Burdick & Jackson Laboratories, Inc., was taken from a freshly opened bottle and, in some instances, passed through a column containing activated neutral alumina to remove water. Tetramethylammonium perchlorate (TMAP), tetraethylammonium perchlorate (TEAP), and tetra-*n*-butylammonium perchlorate (TBAP), from the G. Frederick Smith Chemical Co., were employed without further purification as supporting electrolytes. Heptanoyl chloride and benzoyl chloride, obtained from Aldrich Chemical Co., were transferred from original containers into electrochemical cells with the aid of syringes. Deuterium oxide (Cambridge Isotope Laboratories, 99.83 atom % D), acetonitrile-d_3 (Aldrich, 99.5 atom % D), and diethyl malonate-d_2 (Aldrich, 90 atom % D) were used as received. All deaeration procedures were accomplished with Air Products zero-grade argon.

Electrodes, Instrumentation, and Procedures. A three-electrode cell of conventional design[5] was used for cyclic voltammetric experiments with both carbon and mercury working electrodes. A glassy carbon rod (Tokai Electrode Manufacturing Co., Tokyo, Japan) was press fitted into a shroud of Teflon to provide a disk-shaped working electrode with an area of 0.077 cm^2; details about the construction, polishing, and cleaning of this electrode are available elsewhere.[6] Alternatively, the working electrode was a hanging mercury drop (obtained with a Metrohm Model EA290 capillary system) having an area of 0.014 cm^2. All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride;[7,8] this electrode has a potential of −0.76 V versus the aqueous saturated calomel electrode at 25 °C.

Controlled-potential electrolyses were performed with two-compartment cells that incorporated either reticulated vitreous carbon[6] or mercury pool[9] cathodes. After each experiment, the electrolyzed solution was partitioned between diethyl ether and water. Then the ether extract was dried over anhydrous magnesium sulfate and was concentrated, and the ether-soluble electrolysis products were separated, identified, and quantitated (through the use of tetradecane as an internal standard) by means of gas chromatography, as described in a recent paper;[10] all reported product yields represent the absolute percentage of starting material incorporated into a particular species. To confirm the identities of products, Bruker AM-500 and Nicolet NT-360 instruments were used, respectively, to record ^{1}H and ^{2}H NMR spectra; mass spectra were obtained with a Kratos Model MS80 RFQQ gas chromatograph–mass spectrometer system.

Product Identification. Among the products derived from the electrolysis of heptanoyl chloride, heptaldehyde and heptanoic anhydride were identified by comparison of gas chromatographic retention times for the suspected compounds with those of authentic samples. Heptanoic acid, arising from hydrolysis of the acyl halide in the presence of residual water in the acetonitrile, reacts with the acyl halide to form heptanoic anhydride nonelectrochemically; however, except for a series of special experiments described later, heptanoic acid itself was not found after any electrolysis. Although both heptanoic acid and heptanoic anhydride give gas chromatographic responses, peak areas are not always reproducible, and quantitation of these two species is difficult. A minor product, 7-tetradecene-7,8-diol diheptanoate, was recovered as an oil from some electrolyses; we confirmed the identity of this species by comparing its mass spectrum with that of a pure sample synthesized from 7,8-tetradecanedione[11] and heptanoyl chloride via a procedure published by Trisler and Frye:[12] mass spectrum (30 eV) *m*/*e* (relative intensity) 452, M$^+$ (0.4); 226, M$^+$ − 2(C$_6$H$_{13}$CO) (18); 113, C$_6$H$_{13}$CO$^+$ (100); 85, C$_6$H$_{13}$$^+$ (27).

