JOC Article

Reduction of Diesters of 1,2-Diols. Regioselective C−O Bond Cleavage of the Anionic Forms

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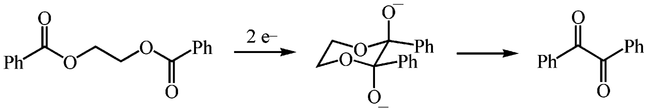
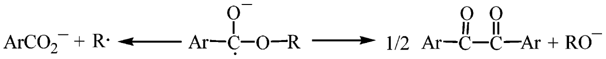


The electrochemical reduction of benzoate diesters of glycols has been studied in acetonitrile and *N*,*N*-dimethylformamide as solvents. The reductions occur in two closely spaced one-electron steps, and it was found that the dianion diradicals decompose by one of two routes, depending on the substituents on the ethylene moiety: cleavage of two benzoates to produce alkene or formation of benzil by way of a postulated cyclic intermediate to produce also the dianion of the diol. These correspond to cleavage of the R−OC(O)Ar bonds and the RO−C(O)Ar bonds, respectively. When the radical formed by the former cleavage is a primary or secondary radical, the reaction is too slow to compete with the latter reaction that produces benzil. However, when that radical is either tertiary or benzylic, the former cleavage reaction is fast and no benzil is detected. The dianions of *p*-cyano- and *p*-nitrobenzoate esters are rather stable on the voltammetric time scale. However, the addition of lithium ions results in detectable formation of 4,4′-dicyanobenzil from four different *p*-cyanobenzoate diesters.

Introduction

Esters of aromatic acids are sufficiently good electron acceptors that formation of anion radicals by electrochemical reduction, though difficult, is achievable within the potential window available in various dipolar aprotic solvents. The anion radicals undergo decomposition by two general paths, cleavage to give $R^\bullet$ and $ArCO_2^-$ and coupling to produce 1,2-diketones and RO^- (Scheme 1). For alkyl benzoates in the presence of tetraalkylammonium counterions, the anion radicals generally cleave to form the alkyl radical and benzoate. The rates of these reactions are similar for the formation of primary and secondary alkyl radicals, larger for tertiary radicals, and largest for benzylic radicals.[1,2] The coupling reaction (right side of Scheme 1) is an electrochemical analogue of the acyloin condensation.[3] It has been shown that coupling is promoted for alkyl benzoates by the addition of magnesium triflate to tetrabutylammonium tetrafluoroborate electrolyte in dimethylformamide.[4] In that work, it was proposed that ion pairing with magnesium favors dimerization of the anion radicals of methyl benzoate to produce a sigma-bonded dimeric dianion that decomposes to benzil and methoxide.[4] Coupling is also observed in the electrochemical reduction of phenyl benzoate.[5]

SCHEME 1



Less attention has been directed to the electrochemical reduction of diesters. Kashimura et al.[6] examined the preparative-scale reductions of symmetrical and asymmetrical diesters of ethylene glycol in tetrahydrofuran with $LiClO_4$ electrolyte. Good yields of symmetrical and unsymmetrical 1,2-diketones were obtained, including a yield of 71% benzil from compound **1** of the present paper. The objective of the present work was to study the mechanism of the decomposition reactions of the anion radicals and dianions formed by reduction of some aromatic diesters of 1,2-diols, **1−14** (Chart 1).

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(1) Wagenknecht, J. H.; Goodin, R. D.; Kinlen, P. J.; Woodard, F. E. *J. Electrochem. Soc.* **1984**, *131*, 1559−1565.

(2) Masnovi, J. *J. Am. Chem. Soc.* **1989**, *111*, 9081−9089.

(3) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 4th edition; Kluwer Academic/Plenum: New York, 2001; Part B, pp 305−306.

(4) Pletcher, D.; Slavin, L. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2005−2012.

(5) Seeber, R.; Magno, F.; Bontempelli, G.; Mazzocchin, G. A. *J. Electroanal. Chem.* **1976**, *72*, 219−228.

(6) Kashimura, S.; Murai, Y.; Washika, C.; Yoshihara, D.; Kataoka, Y.; Murase, H.; Shono, T. *Tetrahedron Lett.* **1997**, *38*, 6717−6720.

