Reduction of Acetylated Tetraphenylethylenes: Electrochemical Behavior and Stability of the Related Reduced Anions

Michael O. Wolf,[†] Harold H. Fox, and Marye Anne Fox*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

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The synthesis and characterization of 1-(4-acetylphenyl)-1,2,2-triphenylethylene (**2**), 1,1-bis(4-acetylphenyl)-2,2-diphenylethylene (**3a**), *trans*-1,2-bis(4-acetylphenyl)-1,2-diphenylethylene (**3b**), *cis*-1,2-bis(4-acetylphenyl)-1,2-diphenylethylene (**3c**), 1,1,2-tris(4-acetylphenyl)-2-phenylethylene (**4**), and 1,1,2,2-tetrakis(4-acetylphenyl)ethylene (**5**) are described. The molecular orbital energies, charge densities, and electronic spectra of the neutral and reduced species of **2** and **3a**−**3c** were calculated using INDO/1 parameters for structures that had been optimized geometrically with AM1 parameters. The calculated electronic spectra for the neutral compounds compare favorably with the experimentally observed absorption spectra. Cyclic voltammetry of these compounds in deoxygenated THF containing 0.3 M [n-Bu$_4$N]PF$_6$ showed that **2** and **3a** have irreversible one-electron first reduction waves, whereas **3b**, **3c**, **4**, and **5** display quasi-reversible two-electron first reduction waves. Chemical reduction of **2**−**4** with Na/Hg in THF results in highly colored solutions, the absorbance spectra of which have been compared to the calculated electronic spectra for the radical anions and dianions of these compounds. Reduction of **2** results in dimerization to a pinacol product, whereas those of **3b** and **4** result only in formation of the tetraarylethane product. **3a** gives both pinacol and tetraarylethane upon reduction.

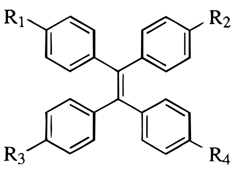
Introduction

Tetraphenylethylene (TPE) (**1**) has been of interest for some time because of its unusual electrochemical behavior and excited state properties.[1−15] Electrochemical reduction of **1** has been shown to yield the radical anion, which rapidly disproportionates according to eq 1.[12]

$$2\mathrm{TPE}^{\bullet-} \underset{k_\mathrm{r}}{\overset{kf}{\rightleftharpoons}} \mathrm{TPE}^{2-} + \mathrm{TPE}\ K_\mathrm{disp} = k_\mathrm{f}/k_\mathrm{r} \qquad (1)$$

The disproportionation equilibrium constant for this reaction, K_disp, is large in relatively polar solvents such as THF or CH$_3$CN, since solvation and ion pairing stabilize the highly charged dianion over the radical anion in these solvents.[1] The cyclic voltammogram of **1** thus contains a single two-electron "reversible" wave, which is actually two closely spaced one-electron waves. We have proposed that tetraphenylethylene derivatives could be used as two-electron transfer catalysts since they can undergo rapid two-electron reduction, and electron transfer can be initiated photochemically.[5,7,14] In this vein, our group has prepared substituted tetraphenylethylenes with varying redox potentials in order to explore the effect of substitution on their observed electrochemical behaviors.[7] The electrochemistry of these compounds was more complex than that observed for **1**. Although reduction waves were sometimes broad and ill-defined, it was clear that K_disp for most of these tetrasubstituted compounds is large.

In an effort to expand our understanding of the geometric changes induced by excitation and/or reduction, we have prepared a series of substituted tetraphenylethylenes **2**−**5** in which the effect of increasing substitution by a single functional group on the electrochemical behavior could be examined. We chose electron-withdrawing acetyl groups for this study, since successive substitutions by Friedel−Crafts acylation proved to be a facile route to multiply substituted tetraphenylethylenes.



1 R$_1$,R$_2$,R$_3$,R$_4$ = H
2 R$_1$ = C(O)CH$_3$; R$_2$,R$_3$,R$_4$ = H
3a R$_1$,R$_2$ = C(O)CH$_3$; R$_3$,R$_4$ = H
3b R$_1$,R$_4$ = C(O)CH$_3$; R$_2$,R$_3$ = H
3c R$_1$,R$_3$ = C(O)CH$_3$; R$_2$,R$_4$ = H
4 R$_1$,R$_2$,R$_3$ = C(O)CH$_3$; R$_1$ = H
5 R$_1$,R$_2$,R$_3$,R$_4$ = C(O)CH$_3$

The acetyl group does not behave solely as an inert substituent in this system, since it can contribute both to the reduction behavior of the compounds and to the reactivity of the reduced species. The structure of the singly and doubly reduced anions in this series is therefore critical in determining the result of electrochemical or chemical reduction of **2**−**5**. In this paper, we describe the observed and calculated absorption spectra of neutral **2**−**5** and the mono- and dianions derived from them. We then correlate this data with the results of the electrochemical and chemical reductions of these compounds.

[†] Current address: Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z1.

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Experimental Section

General. All reactions were carried out under nitrogen, and reaction workups, after quenching, were done in air. Solvents were reagent grade and were used as received. $CDCl_3$ was used as a solvent for ^1H and ^{13}C NMR spectra. Reagents were purchased from Aldrich and were used as received.

1-(4-Acetylphenyl)-1,2,2-triphenylethylene (2). A solution of acetyl chloride (0.21 mL, 3.0 mmol) and $AlCl_3$ (0.40 g, 3.0 mmol) in CH_2Cl_2 (50 mL) was added via cannula to a solution of tetraphenylethylene (1.0 g, 3.0 mmol) in CH_2Cl_2 (50 mL) at room temperature. The solution was stirred for 2 h before being quenched by being poured into water. The crude product was extracted into CH_2Cl_2. The extract was washed with H_2O and brine and was dried over anhyd $MgSO_4$. The solvent was removed *in vacuo*, leaving an oily solid which was purified by chromatography (silica, CH_2Cl_2), yielding pure **2** (0.68 g, 61%): mp = 111 °C. ^1H NMR: 7.67 (d, 2 H, J = 8.4 Hz), 7.15−7.05 (m, 11 H), 7.05−6.95 (m, 6 H), 2.51 (s, 3 H). ^{13}C NMR: 197.6, 149.0, 143.1, 143.1, 143.0, 142.6, 139.8, 134.9, 131.4, 131.2, 131.2, 131.2, 127.8, 127.8, 127.7, 127.7, 126.9, 126.7, 126.7, 26.5. HRMS (CI): m/z calcd for $C_{28}H_{22}O$ $(M)^+$, 374.1671; found, 374.1672.