We identified benzaldehyde and benzyl benzoate, derived from reduction of benzoyl chloride, by matching gas chromatographic retention times of electrolysis products against those of standards. We observed no benzyl alcohol (formed by reduction of benzaldehyde) which reacts with unreduced benzoyl chloride to yield benzyl benzoate, nor was any benzil found. A mixture of *cis*- and *trans*-stilbenediol dibenzoate was obtained as a white solid upon evaporation of ether extracts of electrolyzed solutions of benzoyl chloride. In several instances, the mass of the solid was determined gravimetrically; from electrolyses of benzoyl chloride at a mercury pool held at −0.70 V in acetonitrile containing 0.1 M TEAP, conditions favoring exclusive formation of stilbenediol dibenzoate, up to 89% of the theoretical yield of stilbenediol dibenzoate was recovered. We verified the identity of these products by comparing them with *cis*- and *trans*-stilbenediol dibenzoate prepared from benzil and benzoyl chloride in the manner described by Trisler and Frye:[12] mass spectrum (20 eV) *m*/*e* (relative intensity) 420, M$^+$ (100); 315, M$^+$ − C$_6$H$_5$CO (5); 299, M$^+$ − C$_6$H$_5$CO$_2$ (16); 105, C$_6$H$_5$CO$^+$ (100).

Results and Discussion

Cyclic Voltammetric Behavior of Heptanoyl Chloride. A cyclic voltammogram recorded with a glassy carbon electrode at 50 mV s^{-1} for a 3 mM solution of heptanoyl chloride in acetonitrile containing 0.1 M TEAP exhibits two irreversible reduction waves with peak po-

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Table I. Coulometric Data and Product Distributions for Electrolytic Reduction of Heptanoyl Chloride in Acetonitrile

[C_6H_{13}-COCl], mM	electrode, electrolyte, potential[a]	n	product distribution,[b] % hept-aldehyde	product distribution,[b] % heptanoic anhydride
3	C, TEAP, −1.60	0.75	26	18
3	C, TEAP, −1.60	0.86	77	23
6	C, TEAP, −1.60	0.98	17	33
6	C, TEAP, −1.60	0.72	29	52
6	C, TEAP, −1.60	0.97	43	21
6	C, TEAP, −1.60	0.76	29	1
6	C, TEAP, −1.60	0.91	43	28
6	Hg, TEAP, −1.50	0.97	59	19
6	Hg, TEAP, −1.50	0.88	59	40
12	Hg, TEAP, −1.50	1.06	54	26
6	Hg, TBAP, −1.60	1.01	54	11
6	Hg, TBAP, −1.60	0.96	48	46

[a] C = reticulated vitreous carbon disk; Hg = mercury pool; TEAP = 0.1 M tetraethylammonium perchlorate; TBAP = 0.1 M tetra-*n*-butylammonium perchlorate; potential is in volts versus a saturated cadmium amalgam reference electrode (see the Experimental Section). [b] No unreduced heptanoyl chloride remains; the other electrolysis product is 7-tetradecene-7,8-diol diheptanoate (see text for further discussion).

tentials of −1.47 and −1.80 V. In acetonitrile containing 0.1 M TBAP, the peak potentials are shifted to −1.60 and −1.88 V, and, in the presence of 0.05 M TMAP, the peak potentials are −1.59 and −1.86 V. At a hanging mercury drop, reduction of heptanoyl chloride is an irreversible two-step process with peak potentials of −1.45 and −1.86 V (with TEAP) and −1.55 and −1.88 V (with TBAP) at 50 mV s^{-1}, whereas only a single wave at −1.22 V is seen in the presence of TMAP. We attribute the first step of reduction to one-electron cleavage of the carbon–chlorine bond to yield the acyl radical. In separate experiments we established that the second voltammetric wave for the parent compound arises from combined reductions of heptaldehyde and heptanoic anhydride, the two major electrolysis products; with a glassy carbon electrode in acetonitrile containing 0.1 M TEAP, heptaldehyde and heptanoic anhydride exhibit single cyclic voltammetric waves with peak potentials of −1.82 and −1.85 V, respectively, at a scan rate of 100 mV s^{-1}.

Bulk Electrolyses of Heptanoyl Chloride. Shown in Table I are results obtained from controlled-potential electrolyses of heptanoyl chloride at both reticulated vitreous carbon and mercury pool cathodes under various conditions; for each experiment the potential was maintained so that neither heptaldehyde nor heptanoic anhydride was reducible. Although the two notable products are heptaldehyde and heptanoic anhydride, small amounts (up to 8%) of 7-tetradecene-7,8-diol diheptanoate have been detected in some of our electrolyses.