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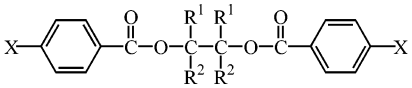
CHART 1



Compound	R^1	R^2	X
1	H	H	H
2	H	H	CN
3	H	H	NO$_2$
4 (*meso*)	CH$_3$	H	H
5 (*dl*)	CH$_3$	H	H
6 (*meso*)	CH$_3$	H	CN
7 (*trans*)	(CH$_2$)$_4$	H	H
8 (*cis*)	(CH$_2$)$_4$	H	H
9 (*trans*)	(CH$_2$)$_4$	H	CN
10 (*meso*)	C$_6$H$_5$	H	H
11 (*dl*)	C$_6$H$_5$	H	H
12 (*meso*)	C$_6$H$_5$	H	CN
13	CH$_3$	CH$_3$	H
14 (*R,R*)	COOCH$_3$	H	H

Results and Discussion

Qualitative Studies in Acetonitrile. All compounds were investigated in acetonitrile to determine the general features of the electrode reactions. A voltammogram for **1** at 3.00 V/s is shown in Figure 1. The height of the cathodic peak corresponds to an overall four-electron process: two-electron reduction of neutral **1** to a dianion diradical, followed by two-electron reduction of benzil that is formed in a subsequent cleavage reaction (see below). The associated anodic peak on the return scan is very small, indicating rapid decomposition of the dianion. Two oxidation peaks are seen near −1.9 and −1.6 V, and, as was demonstrated in separate voltammetric studies of benzil (**16**), they correspond to the stepwise oxidation of the dianion of benzil to its anion radical and neutral forms, respectively. We propose that the decomposition of the dianion diradical occurs through cyclic intermediate **15**. That this is a reasonable intermediate is supported by the existence of the *O*-alkylated forms (methyl and ethyl) of **15** as the trans isomer shown.[7] Also, in the preparative electrochemical reduction of diesters, compounds were isolated that were thought to be magnesium salts of dianions analogous to **15**.[6] The trans isomer is favored by having the negative charges as far apart as possible, having the phenyl groups in equatorial positions and possibly by an anomeric effect of the ring oxygens that could stabilize oxygens in axial positions. We cannot rule out the possibility that the formation of benzil is a concerted double cleavage reaction whose transition state resembles **15**, but we will discuss our results in terms of intermediates such as **15**. The very basic ethylene glycol dianion, **17**, is expected to be protonated by constituents of the medium.

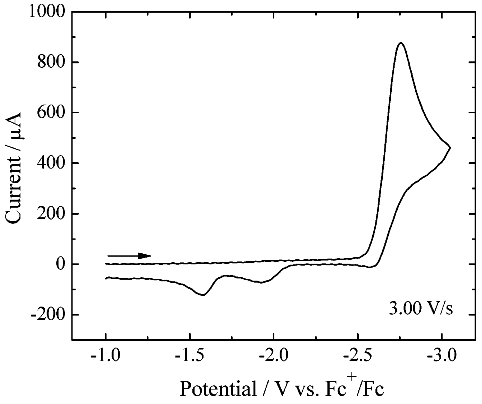
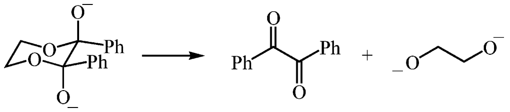


FIGURE 1. Cyclic voltammogram of 2.08 mM **1** in acetonitrile with 0.10 M Bu_4NPF_6. Glassy carbon working electrode. 3.00 V/s.

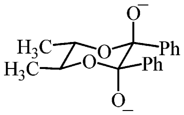


15 **16** **17**

It is possible that the anion radical also decomposes. Such reactions are difficult to detect because one cannot generate the anion radical exclusively, owing to the disproportionation equilibrium that exists in solution near the electrode, $2\,\mathrm{DiEst}^{\bullet -} \rightleftharpoons \mathrm{DiEst} + \mathrm{DiEst}^{2-}$, where DiEst indicates the diester species. However, when the potential was reversed about halfway up the cathodic peak (where the amount of dianion will be smaller than when the scan is extended through the peak), the peaks for the oxidation of benzil anions were almost absent, supporting the notion that the reactions of the anion radical are either slow or do not produce benzil.

Compounds **2** and **3** feature strong electron-withdrawing groups that have two effects: the compounds are much more easily reduced than **1** and the dianion diradicals are stabilized with respect to the cleavage reaction. No benzil is detected in the voltammograms. Each features a two-electron reduction peak composed of two closely spaced one-electron reactions, and the size of the oxidation peak is consistent with the anion radicals and dianions being stable on the voltammetric time scale.