1,1-Bis(4-acetylphenyl)-2,2-diphenylethylene (3a) and *trans*-1,2-Bis(4-acetylphenyl)-1,2-diphenylethylene (3b). A solution of acetyl chloride (1.29 mL, 18.1 mmol) and $AlCl_3$ (2.46 g, 18.4 mmol) in CH_2Cl_2 (50 mL) was added via cannula to a solution of tetraphenylethylene (3.0 g, 9.0 mmol) in CH_2Cl_2 (25 mL) at rt. The solution was stirred for 12 h before being quenched by being poured into water. The crude product was extracted into CH_2Cl_2. The extract was washed with H_2O and brine and was dried over anhyd $MgSO_4$. The solvent was removed *in vacuo*, leaving an oily solid which was purified by chromatography (silica, CH_2Cl_2, followed by ethyl acetate/CH_2Cl_2, 1:100) yielding pure **3a** (0.44 g, 12%) and **3b** (0.34 g, 9%). **3a**: mp = 151 °C. ^1H NMR: 7.69 (d, 4 H, J = 7.5 Hz), 7.2−7.0 (m, 10 H), 7.0−6.9 (m, 4 H), 2.51 (s, 6 H). ^{13}C NMR: 197.5, 148.2, 144.1, 142.5, 138.6, 135.1, 131.4, 131.1, 127.9, 127.9, 127.2, 26.5. HRMS (CI): m/z calcd for $C_{30}H_{24}O_2$ $(M)^+$, 416.1776; found, 416.1769. **3b**: mp = 212 °C. ^1H NMR: 7.68 (d, 4 H, J = 8.4 Hz), 7.1−7.0 (m, 10 H), 7.0−6.9 (m, 4 H), 2.51 (s, 6 H). ^{13}C NMR: 197.7, 148.4, 142.5, 141.4, 135.2, 131.4, 131.2, 128.1, 127.8, 127.2, 26.5. HRMS (CI): m/z calcd for $C_{30}H_{24}O_2$ $(M)^+$, 416.1776; found, 416.1777.

***cis*-1,2-Bis(4-acetylphenyl)-1,2-diphenylethylene (3c).** A solution of **3b** (0.10 g, 0.24 mmol) in benzene (1 mL) was prepared, degassed by thorough purging with nitrogen, and irradiated with a medium pressure Hg lamp in a Pyrex tube for 1 h. The solvent was removed *in vacuo*, and the crude product was purified by chromatography (silica, CH_2Cl_2), yielding pure **3c** (10 mg, 10%). ^1H NMR: 7.69 (d, 4 H, J = 8.4 Hz), 7.2−7.1 (m, 10H), 7.1−7.0 (m, 4 H), 2.51 (s, 6 H). ^{13}C NMR: 197.65, 148.37, 142.43, 141.39, 135.20, 131.39, 131.16, 128.06, 127.80, 127.22, 26.51. HRMS (CI): m/z calcd for $C_{30}H_{24}O_2$ $(M)^+$, 416.1776; found, 416.1774.

1,1,2-Tris(4-acetylphenyl)-2-phenylethylene (4). A solution of acetyl chloride (1.7 mL, 24 mmol) and $AlCl_3$ (3.2 g, 24 mmol) in CH_2Cl_2 (50 mL) was prepared. This was added via cannula to a solution of tetraphenylethylene (1.0 g, 3.0 mmol) in CH_2Cl_2 (50 mL). The solution was stirred for 2 h, and the reaction was quenched by being poured into water. The crude product was extracted into CH_2Cl_2. The extract was washed with H_2O and brine and was dried over anhyd $MgSO_4$. The solvent was removed *in vacuo*, leaving an oily solid which was purified by chromatography (silica, ethyl acetate/CH_2Cl_2, 1:10), yielding pure **4** (0.44 g, 32%): mp = 165 °C. ^1H NMR: 7.7 (m, 6 H), 7.15−7.05 (m, 9 H), 6.96 (m, 2 H), 2.52 (s, 9 H). ^{13}C NMR: 197.4, 197.3, 147.6, 147.5, 147.4, 142.8, 141.9, 140.1, 135.5, 135.4, 131.3, 131.3, 131.3, 131.0, 128.0, 128.0, 127.9, 127.9, 127.5, 26.4 (one resonance obscured in the aryl region). HRMS (CI): m/z calcd for $C_{28}H_{22}O$ $(M)^+$, 459.1960; found, 459.1957.

1,1,2,2-Tetrakis(4-acetylphenyl)ethylene (5). A solution of acetyl chloride (1.7 mL, 24 mmol) and $AlCl_3$ (3.2 g, 24 mmol) in CH_2Cl_2 (50 mL) was added via cannula to a solution of tetraphenylethylene (1.0 g, 3.0 mmol) in CH_2Cl_2 (50 mL). The solution was heated at reflux for 12 h and was then quenched by being poured into water. The crude product was extracted into CH_2Cl_2, washed with H_2O and brine, and dried over anhyd $MgSO_4$. The solvent was removed *in vacuo*, yielding an oily solid which was purified by chromatography (silica, ethyl acetate/CH_2Cl_2, 1:1), yielding pure **5** (0.05 g, 3%): mp = 241 °C. ^1H NMR: 7.71 (d, 8 H, J = 8.4 Hz), 7.07 (d, 8 H, J = 8.4 Hz), 2.52 (s, 12 H). ^{13}C NMR: 197.39, 146.91, 141.62, 135.80, 131.26, 128.13, 25.51. HRMS (CI): m/z calcd for $C_{34}H_{29}O_4$ $(M + H)^+$, 501.2066; found, 501.2056.