There is little doubt that heptanoyl chloride reacts with residual water (at or below the 5 mM level in the acetonitrile used as solvent) to form heptanoic acid, which combines with unreduced heptanoyl chloride to yield heptanoic anhydride. Because in our experiments there was always more unreduced heptanoyl chloride than heptanoic acid, the presence of any heptanoic acid among the final products was precluded by formation of heptanoic anhydride.

Mechanistic Aspects of the Reduction of Heptanoyl Chloride. A central issue has been to identify the electrogenerated intermediate that leads to heptaldehyde. With the aid of experiments involving the use of either deuterium oxide or acetonitrile-d_3, we conclude that heptaldehyde arises via one-electron reduction of starting material to yield the heptanoyl radical which gains a hydrogen (or deuterium) atom from the solvent:

$$C_6H_{13}COCl + e^- \rightarrow C_6H_{13}\dot{C}O + Cl^-$$

$$C_6H_{13}\dot{C}O + CH_3CN \rightarrow C_6H_{13}CHO + {}^{\bullet}CH_2CN$$

This mechanistic interpretation has been corroborated by an examination of the electrochemical reduction of heptanoyl chloride in the presence of acetonitrile-d_3 or diethyl malonate-d_2—the latter a much better proton donor than water. In addition, there is cyclic voltammetric evidence to support the belief that the heptanoyl radical is the key intermediate involved in the production of heptaldehyde.

Electrolyses of 6 mM solutions of heptanoyl chloride were performed at −1.60 V with a mercury pool cathode in acetonitrile containing 0.1 M TEAP and D_2O ranging in concentration from 15 to 1000 mM; in every experiment, a strong ^1H NMR signal at 9.8 ppm indicated the presence of $C_6H_{13}CHO$, whereas a very weak ^2H NMR signal at 10.45 ppm (which grew in intensity as the concentration of D_2O was increased) is consistent with the presence of a trace of $C_6H_{13}COOD$ and with the absence of $C_6H_{13}CDO$. In the mass spectrum (30 eV) for the heptaldehyde formed in the experiment with 1000 mM D_2O, we observed a signal for m/e 114 but nothing for m/e 115, which confirms the presence of $C_6H_{13}CHO$ exclusively. In experiments in which 6 mM solutions of heptanoyl chloride were reduced at mercury in acetonitrile-d_3 containing 0.1 M TEAP at −1.60 V, no ^1H NMR signal was seen downfield from 7.3 ppm, but a ^2H NMR signal for $C_6H_{13}CDO$ appeared at 9.9 ppm; moreover, in the mass spectrum (30 eV) for the heptaldehyde, there was a signal for m/e 115 but not for m/e 114. These results support our contention that heptaldehyde is formed by transfer of a hydrogen (or deuterium) atom from the solvent to an electrogenerated heptanoyl radical and rule out an alternative process in which heptaldehyde is produced through protonation of an electrogenerated heptanoyl anion by either acetonitrile or water; moreover, there is no detectable base-catalyzed proton (or deuteron) exchange at the α carbon atom of heptaldehyde. We believe that the minor product, 7-tetradecene-7,8-diol diheptanoate, appears when heptanoyl chloride reacts chemically with 7-tetradecene-7,8-diolate; the latter is presumably formed by reduction of 7,8-tetradecanedione which arises from coupling of electrogenerated heptanoyl radicals.

Because water and acetonitrile possess nearly identical pK_a values (31.4 and 31.3, respectively, in dimethyl sulfoxide[13]), acetonitrile, present at a much higher concentration than water, could act as a donor of protons as well as hydrogen atoms and could negate the role of water as a proton source. Consequently, we electrolyzed 6 mM solutions of heptanoyl chloride at mercury either in acetonitrile-d_3 containing 0.1 M TEAP and 75 mM diethyl malonate or in acetonitrile containing 0.1 M TEAP and 75 mM diethyl malonate-d_2; use of a higher concentration of diethyl malonate, which interferes with the interpretation of NMR spectra, is precluded by the difficulty of its removal from an electrolyzed solution. Diethyl malonate, with a pK_a of 16.4 in dimethyl sulfoxide,[14] is much more acidic than acetonitrile or water. Because the resulting NMR spectra were similar to those described above, the solvent does not serve as a proton (deuteron) donor, and heptaldehyde is indeed formed via an acyl radical intermediate.