Compounds **4** and **5** behave similarly to **1** in that the anodic peak associated with the reduction peak is small, indicating decomposition of the dianion diradical, and benzil is detected on the return sweep. In the case of **5** (from the dl pair of the diol), in which both methyl groups can occupy equatorial sites in the postulated cyclic intermediate (**18**), the size of the peaks for the oxidation of benzil dianion and the loss of reversibility of the main reduction peak suggest that the rate of decomposition is comparable to that of the dianion diradical of **1**. However, with **4** (from the meso diol), one methyl group must be axial in the cyclic intermediate (**19**), and in this case, it is observed that the peaks for the oxidation of benzil dianion are smaller than those observed for compounds **1** and **5**, suggesting that the rate of decomposition of the dianion of **4** is smaller than that of **1** and **5**. This finding is consistent with a less favorable intermediate for **4** as a result of the 1,3-diaxial interaction between methyl and oxygen.



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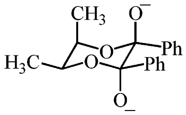

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Analogous behavior is exhibited by **7** and **8** where the amount of benzil formed is larger with **7** compared to **8**. The dianion of **7** would require a *trans*-decalin-type intermediate (**20**), which is certainly much more favorable than the *cis*-decalin-type intermediate (**21**) from **8**. Accordingly, the decomposition rate of the dianion diradicals of **7** is much greater than that of **8**.

In compound **13**, derived from 2,3-dimethyl-2,3-butanediol, a cyclic intermediate would require having two axial methyl groups that would strongly disfavor this reaction path. For **13**,

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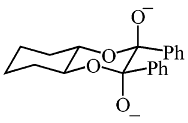
[7] Calò, V.; Lopez, L. *Synthesis* **1984**, *774−776*.



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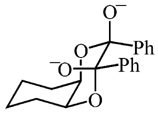

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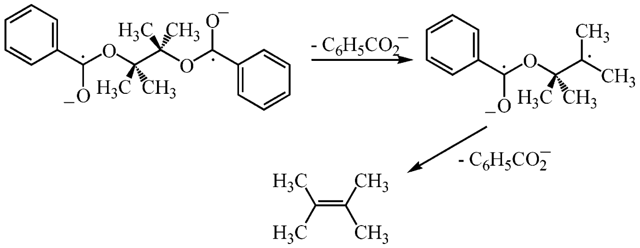
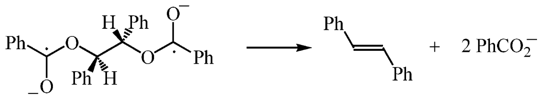
a two-electron reduction peak was observed, and oxidation peaks for the anions of benzil were completely absent. The dianion diradical is not stable and does decompose, as evidenced by the lack of an anodic peak for its oxidation back to the neutral diester at small scan rates. However, when the scan rate was increased to 20 V/s, the anodic peak grew in, suggesting that the decomposition can be easily outrun. In this case, initial cleavage of benzoate is favored because a tertiary alkyl radical is formed (Scheme 2). The cleavage of tertiary radicals from the anion radicals of monoesters is over 100 times faster than cleavage to give primary and secondary radicals.[1] The first cleavage is probably followed by the rapid loss of the second benzoate, producing the alkene, 2,3-dimethyl-2-butene. A qualitative interpretation is that formation of benzil via a cyclic intermediate is not possible for the dianion diradical of **13**, but the dianion diradical can nonetheless react quickly, owing to the formation of a tertiary radical upon loss of benzoate.

SCHEME 2



Compounds **10** and **11** are derived from the diastereomers of hydrobenzoin. As with **13**, rapid decomposition of the dianion diradical (**22**; Scheme 3) occurs, but no benzil is detected. However, in this case, the product formed by cleavage of two benzoates from the dianion diradical, stilbene (**23**), can be detected in the voltammetry through its reversible reduction to the anion radical, which is slightly negative of the main reduction peak. There is also a second irreversible reduction of stilbene near the solvent/electrolyte breakdown potential. In this case, cleavage of the first benzoate leaves behind a benzylic radical, which would rapidly expel the second benzoate to produce stilbene. That this overall reaction is rapid is consistent with the observation[2] that cleavages producing benzylic radicals from anion radicals of alkyl benzoates have the largest rates measured. Voltammetry does not allow the determination of the isomeric identity of the stilbene that is formed, because the reduction potentials of *cis*- and *trans*-stilbene are almost identical.[8]

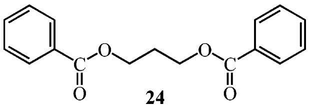
SCHEME 3



22 **23**

Compound **14**, derived from dimethyl *R*,*R*-tartrate, behaved similarly to the hydrobenzoin derivatives, **10** and **11**, in the sense that cleavage of the dianion diradical produced the corresponding olefin and benzoate. This diester was studied in DMF. The olefin, dimethyl fumarate, was detected on the return sweep of the voltammogram by the oxidation of its anion radical at about −1.8 V. The reduction of **14** was completely irreversible, attesting to the very rapid decomposition of the dianion diradical. The peak height corresponded to approximately four electrons per molecule of **14**. Dimethyl fumarate, as shown by separate voltammetric experiments, is reduced to the anion radical near −1.8 V, and the second step of reduction coincides almost exactly with the reduction peak for **14**. Quantitative interpretation of the voltammetry was hindered by the complex electrochemical behavior of dimethyl fumarate whose anion radical undergoes dimerization.[9]