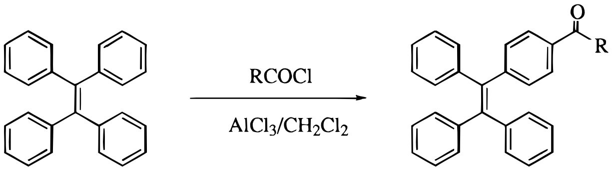
Electrochemistry. $[n\text{-}Bu_4N]PF_6$ (Aldrich) was recrystallized three times from absolute ethanol. THF was distilled from Na/benzophenone immediately before use and degassed by three freeze−pump−thaw cycles. Experiments were done in a three-electrode cell with a platinum mesh counter electrode, a silver wire quasi-reference electrode, and a platinum working electrode. Potentials were referenced internally to added ferrocene and are reported against SCE. Bulk electrolysis was conducted in the same cell at constant potential (−2.00 V vs Ag) under a N_2 atmosphere.

Chemical Reductions. The compound to be reduced was dissolved in dry THF and stirred with an excess (10−20 equiv) of 5 wt % Na in Hg. After the reaction was complete, the mixture was poured into water, and the product was extracted into CH_2Cl_2 and dried over anhyd $MgSO_4$. The solvents were then removed *in vacuo*.

Molecular Orbital Calculations. Structural minimizations for all neutral compounds were conducted with MOPAC 6.01 and AM1 parameters.[16] Geometry optimization was achieved when the energy change was less than 0.0002 kcal mol^{-1}; the resulting structures were then used in all subsequent calculations. Semiempirical electronic structure calculations for **1**−**3** were carried out using the ZINDO package included in the CAChe 3.7 software package. Compounds **4** and **5** were too large to be handled by this software. The INDO/1 parameters used in these calculations were taken from the literature.[17] Singlet RHF and doublet ROHF calculations were performed on the neutral and monoanions, respectively. The dianions of **1**, **2**, **3a**, and **3b** were treated as singlets (RHF). The spectral calculations were performed following the procedure (CI) included in the ZINDO software. The solvent parameters for CH_2Cl_2 (ρ = 1.4218, ϵ = 9.08; used for the neutral compounds) or THF (ρ = 1.407, ϵ = 7.58; used for the reduced compounds) were included as a dielectric continuum in the model. Molecular radii were determined directly from the minimized structures.

Results

Synthesis. We prepared acetylated tetraphenylethylenes **2**−**5** by Friedel−Crafts acylation of **1** in CH_2Cl_2 using $AlCl_3$, as shown for the preparation of **2** in eq 2.



1 **2** (2)

Compounds **2**−**4** were obtained by controlling the molar ratio of acetyl chloride and $AlCl_3$ to TPE at room temperature. In order to obtain **5**, it was necessary to heat the reaction mixture at reflux. However, by this method the compound could be isolated only in very low yield (~3%). All of the acetylated compounds were purified by column chromatography on silica and were obtained as crystalline solids.

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Table 1. INDO/1 Calculations of Formal Charge on Olefinic and Carbonyl Atoms in Acetophenone and 1−3 as Neutral and Singly and Doubly Reduced Ions

compound	formal charge[a]					
	C1 olefin	C2 olefin	C carbonyl 1	O carbonyl 1	C carbonyl 2	O carbonyl 2
1	−0.001	−0.002				
1$^{\bullet-}$	−0.134	−0.135				
1^{2-}	−0.154	−0.151				
2	−0.011	0.010	0.401	−0.620		
2$^{\bullet-}$	0.010	−0.030	0.256	−0.779		
2^{2-}	−0.041	−0.110	0.272	−0.801		
3a	−0.010	0.010	0.403	−0.617	0.403	−0.618
3a$^{\bullet-}$	0.011	−0.039	0.290	−0.756	0.396	−0.639
3a^{2-}	0.013	−0.082	0.294	−0.776	0.308	−0.755
3b	0.001	0.000	0.403	−0.616	0.403	−0.617
3b$^{\bullet-}$	0.021	−0.049	0.297	−0.751	0.396	−0.638
3b^{2-}	−0.076	−0.081	0.240	−0.677	0.240	−0.675
3c	0.001	−0.003	0.404	−0.615	0.403	−0.616
3c$^{\bullet-}$	0.026	−0.034	0.267	−0.771	0.399	−0.633
acetophenone			0.388	−0.625		
acetophenone$^{\bullet-}$			0.185	−0.820		

[a] C1 olefin and C2 olefin are defined as the olefinic carbon atoms in **1**−**3**. C carbonyl 1 and O carbonyl 1 are defined as the carbon and oxygen atoms of the carbonyl group located closest to C olefin 1. C carbonyl 2 and O carbonyl 2 are defined as the carbon and oxygen atoms of the second carbonyl group in **3a** or those located closest to C olefin 2 in **3b** and **3c**.

Molecular Orbital Calculations. The AM1-optimized geometries of the acetyl-substituted tetraphenylethylenes **1**−**3** have been investigated with the goal of supporting the experimental results reported herein. All of the minimized structures are propeller-shaped, similar to the known structure of **1**,[18] with the acetyl groups in **2** and **3** lying in the plane of the attached phenyl rings. The minimized structures of **1**−**3** were used in the calculation of molecular orbital energies, charge densities, and absorption spectra of the neutral and reduced species using INDO/1 parameters. Compounds **4** and **5** could not be studied directly because of software limitations. The structures of the reduced species were not minimized further in order to facilitate comparison of the electronic structure of the neutral, radical anions, and dianions, although it is known that the structure of the dianion of **1** is slightly twisted (~30°) about the olefin.[14]

The formal charges of the olefinic carbon atoms and carbonyl carbon and oxygen atoms for acetophenone and **1**−**3** and their related mono- and dianions are listed in Table 1. As **1** is reduced, there is an increased negative charge (decreased formal charge) on the olefinic carbon atoms, consistent with reduction of the C−C π-bond, as is observed in the literature.[15] In **2**, the carbonyl of the acetyl group is the site of significant reduction; the formal charge on the carbonyl C and O became significantly more negative upon addition of one electron, whereas the olefinic carbons become only slightly more negative. When the dianion is produced, a greater fraction of negative charge resides on the olefin carbons as well. Compound **3a** behaves in a similar fashion to **2** when reduced by one electron, but both carbonyl groups and the olefin bear more negative charge in the dianion of **3a**. A similar response is observed for the dianion of **3b**, except that charge is more evenly distributed across the molecule. Thus, these calculations indicate that reduction of acetyl-substituted tetraphenylethylenes affects both the carbonyl and olefinic moieties.

