−1480, $[\theta]_{266}$ −1840, $[\theta]_{262}$ −360, $[\theta]_{259}$ −640, $[\theta]_{235}$ −17 200, $[\theta]_{231}$ −16 400, $[\theta]_{211}$ −42 400, $[\theta]_{203}$ 0, $[\theta]_{195}$ +57600. Free base $[\alpha]$ +0.57° (*c* 1.9, CH_3OH). ^1H NMR and MS spectra are identical with those of compound (+)-**9**·HCl. Anal. Calcd for $C_{18}H_{22}NO_2Cl\cdot{}^1/_3H_2O$: C, 66.35; H, 6.80; N, 4.30; Cl, 10.88. Found: C, 66.30; H, 6.85; N, 4.29; Cl, 10.94.

It is worth noting that (+)-base **9** affords a hydrochloride with a negative specific rotation when measured in methanol.

CD Spectrum of (−)-(1*S*)-Norreticuline: (*c* = 0.005 M, CH_3OH) $[\theta]_{310}$ 0, $[\theta]_{291}$ +5360, $[\theta]_{272}$ 0, $[\theta]_{262}$ +160, $[\theta]_{248}$ 0, $[\theta]_{243}$ −620, $[\theta]_{240}$ 0, $[\theta]_{236}$ + 2500, $[\theta]_{227}$ +900, $[\theta]_{213}$ +16 000, $[\theta]_{207}$ 0, $[\theta]_{202}$ −16 800, $[\theta]_{195}$ −8000.

Acknowledgment. We thank Dr. Voldemar Toome and Bogda Wegrzynski of the Research Division of Hoffmann-La Roche, Inc., Nutley, NJ, for having measured CD spectra of the optically active isoquinolines as described herein.

Registry No. 1, 22190-45-0; (−)-**2**, 120142-61-2; (+)-**2**, 120142-62-3; (±)-**2**, 120034-51-7; (±)-**3**, 120034-52-8; (−)-**4a**, 120034-53-9; (−)-**4b**, 120142-59-8; **5** (isomer 1), 120142-60-1; **5** (isomer 2), 120142-67-8; (+)-**6**, 120142-63-4; (−)-**6**, 120142-64-5; (±)-**6**, 120142-65-6; (±)-**7**, 120142-66-7; (+)-**8a**, 120034-55-1; (−)-**8b**, 120034-56-2; (−)-**9**, 47145-37-9; (+)-9·HCl, 14546-74-8; (+)-**9**, 47145-36-8; (−)-**9**·HCl, 14546-73-7; (±)-**9**, 3901-25-5; (±)-10, 120034-54-0; (*R*)-(+)-1-phenylethyl isocyanate, 33375-06-3; (−)-(1*S*)-norreticuline, 4781-58-2.

Cathodic Acylation of 1,2-Acenaphthenedione

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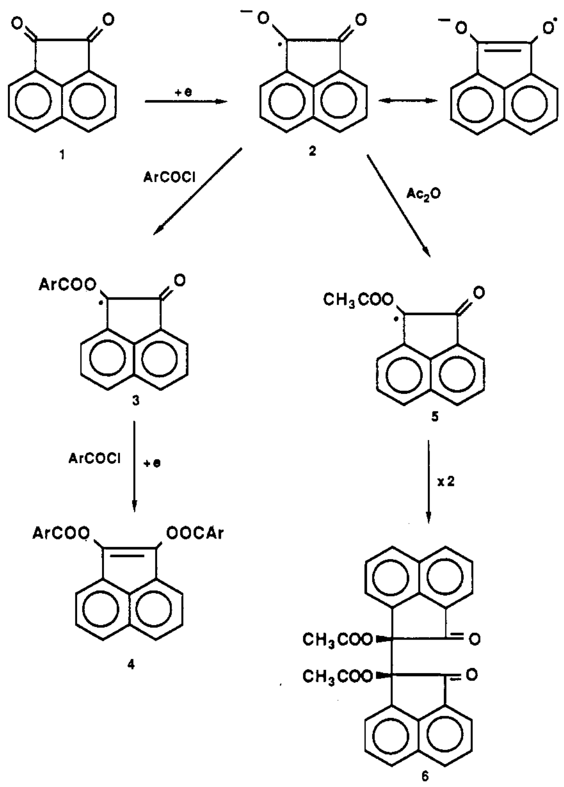
Received October 18, 1988

The papers about cathodic reduction of aryl α-diketones have been mainly focused on benzil,[2-6] with the majority of the electrolyses being carried out in protic media. The first products are *cis*- and *trans*-stilbenediols which later are converted into benzoin by ketolization. Overall the reaction corresponds to a two-electron, two-proton process. Either a direct two-electron transfer or two electrochemical steps, each with single-electron transfer, via the semidione radical anion, have been postulated.