Finally, a qualitative investigation of 1,3-propanediol dibenzoate, **24**, showed two closely spaced reversible one-electron reduction steps. Both benzoate ester functions are reduced almost independently, and the resulting dianion diradical has a stability comparable to the anion radical of other primary alkyl benzoates such as methyl benzoate.[4] Benzil was not detected on the voltammetric time scale. A seven-membered ring intermediate would be required for the formation of benzil.



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Quantitative Studies in *N*,*N*-Dimethylformamide. The decomposition reactions of some of the diester dianion diradicals are rather rapid in acetonitrile, meaning that relatively large scan rates would be required for the quantitative evaluation of reaction rates and the overall mechanism. The rates are significantly lower in *N*,*N*-dimethylformamide (DMF), so this solvent was selected for quantitative studies. Figure 2 shows a voltammogram of 3.02 mM **1**, obtained at a glassy carbon electrode at 0.30 V/s. The fact that the cathodic peak at −2.8 V is a composite of two closely spaced reductions is quite evident in Figure 2, as is the small anodic peak near −2.6 V. The peaks for the stepwise oxidation of the benzil dianion appear at −1.9 (shoulder) and −1.56 V. The very broad and low plateau at −1.9 V for the oxidation of the benzil dianion was also found

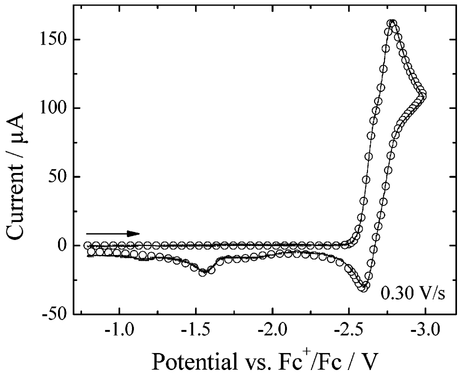

FIGURE 2. Cyclic voltammogram of 3.02 mM **1** in DMF with 0.10 M Bu_4NPF_6. Glassy carbon working electrode. 0.30 V/s. Symbols: simulation. Curve: background-corrected voltammogram.

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(8) Sioda, R. E.; Cowan, D. O.; Koski, W. S. *J. Am. Chem. Soc.* **1967**, *89*, 230−235.

(9) Doherty, A. P.; Scott, K. *J. Electroanal. Chem.* **1998**, *442*, 35−40.

TABLE 1. Simulation Parameters for 1, 4, 5, 7, and 8[a]

reaction	parameter (unit)	**1**	**4**	**5**	**7**	**8**
$\mathrm{DiEst} + e^- \rightleftharpoons \mathrm{DiEst}^{\bullet -}$	$E°_1$ (V)	−2.632 ± 0.006	−2.645	−2.654	−2.658 ± 0.002	−2.645
$\mathrm{DiEst}^{\bullet -} + e^- \rightleftharpoons \mathrm{DiEst}^{2-}$	$E°_2$ (V)	−2.737 ± 0.007	−2.756	−2.762	−2.780 ± 0.002	−2.754
$\mathrm{DiEst}^{2-} \rightarrow \mathrm{Bz}$	$k_{f,5}$ (s^{-1})	2.2 ± 0.1	0.5	1.3	16 ± 1	130

[a] Results for **1** are the averages of four data sets obtained at four different concentrations, 0.97, 1.95, 2.08, and 3.02 mM. For **7**, two data sets were obtained at 1.83 and 1.96 mM.

in studies of benzil alone, as was the small peak near −1.2 V. Also shown in Figure 2 is a simulation (symbols) of the voltammogram. The reaction scheme used for the simulation is given by reactions 1−11, along with the equilibrium and kinetic parameters associated with each reaction.