The calculated energies of the HOMO and LUMO of **1**−**3** and the corresponding reduced anions are listed in Table 2. The energies of both the HOMO and LUMO increase upon reduction, as expected. In addition, the HOMO−LUMO gaps decrease substantially in the monoanions.

Table 2. INDO/1 Calculations of HOMO[a] and LUMO Energies of 1−3 and the Related Anions

compound	HOMO[a] (eV)	LUMO (eV)
1	−7.385	0.280
1$^{\bullet-}$	−1.017[a]	3.680
1^{2-}	3.158	6.486
2	−7.609	−0.368
2$^{\bullet-}$	−1.238[a]	2.639
2^{2-}	2.741	5.591
3a	−7.850	−0.610
3a$^{\bullet-}$	−1.397[a]	1.766
3a^{2-}	2.286	4.883
3b	−7.804	−0.662
3b$^{\bullet-}$	−1.387[a]	1.537
3b^{2-}	2.077	4.072
3c	−7.820	−0.535
3c$^{\bullet-}$	−1.335[a]	1.804

[a] The HOMO of a radical anion might appropriately be called a SOMO, but in order to facilitate direct comparison with the related orbitals in the closed shell neutral and dianion, the more general term (HOMO) is employed here.

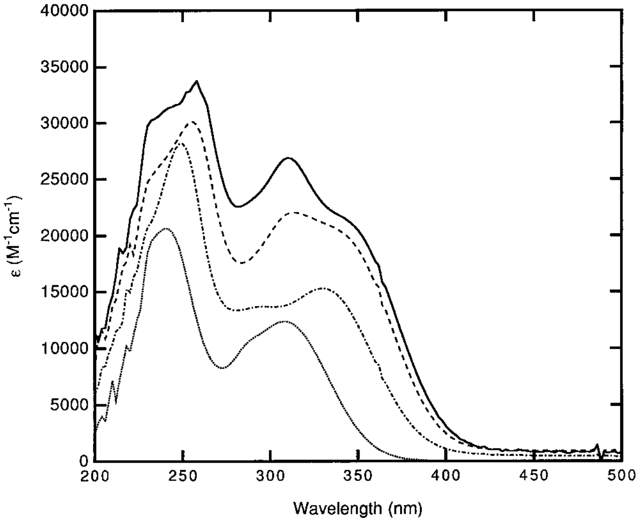

Figure 1. Absorption spectra of **1** (· · ·), **2** (−·−), **4** (- - -), and **5** (−) in CH_2Cl_2.

Absorption Spectra. The absorption spectra of **1-5** in CH_2Cl_2 shown in Figures 1 and 3 can be compared with the calculated (INDO/1) electronic spectra of **1**−**3** shown in Figures 2 and 4. The calculated and observed spectra

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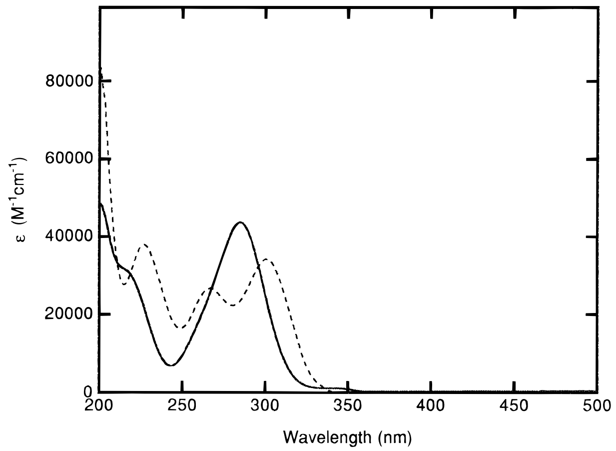

Figure 2. Calculated (INDO/1) absorption spectra of **1** (—) and **2** (- - -).

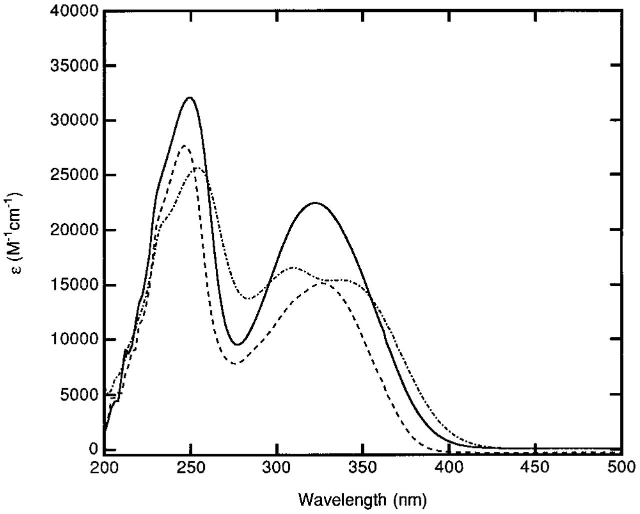

Figure 3. Absorption spectra of **3a** (—), **3b** (- - -), and **3c** (—•—) in CH_2Cl_2.