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Cyclic voltammetric experiments provide additional confirmation that acyl anions are not formed when heptanoyl chloride is reduced electrochemically. In previous work,[5] we observed that electrogeneration of the *tert*-butyl carbanion at mercury in the presence of the tetramethylammonium cation leads to the appearance of a reversible redox process attributed to trimethylammonium methylide assisted oxidation of mercury; the nitrogen ylide presumably arises because the electrogenerated carbanion deprotonates the tetramethylammonium ion. A cyclic voltammogram obtained at a scan rate of 1 V s^{-1} for reduction of a 6 mM solution of heptanoyl chloride at a hanging mercury drop electrode in acetonitrile containing either 0.05 M TMAP or 0.1 M tetramethylammonium tetrafluoroborate shows no redox process in the region of potentials corresponding to trimethylammonium methylide assisted oxidation of mercury.

It is of interest to compare our observations pertaining to the role of acetonitrile as a hydrogen atom donor with those of previous investigators. M'Halla, Pinson, and Savêant,[15] using either acetonitrile-d_3 or deuterium oxide, found that reduction of 4-bromoacetophenone at mercury in acetonitrile containing TEAP generates an aryl radical which abstracts a hydrogen atom from the solvent, and these authors reached the same conclusion in a study[16] of the electrochemistry of 4-halobenzonitriles at mercury cathodes in acetonitrile; no evidence for significant participation of the solvent as a proton donor was seen. For the reduction of diazodiphenylmethane at mercury in acetonitrile, Bethell and Parker[17] indicate that the solvent donates a hydrogen atom to the electrogenerated radical anion of the starting material. In contrast, Bellamy and co-workers[18,19] reported that electrolyses of acetophenone at mercury in acetonitrile containing tetraethylammonium tetrafluoroborate afford mixtures of 3-phenylbutyronitrile and 3-methyl-3-phenylglutaronitrile but yield negligible quantities of an alcohol or pinacol; they concluded that deprotonation of acetonitrile by an electrogenerated base is followed by attack of $^-CH_2CN$ on the aromatic carbonyl compound. According to Pons and Khoo,[20] electrolysis of dry acetonitrile containing tetra-*n*-butylammonium tetrafluoroborate at a platinum cathode and at a very negative potential produces $^-CH_2CN$; this anion was detected by the formation of 3-hydroxy-4-methylvaleronitrile when isobutyraldehyde was added to the system at the end of an electrolysis, and other compounds requiring reaction of $^-CH_2CN$ with the solvent were identified. In a study of the reduction of benzyl iodide at platinum in acetonitrile containing TEAP, separate experiments with acetonitrile-d_3 and D_2O were employed by Koch, Henne, and Bartak[21] to demonstrate that acetonitrile, not water, is the major source of protons for electrogenerated benzyl carbanions.

Examination of Table I reveals a lack of agreement between the coulometric *n* values and the yields of heptaldehyde. Characteristically, the *n* value is greater than what is expected from the quantity of the aldehyde and from any small amount of 7-tetradecene-7,8-diol diheptanoate, both of which arise via one-electron processes. Thus, other electron-transfer reactions must occur during electrolysis of the acyl chloride. Inasmuch as our studies with acetonitrile-d_3 indicate that $^{\bullet}CD_2CN$ (or $^{\bullet}CH_2CN$) is formed transiently, we have searched for products derived from such species. We have failed to detect any succinonitrile (formed from the coupling of $^{\bullet}CH_2CN$) or any compound produced by attack of $^-CH_2CN$ (arising from one-electron reduction of $^{\bullet}CH_2CN$) on the carbonyl moieties[18,19] of heptanoyl chloride, heptaldehyde, and heptanoic anhydride. Nevertheless, we propose that $^{\bullet}CH_2CN$, formed by abstraction of a hydrogen atom from solvent by a heptanoyl radical, could undergo subsequent reduction to $^-CH_2CN$ and that the latter anion could be protonated by adventitious water to give acetonitrile again; such a sequence of reactions would lead to anomalously high *n* values without affording novel products. Although ^2H NMR spectra obtained in the aforementioned experiments involving electrolysis of heptanoyl chloride in CH_3CN containing D_2O exhibited signals that could conceivably be due to a species such as CDH_2CN (formed by reaction of $^-CH_2CN$ with D_2O), we cannot yet confirm our hypothesis. However, with the aid of gas chromatography, we have detected substantial quantities of triethylamine and tri-*n*-butylamine which arise, respectively, via the Hofmann eliminations that would follow deprotonation of tetraethylammonium and tetra-*n*-butylammonium cations (comprising the supporting electrolytes) by either $^-CH_2CN$ or OH^-.