$$\mathrm{DiEst} + e^- \rightleftharpoons \mathrm{DiEst}^{\bullet -} \qquad E°_1, k_{s,1}, \alpha_1 \tag{1}$$

$$\mathrm{DiEst}^{\bullet -} + e^- \rightleftharpoons \mathrm{DiEst}^{2-} \qquad E°_2, k_{s,2}, \alpha_2 \tag{2}$$

$$\mathrm{Bz} + e^- \rightleftharpoons \mathrm{Bz}^{\bullet -} \qquad E°_3, k_{s,3}, \alpha_3 \tag{3}$$

$$\mathrm{Bz}^{\bullet -} + e^- \rightleftharpoons \mathrm{Bz}^{2-} \qquad E°_4, k_{s,4}, \alpha_4 \tag{4}$$

$$\mathrm{DiEst}^{2-} \rightarrow \mathrm{Bz} \qquad k_{f,5} \tag{5}$$

$$\mathrm{Bz}^{2-} \rightarrow \mathrm{product} \qquad k_{f,6} \tag{6}$$

$$2\,\mathrm{DiEst}^{\bullet -} \rightleftharpoons \mathrm{DiEst}^{2-} + \mathrm{DiEst} \qquad K_7, k_{f,7}, k_{b,7} \tag{7}$$

$$\mathrm{Bz} + \mathrm{DiEst}^{2-} \rightleftharpoons \mathrm{Bz}^{\bullet -} + \mathrm{DiEst}^{\bullet -} \qquad K_8, k_{f,8}, k_{b,8} \tag{8}$$

$$\mathrm{Bz}^{\bullet -} + \mathrm{DiEst}^{2-} \rightleftharpoons \mathrm{Bz}^{2-} + \mathrm{DiEst}^{\bullet -} \qquad K_9, k_{f,9}, k_{b,9} \tag{9}$$

$$\mathrm{Bz} + \mathrm{DiEst}^{\bullet -} \rightleftharpoons \mathrm{Bz}^{\bullet -} + \mathrm{DiEst} \qquad K_{10}, k_{f,10}, k_{b,10} \tag{10}$$

$$\mathrm{Bz}^{\bullet -} + \mathrm{DiEst}^{\bullet -} \rightleftharpoons \mathrm{Bz}^{2-} + \mathrm{DiEst} \qquad K_{11}, k_{f,11}, k_{b,11} \tag{11}$$

Here DiEst denotes the various diester species and Bz denotes benzil. DiEst^{2-} is the dianion diradical. $E°_j$, $k_{s,j}$ and α_j are the standard potential, the standard electron-transfer rate constant, and the electron-transfer coefficient of electrode reaction j. K_k, $k_{f,k}$ and $k_{b,k}$ are the equilibrium constant, the forward rate constant, and the backward rate constant of chemical reaction k. Reactions 1−4 are the electrode reactions of the diester and benzil. The key chemical step is reaction 5, which produces benzil from the dianion diradical of the diester. It is considered to be completely irreversible. As indicated earlier, the reaction may proceed through a cyclic intermediate dianion, but that detail is omitted and reaction 5 is simply written as an irreversible reaction that is first-order in the dianion diradical. The other product, the ethylene glycol dianion, was not included in the simulation. Reaction 6 results in an irreversible loss of some of the dianion of benzil. Inclusion of a small value for $k_{f,6}$ improved the fits of simulation to the data. Studies of the reduction of benzil itself confirmed that the dianion is not perfectly stable under the reaction conditions.

Reactions 7−11 are electron-transfer reactions occurring among the six solution-phase redox species. The equilibrium constants of these reactions are dictated by the values of the standard potentials used for reactions 1−4. As these are simple electron-transfer reactions that do not involve large reorganization energies, their rate constants were made large. These reactions produce a state of redox equilibrium in the solution in the diffusion layer. It is probably not necessary to include all of them, as only two or three should be sufficient to bring about equilibrium. We did not attempt to remove this redundancy. It should be mentioned that reasonable fits of simulations to experiment could be obtained with only reactions 1−5. However, inclusion of the solution-phase electron-transfer reactions improved the agreement noticeably.

The adequacy of this reaction scheme was tested thoroughly with **1**. Experiments were performed at four concentrations between 1 and 3 mM and at scan rates from 0.10 to 10.0 V/s. At each concentration, the fits were optimized by varying all simulation parameters to find the best agreement with experiment for all scan rates. The simulation shown in Figure 2 used this optimized parameter set. All simulation parameters are tabulated in the Supporting Information.

The most important parameter controlling the various peak heights in the simulated voltammograms is $k_{f,5}$. The average value found for the four concentrations was 2.2 ± 0.1 s^{-1}. When $k_{f,5}$ is set equal to zero, the cathodic peak is too small and there are no anodic peaks associated with benzil. When the value of $k_{f,5}$ is too large, the cathodic peak exceeds the experimental value and the benzil peaks are too large. The reason that the cathodic peak grows as $k_{f,5}$ is increased is that reaction 5 produces benzil, which is more easily reduced than the diester, so it is reduced at the potential of the diester reduction, giving more current. The fact that the growth of the cathodic peak and the growth of the peaks for benzil is well accounted for by the simulations is good support for the stoichiometry inherent in the reaction scheme. This suggests that alternate reactions, such as cleavage to give benzoate and ethylene, are unimportant. Also, the fact that nearly identical parameters provide fits for concentrations from 1 to 3 mM, while assuming that reaction 5 is first order, argues against any second-order reactions playing an important role.