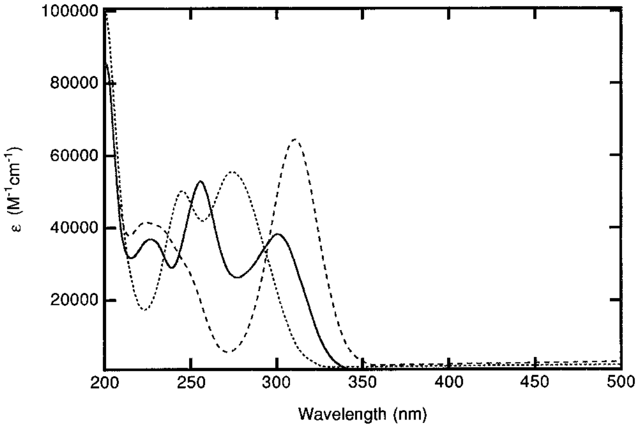

Figure 4. Calculated (INDO/1) absorption spectra of **3a** (—), **3b** (- - -), and **3c** (• • •).

are similar in shape, although the peaks in the observed spectra are less well-defined. Each of the observed spectra contains at least two distinct bands, and, in some cases, shoulders. Both the higher and lower energy bands are red-shifted with increasing acetylation, with the intensities of both bands increasing with substitution. The absorption spectrum of **2** is significantly red-shifted from that of **1**, and a third band appears at ~275 nm. Since acetophenone has strong absorptions at 240 and 275 nm,[19] the new band in the spectrum of **2** can likely be assigned to the carbonyl group. The three diacetyl isomers **3a**−**c** have slightly different spectra, although the two principal bands appear at approximately the same energy, Figure 3. In the spectrum of the *cis* isomer **3c**, the low-energy band is split, exhibiting two maxima at 310 and 340 nm, whereas in both **3a** and the *trans* isomer **3b** the low-energy band exists as a single peak at ~325 nm. Compounds **4** and **5** have similar absorption spectra, Figure 1, in which the strongest absorption is observed in the low-energy band (at 300 nm) and in which a low energy shoulder is present.

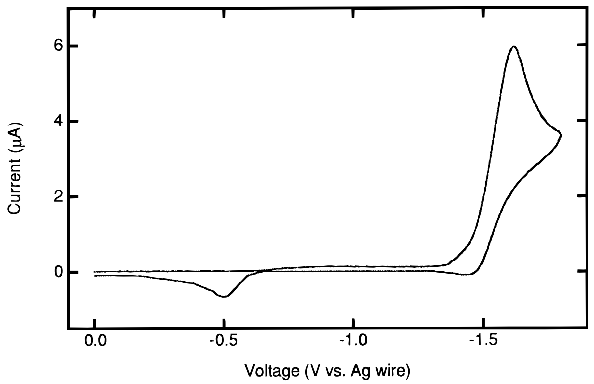

Figure 5. Cyclic voltammogram of **2** (~10 mM) at Pt in deaerated 0.3 M [n-Bu_4N]PF_6 in THF at room temperature. Scan rate = 100 mV/s.

Table 3. Cyclic Voltammetry Data of 1−5 and Acetophenone

compound	E1/2 vs SCE (V ± 0.05 V)	no. of electrons	i_{pc}/i_{pa}[a]	$E_{pc} - E_{pa}$[b] (mV)
1	−3.01	2		
2	−2.83	1	irreversible	
3a	−2.69	1	irreversible	
3b	−2.44	2	0.98	210
3c	−2.44		1.00	183
4	−2.32	2	0.96	220
5	−2.18	2	0.96	140
acetophenone	−2.93	1	irreversible	

[a] i_{pc} = peak cathodic current; i_{pa} = peak anodic current. [b] Scan rate = 100 mV/s.

Cyclic Voltammetry. Cyclic voltammograms of **2**−**5** were measured in deaerated THF containing 0.3 M [n-Bu_4N]PF_6 as the supporting electrolyte. The cyclic voltammogram of **2** shows an irreversible reduction wave and a broad reoxidation wave at −0.5 V vs Ag which appears only after scanning through the reduction wave, Figure 5. The cyclic voltammogram of **3a** is similar (from 0 to −2.0 V vs Ag) to that of **2**, except that the reduction wave appears at a slightly less negative potential, Table 3. The peak position of the reduction wave ($E_{p,c}$) of **2** shifts negatively with increasing scan rate, while the maximum cathodic current ($i_{p,c}$) increases, Figure 6. Interestingly, at fast scan rates (>1 V/s), an oxidation wave directly associated with the reduction wave appears. This anodic wave also increases in intensity with increasing scan rate, suggesting that at fast scan rates some of the initial reduced species is oxidized back to the neutral species before it could have been converted to the secondary product. Since the oxidation wave at ~−0.5 V is less intense than the cathodic wave, it is likely that

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(19) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1993.

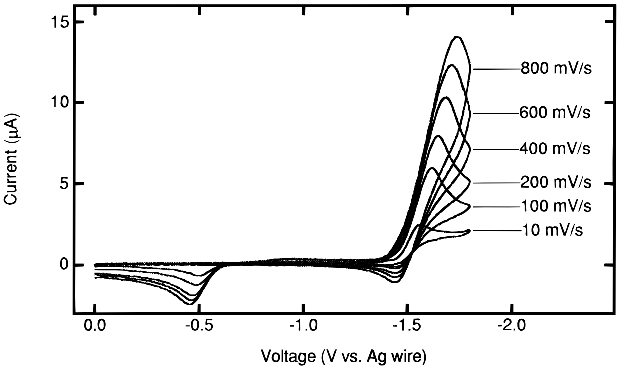

Figure 6. Scan rate dependence of the cyclic voltammogram of a deaerated ~10 mM solution of **2** in 0.3 M [*n*-Bu_4N]PF_6 in THF at Pt at room temperature.

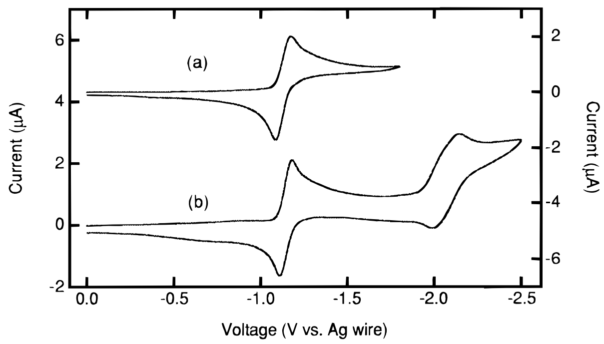

Figure 7. Cyclic voltammogram of ~10 mM **5** in deaerated 0.3 M [*n*-Bu_4N]PF_6 in THF at Pt at room temperature over the potential range (a) 0 to −1.75 V and (b) 0 to −2.5 V. Scan rate = 100 mV/s.

the chemically produced secondary product either is unstable or is not formed quantitatively. We attribute this behavior to an ECE process in which the initial reduction product reacts rapidly, and the resulting product is subsequently oxidized at ~−0.5 V vs Ag.