The electrochemical reduction of simple carbonyl compounds by single-electron transfer, protonation, and coupling processes lead to the corresponding glycols or pinacols through ketil radical anion intermediates.[7] In contrast, a similar dimerization for aryl 1,2-diketones giving diketopinacols has not been observed. This probably happens because fast protonation of the first radical anion intermediate gives a neutral radical, which is easily reduced to a relatively stable enolate anion. Thus, the radical species is too short-lived to undergo a coupling process.

Scheme I



After studying the cathodic reduction of aroyl chlorides,[8,9] we postulate a ECEC-type reaction mechanism. The first electrochemical step with single-electron transfer leads to the corresponding aroyl free radicals. A second chemical step with coupling of the generated aroyl radicals gives the corresponding aryl 1,2-diketones, which are reduced in the same way as benzil in protic medium but with acylation of the anionic electrogenerated intermediates instead of protonation, e.g. reduction of benzoyl chloride which gives *cis*- and *trans*-stilbenediol dibenzoates in high yield. This mechanism was later studied in detail.[10] In spite of the fact that acylation is relatively slower than protonation, intermolecular coupling giving pinacol derivatives has not been detected.

However, we now report that electroacylation of 1,2-acenaphthenedione by its selective cathodic reduction in the presence of nonelectroactive acylating reagents provides two different types of products in good yields. The compounds are either diacylated two-electron reduction products or a diketopinacol diester, which arises by single-electron transfer and by coupling of the electrogenerated intermediates. The behavior disparity depends exclusively on the acylating reagent used. This is the first time that this peculiar reactivity has been observed in this class of diketones.

Cathodic reductions of 1,2-acenaphthenedione (**1**) were carried out at mercury pool cathode under constant potential with the catholyte solution containing either benzoyl or *p*-toluyl chlorides. The electricity consumption was 2 F/mol of 1,2-acenaphthenedione. The reaction products were characterized on the basis of their elemental analyses and their MS, IR, and ^1H NMR spectra as the corresponding 1,2-bis(aroyloxy)acenaphthylenes **4**. However,

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0022-3263/89/1954-3205$01.50/0

when the reduction was carried out under identical experimental conditions but with acetic anhydride instead of the aroyl chlorides, a change in the reaction process was observed. Thus, integration of the current passed during the electrolysis was in agreement with a electricity consumption of 1.2 F/mol of 1,2-acenaphthenedione, and by microanalysis and high-resolution mass spectrometry the isolated compound showed $C_{28}H_{18}O_6$ composition. IR, ^{1}H NMR, and ^{13}C NMR spectra provided data in agreement with the structure of bi(1-acetoxy-2-oxoacenaphthen–1-yl) **6**. Unequivocal determination of the configuration of this product as the meso diastereoisomer was achieved by X-ray structural analysis.

The results of the cathodic reactions can be rationalized through reaction mechanisms outlined in Scheme I. The evolution of the first anionic electrogenerated intermediate **2** can follow two routes, depending on its relative acylation rate. If acylation of the radical anion is fast, e.g. with benzoyl chloride, the resulting neutral intermediate **3** can undergo a second electron transfer, leading to an anion which reacts with a further molecule of benzoyl chloride to give the product **4**. However, in the case of a relatively slower reaction of intermediate **2** with acetic anhydride, the negative charge can prevent the second electron transfer. Thus, the acylation that takes place far from the electrode should give the radical **5**, whose coupling gives the product **6**.

The observed stereoselectivity toward the meso diastereoisomer can be explained on the basis of nonbonded interactions between two radical species **5** just prior to dimerization.[11,12] Thus, steric and polar repulsions for the dimerization step giving the meso form are smaller than those repulsions corresponding to the *d,l* pair formation. The above electrolyses were similarly applied to benzil, however, and now the respective stilbenediol diesters were obtained, both in those reactions carried out with aroyl chlorides as well as in those carried out with acetic anhydride.

Experimental Section

NMR spectra were determined on Brucker WP 80 or A 250 instruments with tetramethylsilane as internal reference. Electron-impact mass spectra were obtained on HP 5995 GC/MS or MS 902 instruments with direct insertion probe and an ionizing voltage of 70 eV. IR spectra were recorded on a Perkin-Elmer Model 177 grating spectrophotometer. Microanalyses were performed on a Perkin-Elmer 240 analyzer. Analytical gas chromatography was carried out with use of an OV-101 capillary column (12 m). Electrochemical experiments were performed with an Amel 557 potentiostat and Amel 558 integrator. Reagents and solvents were obtained from Fluka AG and were used without purification except acetone, which was dried and distilled according to a described method.[13] Yields are given for isolated crystalline products.