The standard potentials of reactions 1−2 are well defined by the simulation, and the values are summarized in Table 1 along with $k_{f,5}$. (Tables of all simulation parameters are included in the Supporting Information). Data for other compounds that produce benzil on reduction (**4**, **5**, **7**, and **8**) are also included in Table 1, and examples of fits of simulation to experimental voltammograms for **4** and **7** are presented in Figures 3 and 4. It is interesting to note in Table 1 that the two standard potentials are close to one another, $E°_1 - E°_2$ ranging from 0.10 to 0.12 V. This indicates that the two identical ester functions are sufficiently separated to be reduced almost independently of one another. The values of the potentials are remarkably constant among the five compounds, indicating that the nature of the substituents on the ethylene group has little effect on the electron affinity of the ester groups. Also note that the relative values of $k_{f,5}$ are consistent with the qualitative results in acetonitrile that were presented and discussed earlier.

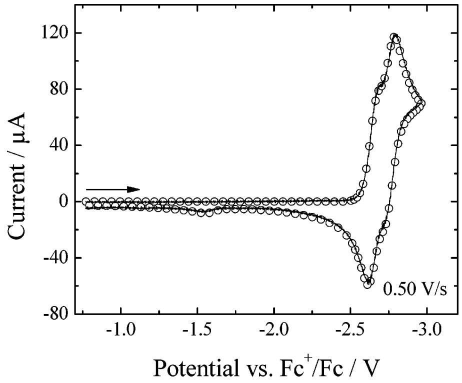

FIGURE 3. Cyclic voltammogram of 2.06 mM **4** at 0.50 V/s. Other conditions as in Figure 2.

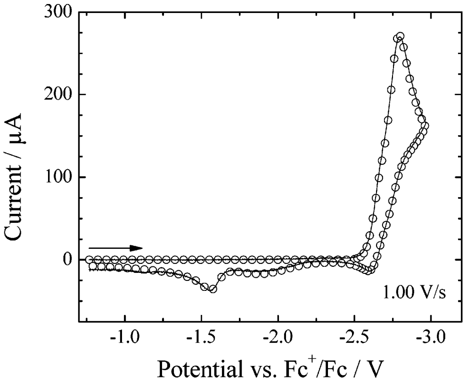

FIGURE 4. Cyclic voltammogram of 2.03 mM **7** at 1.00 V/s. Other conditions as in Figure 2.

For these compounds (**1**, **4**, **5**, **7**, and **8**), the competing reaction of cleavage of two benzoates leaving the alkene is too slow to affect the results. As shown earlier,[1,2] cleavage of benzoate to produce primary or secondary radicals is slow and occurs at about the same rate. Cleavage to produce tertiary radicals is faster, and the production of benzylic radicals is still faster. For the present compounds, cleavage of the first benzoate from the dianion diradical would give a primary (**1**) or secondary (**4**, **5**, **8**, and **9**) radical, a reaction which is apparently too slow to compete with the formation of benzil. Earlier, it was observed that the dianion diradical of **13** reacted rapidly and did not form any detectable benzil. For this compound, cleavage of the first benzoate leaves a tertiary radical, and this reaction is fast enough to compete successfully with benzil formation, which, in addition, would require a congested cyclic intermediate.

Let us turn now to compounds **10** and **11**, which form stilbene upon reduction. Here, cleavage of the first benzoate from the dianion diradical produced a benzylic radical, and this reaction is fast enough to compete successfully with the formation of benzil, which again would require a congested cyclic intermediate. The stilbene that is formed is reversibly reduced to its anion radical at potentials slightly negative of the reduction peak of the diester. A peak corresponding to the reduction of the stilbene anion radical is also observed. Figure 5 shows a voltammogram for 1.91 mM **10** at 0.30 V/s along with a simulation according to reactions 1−11. In these reactions, the benzil species (Bz, $Bz^{\bullet-}$, and Bz^{2-}) were replaced by the corresponding stilbene species (Stb, $Stb^{\bullet-}$, and Stb^{2-}). No other changes were necessary, as each of the two different types of cleavage reactions produces electroactive products, Bz or Stb, with the same stoichiometry (1:1, dianion/Bz or dianion/Stb), and both Bz and Stb take part in stepwise two-electron reductions.