Cyclic voltammetry of acetophenone under the same conditions shows similar features. The radical anion of acetophenone undergoes a rapid coupling reaction to yield a pinacol (1,2-diphenyl-1,2-ethanediol).[20] The oxidation waves at ~−0.5 V in both acetophenone and **2** and **3a** are assigned to oxidation of the pinacol product. We conclude that the electrochemical reduction of **2** and **3a** in THF generates carbonyl-based radical anions which dimerize rapidly.

The cyclic voltammograms obtained at a scan rate of 100 mV/s of **3b**, **3c**, **4**, and **5** all have quasi-reversible first reduction waves like that shown for **5**, Figure 7a. The quasi-reversibility of this wave indicates the production of a reduced species that dimerizes less rapidly than the radical anion of **2** or **3a**. The reduction waves for **3b**, **3c**, **4**, and **5** remain quasi-reversible even at the slowest scan rates (10 mV/s). The electrochemical behavior of **3a** and **3b** is particularly interesting, as these geometric isomers differ markedly, Figure 8. The cyclic voltammogram of **5** also contains a second two-electron cathodic wave, Figure 7b. The asymmetry of this wave implies two closely spaced reductions involving the same number of electrons as in first wave. This electrochemical behavior is very similar to that observed for 1,1,2,2-tetrakis(4-nitrophenyl)ethylene in CH_3CN and DMF, where two successive two-electron waves have been reported.[21]

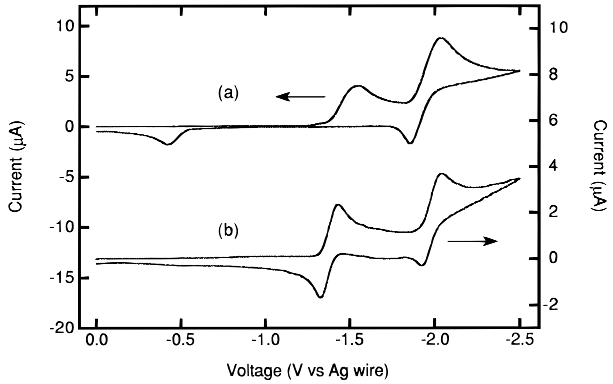

Figure 8. Cyclic voltammogram of (a) ~10 mM **3a** and (b) ~10 mM **3b** in deaerated 0.3 M [*n*-Bu_4N]PF_6 in THF at Pt at room temperature containing 1 equiv of **1**. Scan rate = 100 mV/s.

The cyclic voltammograms of **3b** and **3c** are identical. Since these compounds may interconvert by rotation about the ethylenic bond, we suggest that reduction produces a common species by rapid rotation about this bond. This process is too rapid to be observed directly, and so the cyclic voltammograms appear identical. Bulk electrolysis of **3b** yielded some **3c** after workup, as would be expected if rotation about the ethylenic bond occurs in the intermediate reduced species. Our results are consistent with literature measurements for *cis*- and *trans*-1,2-bis(4-cyanophenyl)-1,2-bis(4-methoxyphenyl)ethylene, in which both isomers exhibit identical reduction potentials.[9]

In order to determine the number of electrons involved in each reduction of **2**−**5**, we examined the cyclic voltammograms of these compounds in the presence of an equimolar quantity of **1**. We chose **1** as the internal standard for these experiments because its diffusion characteristics are expected to be similar to those of the acetylated derivatives. The cyclic voltammograms for **3a** and **3b** in the presence of **1** are shown in Figure 8. Those compounds with an irreversible reduction wave (**2** and **3a**) display single-electron reductions by cyclic voltammetry, whereas **1**, **3b**, **3c**, **4**, and **5** all display two electron quasi-reversible reduction waves, Table 3.

Chemical Reductions. Compounds **2**−**5** can be chemically reduced upon reaction with Na/Hg amalgam. Reduction of a solution of **2** gives a red solution, the absorption spectrum of which is shown in Figure 9. The addition of water to the reduction mixture causes the red color to disappear rapidly. Workup of the resulting mixture yields both diastereomers of pinacol **6**,[22] in addition to recovered **2**. The presence of residual **2** after workup, even when excess Na/Hg was used, is likely the result of equilibration between $\mathbf{6}^{2-}$ and $\mathbf{2}^{\bullet-}$, analogous to that reported for other pinacols.[23] The observed cyclic voltammetry of **2** (*vide supra*) suggests that dimerization is rapid on the operative electrochemical time scale. The calculated absorbance spectrum for **2** as a radical anion,

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[20] Wawzonek, S.; Gunderson, A. *J. Electrochem. Soc.* **1960**, *107*, 537−540.

[21] Ammar, F.; Savéant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *47*, 115−125.

[22] Mattielo, L.; Rampazzo, L. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2243−2247.

[23] Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1962**, *84*, 4155−4157.

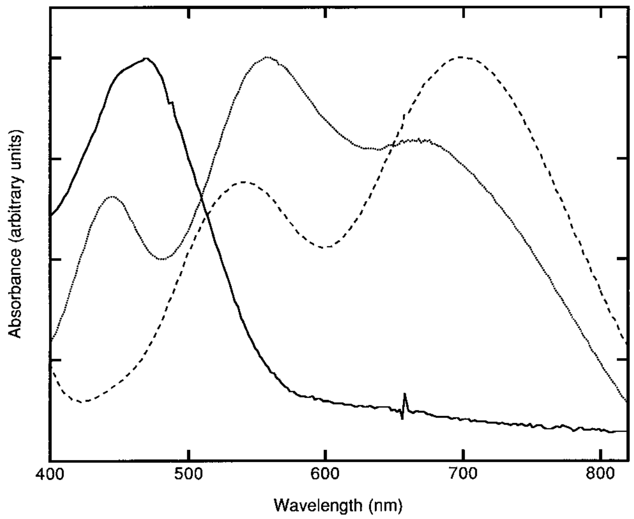


Figure 9. Absorption spectra of **2** (—), **4** (· · ·), and **5** (- - -) after treatment with Na/Hg in THF.