General Electrolysis Procedure. Electrolyses were carried out in a concentric cylindrical cell with two compartments separated by a circular glass frit (medium) diaphragm. A mercury pool (diameter 5 cm) was used as the cathode and a platinum plate as the anode. The catholyte was magnetically stirred. The reductions were carried out in dry acetone–anhydrous lithium perchlorate, 0.4 M. Approximately 70 mL and 20 mL of this solution were placed into the cathodic and the anodic compartments, respectively. A flow of dry nitrogen saturated with dry acetone was bubbled through the catholyte solution, and the temperature was kept at 15 °C by external cooling. To prevention of the accumulation of electrogenerated acid in the anode compartment, anhydrous sodium carbonate (3 g) was placed on the anodic compartment. Solutions of 1,2-acenaphthenedione (1.82 g, 10 mmol) with the appropriate acylating reagent (30 mmol) were electrolyzed under a constant cathodic potential of −0.6 V vs SCE. Crude reaction products were obtained by removing the acetone under reduced pressure and then water (100 mL) was added to dissolve the electrolyte; an oil separated, which was extracted with chloroform. Crystalline compounds were obtained from chloroform/methanol. Several electrolyses were carried out with variation of the relative proportion of acylating reagent with respect to a fixed amount of 1,2-acenaphthenedione. Yields are high under a ratio as indicated above, but they decrease if the proportion of acylating reagent decreases.

1,2-Bis(benzoyloxy)acenaphthylene: 73% yield; mp 311–313 °C; IR (KBr) ν max 1728, 1270, 1106, 788, 712 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) only aromatic protons δ 7.02–7.89; mass spectrum, *m/z* (relative intensity) 392 (5, M$^+$), 154 (4) 126 (4), 105 (100), 77 (21). Anal. Calcd for $C_{26}H_{16}O_4$: C, 79.58; H, 4.11. Found: C, 79.72; H, 4.18.

1,2-Bis[(4-methylbenzoyl)oxy]acenaphthylene: 75% yield; mp 326–328 °C; IR (KBr) ν max 1720, 1616, 1725, 1180, 1100, 838, 785, 702 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 7.02–7.97 (m, 7 H); mass spectrum, *m/z* (relative intensity) 420 (3, M$^+$), 154 (4), 126 (3), 119 (100), 91 (18). Anal. Calcd for $C_{28}H_{20}O_4$: C, 79.98; H, 4.79. Found: C, 79.69; H, 4.69.

***meso*-Bi(1-acetoxy-2-oxoacenaphthen-1-yl)**: 61% yield; mp 285–287 °C; IR (KBr) ν max 1740, 1368, 1248, 1215, 1008, 835, 790 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.21 (s, 1 H), 6.82–8.02 (m, 2 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 20.60, 85.11, 121.76, 121.96, 126.77, 127.55, 128.32, 129.93, 131.22, 131.94, 133.07, 141.34, 168.86, 194.96; mass spectrum, *m/z* (relative intensity) 450 (19, M$^+$), 348 (23), 347 (42), 268 (48), 226 (37), 184 (100), 183 (31), 43 (58); HRMS, *m/z* 450.1104 ($C_{28}H_{18}O_6$ requires 450.1103). Anal. Calcd for $C_{28}H_{18}O_6$: C, 74.66; H, 4.03. Found: C, 74.58; H, 3.96.

Diastereoisomeric purity (100% meso) for this product was established as follows: by high field ^{1}H NMR and ^{13}C NMR spectroscopy, signals were not unfolded, GLC (capillary column) showed a single peak, moreover the melting points of several single crystals obtained by the diffusion double layer ($CHCl_3$/MeOH) method were identical. The meso configuration was determined as is detailed in the X-ray crystallographic experimental data. No significant amount of the *d,l* diastereoisomers was detected between crude reaction products by means of TLC and GC–MS (capillary column) analyses.

X-ray Crystallography. The crystals used for the X-ray study were obtained from chloroform/methanol. Unit cell parameters and intensity data were obtained by using a CAD4 diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å), in a manner previously described in detail.[14]

The structure was solved via direct methods and refined by least squares. Non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen ones with individual isotropic thermal parameters. Crystallographic data are as follow: $C_{28}H_{18}O_6$, $M = 450.43$, monoclinic, $a = 10.796$ (1) Å, $b = 13.660$ (1) Å, $c = 14.742$ (1) Å, $\beta = 97.38$ (1)°, $U = 2155.9$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.39$ g cm^{-3}. Data collection: $\omega/2\theta$ scand mode, ω width $= 0.8 + 0.4 \tan \theta$, scand speed 1.27–6.77 deg min^{-1}, $2.0 \leq \theta \leq 60.0°$, 3500 data, 3203 unique, observed $[I > \sigma(I)]$. Structure refinement: no. parameters 379, weights $\omega = 1/[\sigma^2(F) + 0.0002F_o^{\,2}]$, $R = 0.0517$, $R_w = 0.0418$.

Registry No. 1, 82-86-0; **4** (R = Ph), 92825-47-3; **4** (R = *p*-MeC_4H_6), 92825-50-8; **6**, 120417-89-2; benzoyl chloride, 98-88-4; 4-methylbenzoyl chloride, 874-60-2; acetic anhydride, 108-24-7; benzil, 134-81-6.

Supplementary Material Available: Molecular diagram with crystallographic atomic numbering, tables of fractional coordinates, anisotropic thermal parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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