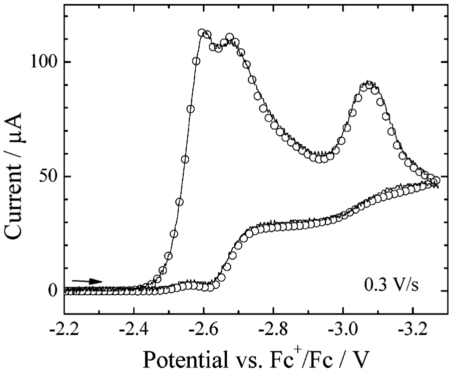

FIGURE 5. Cyclic voltammogram of 1.91 mM **10** at 0.30 V/s. Other conditions as in Figure 2.

TABLE 2. Standard Potentials from Simulations of Voltammograms of 10 and Stilbene

reaction	parameter (unit)	**10**	stilbene
$\mathrm{DiEst} + e^- \rightleftharpoons \mathrm{DiEst}^{\bullet-}$	$E°_1$ (V)	−2.638	
$\mathrm{DiEst}^{\bullet-} + e^- \rightleftharpoons \mathrm{DiEst}^{2-}$	$E°_2$ (V)	−2.589	
$\mathrm{Stb} + e^- \rightleftharpoons \mathrm{Stb}^{\bullet-}$	$E°_3$ (V)	−2.654	−2.647

In Figure 5, the one-electron reduction of stilbene follows shortly after the two-electron reduction of diester **10**. The small anodic peak seen at about −2.6 V is due to the oxidation of the anion radical of stilbene. The second irreversible reduction of stilbene appears at about −3.1 V. The fact that the height of this peak is well accounted for by the simulation is good evidence that the decomposition of the dianion proceeds exclusively to stilbene. Consistent with this conclusion is the observation that no peaks for benzil are seen. The rate constant for the decomposition of the dianion, $k_{f,5}$, is very large, with a lower limit of about 1000 s^{-1}. We did not attempt to evaluate this overall rate constant. It should be noted that the rate constant for cleavage of benzylic radicals from anion radicals of alkyl benzoates is of the order of 10^5 s^{-1} in ethanol.[2]

The same set of parameters was used to fit scan rates from 0.10 to 10.0 V/s and these are listed in the Supporting Information. The standard potentials for the two one-electron reductions of **10** along with that of the first step of reduction of stilbene are given in Table 2. Included are the results for stilbene itself. The values of $E°_1$ and $E°_2$ for **10** are very similar, indicating a very weak interaction between the two ester groups being reduced.

Cyanobenzoates **2**, **6**, **9**, and **12** were also studied in DMF. As indicated earlier, the dianion diradicals are quite stable, and the voltammograms could be readily simulated including only reactions 1 and 2 with $k_{f,5} = 0$, except for the lowest scan rates, where some loss of the dianion was indicated. Here we examined the effect of added metal ions. It was found that replacement of 0.10 M tetrabutylammonium ion by 0.10 M sodium ion in the electrolyte had no effect. However, small amounts of lithium ion, added as lithium perchlorate, resulted in the formation of 4,4′-dicyanobenzil, and $k_{f,5}$ could be evaluated. Selected simulation parameters are included in Table 3, and a listing of all parameters is in the Supporting Information.

As mentioned earlier, the cyanobenzoates are about 0.6 V more easily reduced than the corresponding benzoates. The

TABLE 3. Simulation Parameters for Cyanobenzoate Esters, 2, 6, 9, and 12[a]

compound (concentration/mM)	concentration of $LiClO_4$/ mM	E°_1 (V)	E°_2 (V)	E°_3 (V)	E°_4 (V)	$k_{f,5}$ (s^{-1})
	0	−2.016	−2.092			0
2 (1.91)	4	−2.016	−2.092	−1.290	−1.322	0.55
	8	−2.016	−2.092	−1.300	−1.307	1.16
	0	−2.037	−2.124			0
6 (2.01)	4	−2.039	−2.123	−1.266	−1.325	0.80
	8	−2.039	−2.123	−1.304	−1.317	3.00
	0	−2.040	−2.134			0
9 (2.00)	4	−2.040	−2.131	−1.266	−1.325	0.74
	8	−2.039	−2.127	−1.332	−1.320	2.03
	0	−1.986	−2.078			0
12 (1.94)	4	−1.987	−2.076	−1.363	−1.291	1.43
	8	−1.987	−2.076	−1.291	−1.278	6.95

[a] Each entry is the parameter value used for simulations from 0.100 to 10.0 V/s.

standard potentials, E°_1 and E°_2, are scarcely affected by the low concentrations of lithium perchlorate used here. However, the rate of formation of 4,4′-dicyanobenzil is greatly increased. This is likely due to ion pairing between the dianion of the diester and the lithium ions, which should facilitate the formation of the cyclic intermediate. Interestingly, for compound **12**, there is a change in mechanism compared to compound **10**. Both of these diesters are derived from *meso*-hydrobenzoin, but **12**, in the presence of lithium ions, produces 4,4′-dicyanobenzil, whereas **10** undergoes the opposite type of cleavage giving stilbene.