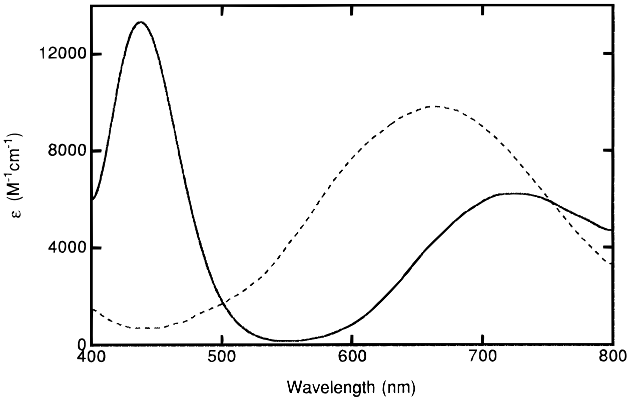
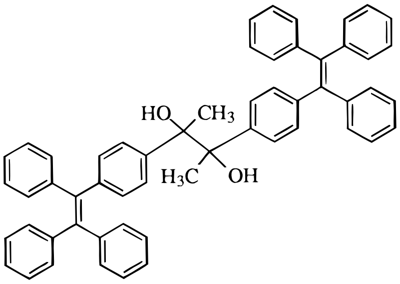


Figure 10. Calculated absorption spectra of **1**$^{\bullet-}$ (—) and **2**$^{\bullet-}$ (- - -).

2$^{\bullet-}$, Figure 10, displays a broad absorbance around 710 nm similar to that expected for a ketyl radical anion. This contrasts with the observed maximum of 450 nm, suggesting that the observed species may be the pinacol of **6** which has been further reduced by excess Na/Hg amalgam.



6

The product mixture showed no evidence for the formation of semidione.[24] Semidione formation is unlikely under our experimental conditions which were more mildly reducing, in a less polar solvent, and in the absence of air, all of which differentiate our experiment from those described earlier as conducive of semidione formation.

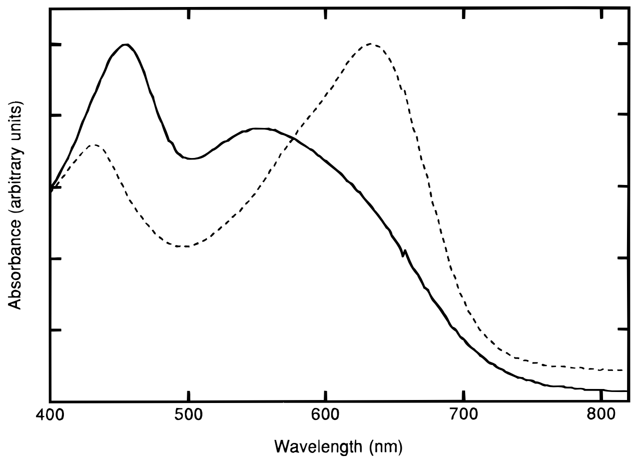


Figure 11. Absorption spectra of **3a** (- - -) and **3b** (—) after treatment with Na/Hg in THF.

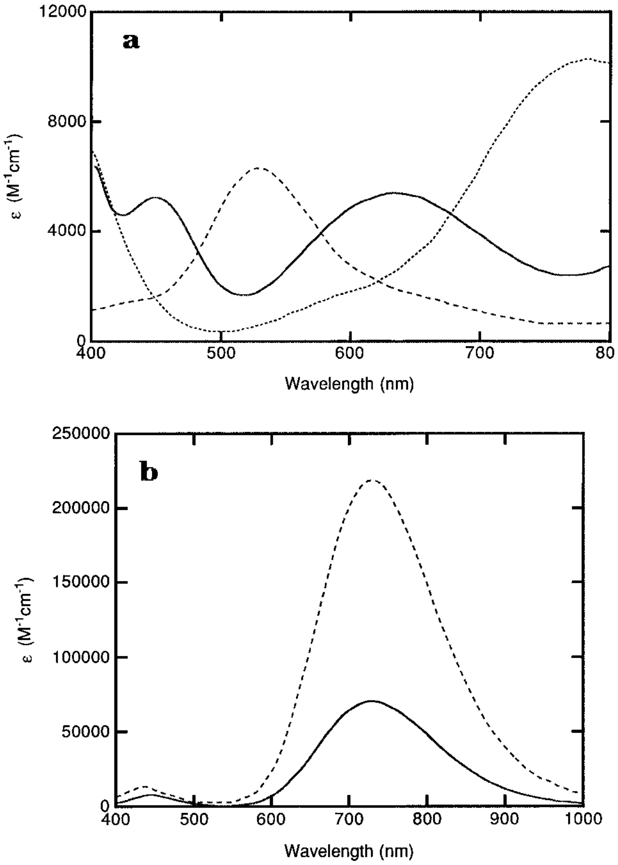


Figure 12. Calculated absorption spectra of (a) **3a**$^{\bullet-}$ (· · ·), **3b**$^{\bullet-}$ (—), and **3c**$^{\bullet-}$ (- - -) and (b) **1**$^{2-}$ (—) and **3b**$^{2-}$ (- - -).

The reductions of **3a** and **3b** with Na/Hg give dark red solutions, the absorbance spectra of which are shown in Figure 11. The calculated spectra of **3a**$^{\bullet-}$ and **3b**$^{\bullet-}$, Figure 12a, are somewhat similar to the observed spectra, although shifted from the observed maximum absorbances. In addition there is an absorbance near 450 nm that is similar to that observed for reduced **2** in Figure 9. Quenching the reduced **3a** solution with water, followed by workup, yields a product mixture containing the pinacols of **3a** as well as **7a**. Dimerization appears to be slower in **3a** than in **2**, leading to concomitant spectroscopic observation of bands attributable to **3a**$^{\bullet-}$ at wavelengths longer than 600 nm and to the pinacol

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[24] Russell, G. A.; Strom, E. T.; Talaty, E. R.; Weiner, S. A. *J. Am. Chem. Soc.* **1966**, *88*, 1998.