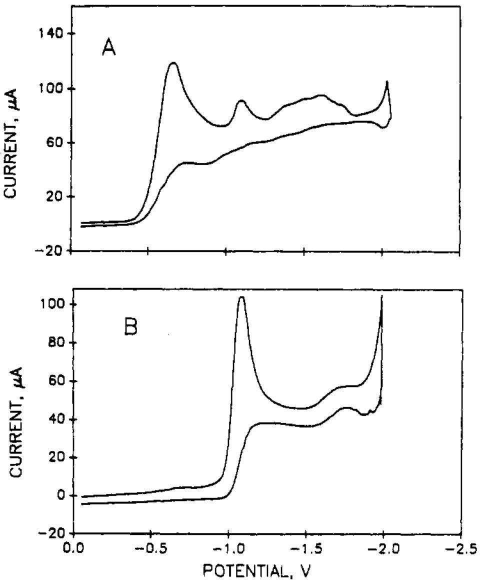

Figure 1. Cyclic voltammograms recorded at 100 mV s^{-1} with a glassy carbon electrode (area = 0.077 cm^2) in acetonitrile containing 0.1 M TEAP. (A) 3 mM benzoyl chloride; (B) 4 mM benzaldehyde.

Another process that could be linked to the anomalously high coulometric *n* values in Table I is decarbonylation of the electrogenerated heptanoyl radical, which would be expected to lead to the production of hexane via capture of a hydrogen atom from the solvent by a hexyl radical. If decarbonylation of the acyl radical does take place, a corresponding quantity of heptaldehyde will not be found among the products listed in Table I and the *n* value will appear to be too large. We have attempted to detect and quantitate hexane in electrolyzed solutions of heptanoyl chloride. No gas chromatographic peak and no individual mass spectrometric signal for hexane were seen for any ether extract; however, *a total ion chromatogram for the*

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Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of Benzoyl Chloride in Acetonitrile

			product distribution, %		
[C_6H_5COCl], mM	electrode, electrolyte, potential[a]	n	benzaldehyde	benzyl benzoate	stilbenediol dibenzoate
6	Hg, TEAP, −0.70	1.01	–	–	100
6	Hg, TBAP, −0.70	1.03	–	–	100
6	Hg, TEAP, −0.90	1.50	17	19	64
12	Hg, TEAP, −0.90	1.48	9	16	75
6	C, TEAP, −0.90	1.07	12	2	86
6	Hg, TBAP, −0.95	1.40	6	12	82

[a] Hg = mercury pool; C = reticulated vitreous carbon disk; TEAP = 0.1 M tetraethylammonium perchlorate; TBAP = 0.1 M tetra-*n*-butylammonium perchlorate; potential is in volts versus a saturated cadmium amalgam reference electrode (see the Experimental Section).

solvent front did show a signal for m/e 86 that we attribute to the presence of hexane. Though there is some evidence for the presence of hexane, *and thus for the occurrence of decarbonylation of the heptanoyl radical,* we have been unable to determine how important this process is.

Cyclic Voltammetric Behavior of Benzoyl Chloride. Although the electrochemical reduction of benzoyl chloride has been the subject of two earlier publications,[1,4] we have reexamined its behavior with particular emphasis on the production of benzaldehyde. Illustrated in Figure 1A is a cyclic voltammogram, recorded at 100 mV s^{-1} with a glassy carbon electrode, for benzoyl chloride in acetonitrile containing 0.1 M TEAP. With a peak potential of −0.62 V, the first wave is due to reductive cleavage of the carbon–chlorine bond of the acyl chloride; the second wave with a peak potential of −1.07 V is attributable to reduction of benzaldehyde (Figure 1B), a process not previously observed in cyclic voltammograms for benzoyl chloride. Additional poorly resolved waves seen in Figure 1A in the region from approximately −1.3 to −1.7 V arise from reductions of stilbenediol dibenzoate and diphenylacetylene, as reported by Cheek and Horine.[4]