These results show that the addition of lithium ions to the electrolyte favors the formation of benzil for these cyanobenzoate esters where the dianion diradical is quite stable. In experiments with **10**, whose dianion diradical preferentially cleaves benzoate to produce stilbene, the addition of 10 mM $LiClO_4$ caused a transition from stilbene formation to benzil formation by way of the now favored cyclic intermediate. Specifically, at 1 V/s, peaks for both stilbene and benzil appear in the voltammogram, whereas only stilbene is detected in the absence of lithium ions.

Conclusions

The dianions of dibenzoate esters of glycols decompose by two routes giving either benzil and the dianion of the diol or two benzoates and olefin. The latter reaction occurs exclusively for cases where cleavage of the first benzoate leaves a tertiary radical or a benzylic radical. Benzil formation is observed when cleavage of benzoate would leave a primary or secondary radical. For these compounds, benzil formation can compete with alkene formation by cleavage of benzoate. Benzil formation is postulated to proceed by way of a cyclic intermediate dianion. When benzoate is replaced by *p*-cyano- or *p*-nitrobenzoate, the corresponding dianion diradicals are rather stable on the voltammetric time scale. In the case of the cyanobenzoate esters, slow formation of benzil is observed when 4−8 mM lithium salts are added to the electrolyte.

Experimental Section

Chemicals and Reagents. The solvent for electrochemistry was acetonitrile or *N*,*N*-dimethylformamide, and the electrolyte was tetrabutylammonium hexafluorophosphate. Sources and treatment of the solvents and electrolyte have been described.[10] Diesters **1**−**4**, **6**, **7**, and **9**−**13** were synthesized by the reaction of one mole of the corresponding diol with two moles of benzoyl chloride, 4-cyanobenzoyl chloride, or 4-nitrobenzoyl chloride in ether, dichloromethane, or chloroform at room temperature using pyridine as the catalyst, according to standard methodology.[11] For compounds **10**−**12**, the temperature of the reaction was increased to 50 °C. Diesters **5** and **8** were synthesized by a similar methodology using dichloromethane as solvent at room temperature and using 4-pyrrolidinopyridine/Et_3N as the catalyst system.[12,13] For diester **14**, the reaction was carried out in toluene at 140 °C using Et_3N as the catalyst.[14]

Electrochemical Cells, Electrodes, and Instrumentation. These were as described earlier.[10] The working electrode was a 0.3-cm diameter glassy carbon electrode whose area was determined to be 0.0814 cm^2. The reference electrode was a silver wire immersed in 0.10 M Bu_4NPF_6/0.010 M $AgNO_3$ in acetonitrile. The potential of this reference electrode was periodically measured versus the reversible ferrocene/ferrocenium potential, and all potentials reported in this work are with respect to ferrocene. The temperature was maintained at 298 K.

Digital simulations were conducted using DigiElch, version 2.0, a free software package for the digital simulation of common electrochemical experiments (http://www.digielch.de).[15]

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Supporting Information Available: Tables of simulation parameters for **1**, **2**, **4**−**10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Macías-Ruvalcaba, N. A.; Evans, D. H. *J. Phys. Chem. B* **2005**, *109*, 14642−14647.

(11) Reimschuessel, H. K.; Debona, B. T.; Murthy, A. K. S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3217−39.

(12) Höfle, G.; Steglich, W.; Vorbrüeggen, H. *Angew. Chem., Int. Ed. Eng.* **1978**, *17*, 569−583.

(13) Wolfe, M. S. *Synth. Commun.* **1997**, *27*, 2975−2984.

(14) Caddick, S.; McCarroll, A. J.; Sandham, D. A. *Tetrahedron* **2001**, *57*, 6305−6310.

(15) (a) Rudolph, M. *J. Electroanal. Chem.* **2003**, *543*, 23−29. (b) Rudolph, M. *J. Electroanal. Chem.* **2004**, *571*, 289−307. (c) Rudolph, M. *J. Electroanal. Chem.* **2003**, *558*, 171−176. (d) Rudolph, M. *J. Comput. Chem.* **2005**, *26*, 619−632. (e) Rudolph, M. *J. Comput. Chem.* **2005**, *26*, 633−641. (f) Rudolph, M. *J. Comput. Chem.* **2005**, *26*, 1193−1204.