Bulk Electrolyses of Benzoyl Chloride. Compiled in Table II are results from six electrolyses of benzoyl chloride. For an electrolysis at a mercury pool cathode held at −0.70 V, stilbenediol dibenzoate is the only product and the coulometric *n* value is essentially unity (Table II); these results mimic closely those reported by Cheek and Horine.[4] On the other hand, for potentials (−0.90 and −0.95 V) corresponding to the foot of the wave for reduction of benzaldehyde, electrolyses of benzoyl chloride at mercury lead to benzaldehyde and benzyl benzoate in moderate yields, although stilbenediol dibenzoate remains the major product, and the *n* value ranges from 1.4 to 1.5. Finally, the distribution of products obtained from electrolysis of benzoyl chloride at reticulated vitreous carbon is quite similar to those seen in Table II for electrolyses at mercury pool electrodes held at −0.90 or −0.95 V, although the *n* value is close to unity.

Mechanistic Aspects of the Reduction of Benzoyl Chloride. Because electrolyses of benzoyl chloride at potentials near or at the peak of the first voltammetric wave involve the transfer of only one electron per molecule, we conclude, in agreement with earlier proposals,[1,4] that stilbenediol dibenzoate is formed by reaction of unreduced benzoyl chloride with stilbenediolate. Electroreduction of benzaldehyde to benzyl alcohol, followed by reaction of the alcohol with unreduced benzoyl chloride, can account for the appearance of benzyl benzoate and for higher *n* values at more negative potentials in Table II.

In seeking to identify the intermediate that gives rise to benzaldehyde, we electrolyzed 6 mM solutions of benzoyl chloride at both mercury and carbon held at −0.90 V in acetonitrile containing 0.1 M TEAP and 200 mM D_2O and observed an average ratio of close to 3:1 for the relative intensities of mass spectrometric signals (30 eV) for benzaldehyde corresponding to, respectively, *m/e* 106 (C_6H_5CHO) and *m/e* 107 (C_6H_5CDO). Similar experiments, involving electrolysis of benzoyl chloride in acetonitrile-d_3 containing 0.1 M TEAP and residual H_2O, gave a ratio of approximately 1:9 for the *m/e* 106 and *m/e* 107 signals. There can be no doubt that benzoyl radicals and anions are both involved as intermediates in the reduction of benzoyl chloride, but most of the benzaldehyde appears to be produced from benzoyl radicals:

$$C_6H_5COCl + e^- \longrightarrow C_6H_5\dot{C}O + Cl^-$$

$$\left\{\begin{array}{c} C_6H_5\dot{C}O + CH_3CN \longrightarrow C_6H_5CHO + {}^{\bullet}CH_2CN \\ \text{or} \\ C_6H_5\dot{C}O + e^- \longrightarrow C_6H_5CO^- \end{array}\right\}$$

$$C_6H_5CO^- + H_2O \longrightarrow C_6H_5CHO + OH^-$$

To probe the possibility that decarbonylation of the electrogenerated benzoyl radical results in the production of benzene, we performed experiments analogous to those described above for reduction of heptanoyl chloride, and we found evidence for the presence of a small quantity of benzene (*m/e* 78) only in the total ion chromatogram for the solvent front.

Registry No. Heptanoyl chloride, 2528-61-2; benzoyl chloride, 98-88-4; heptaldehyde, 111-71-7; hepatonic anhydride, 626-27-7; 7-tetradecene-7,8-diol diheptanoate, 137721-14-3; benzaldehyde, 100-52-7; benzyl benzoate, 93-97-0; stilbenediol dibenzoate, 96276-54-9.

Direct Synthesis of Calix[4]arenes with Two Different Phenolic Units in Alternating Order

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The chemistry of calix[4]arenes has reached a stage where not only are various derivatives available, but also selective functionalization becomes more and more possible.[1] Thus, the easy and efficient formation of 1,3-ester[2] or 1,3-ether derivatives[3] has led to the synthesis of various calix[4]arenes of the type ABAB (where A and B symbolize two different phenolic units) either by selective debutylation or by selective substitution of the free phenolic

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