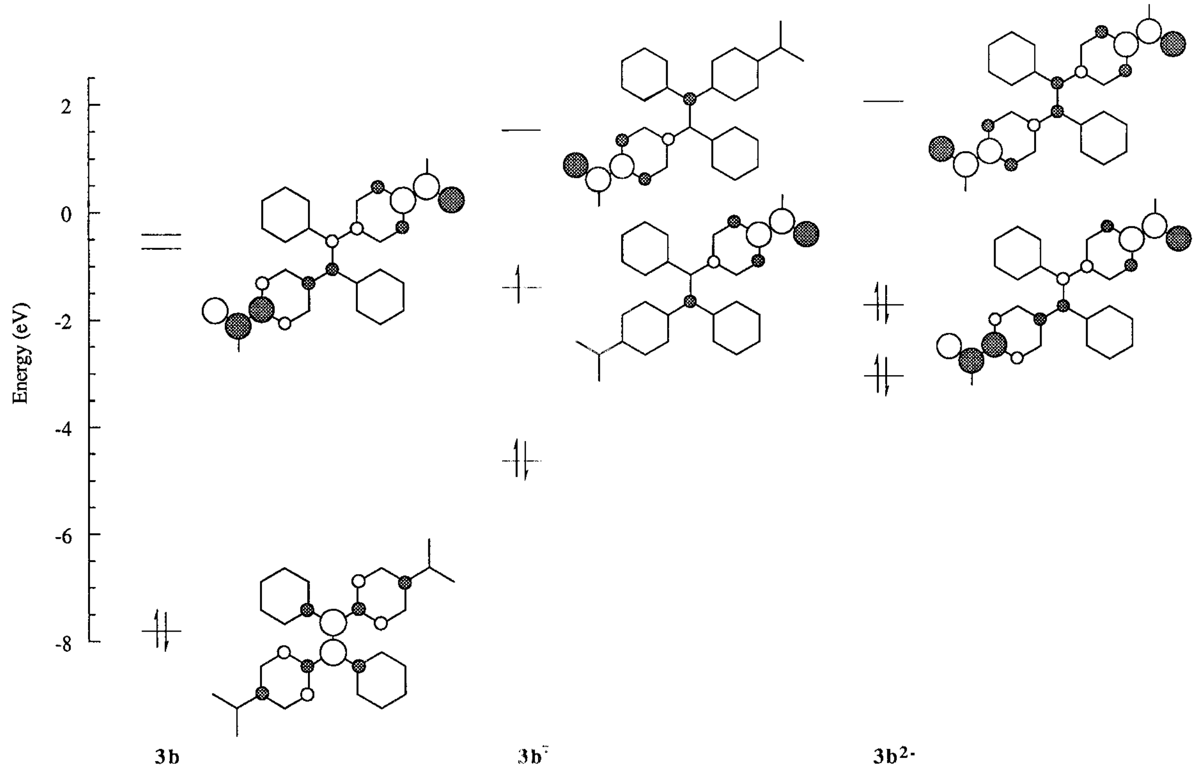
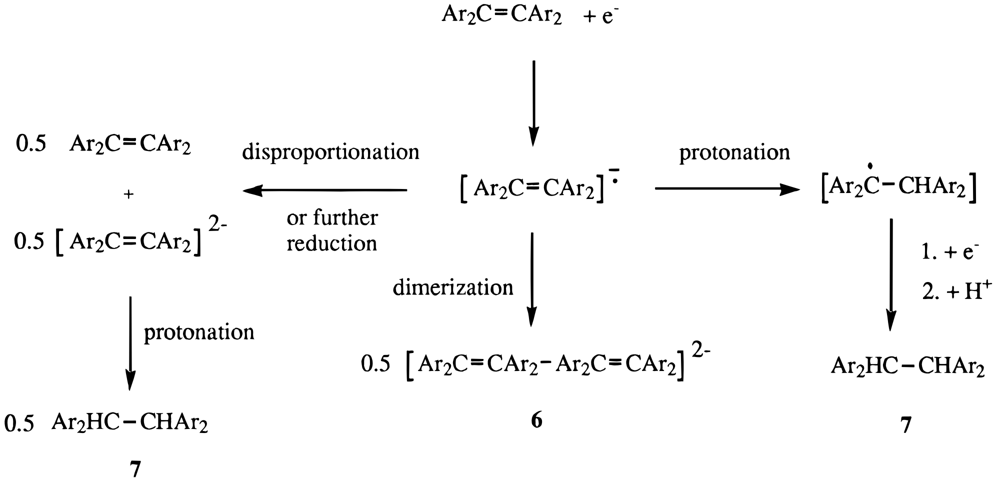
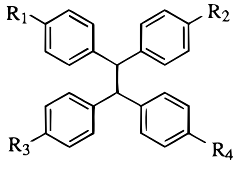


Figure 13. Energy and charge density changes in the HOMO and LUMO of **3b** upon reduction to the radical anion and dianion.

Scheme 1. Reaction Pathways of Reduced 1−5



dianion at 450 nm.



7a $R_1,R_2 = C(O)CH_3$; $R_3,R_4 = H$
7b $R_1,R_4 = C(O)CH_3$; $R_2,R_3 = H$
7c $R_1,R_2,R_3 = C(O)CH_3$; $R_1 = H$

The major product obtained upon chemical reduction of **3b** is assigned from the ^{1}H spectrum to the symmetric ethane **7b** resulting from reduction of the double bond. There is no evidence for the formation of any products arising from reduction of the carbonyl group. The calculated positions of the long wavelength bonds for singly and doubly reduced **3b** (**3b**$^{\bullet-}$ and **3b**$^{2-}$), Figure 12, are essentially identical albeit with different extinction coefficients. Thus, the absorbing species in the observed spectrum, Figure 11, may be either the mono- or dianion of **3b**.

The reduced olefin **7c** was obtained from the reduction of **4** with Na/Hg in THF. The absorption spectra of the freshly reduced solutions of **4** and **5** are shown in Figure 9. The solution of reduced **4** is blue and that of reduced **5** is purple: these colors are also observed close to the working electrode during bulk electrochemical reduction of these compounds.

Discussion

The differences observed in the reactivity of reduced **2**−**5** are caused by differences in the stabilities of the corresponding radical anions. We propose Scheme 1 to account for the reactivity of this series of compounds.

The radical anion formed upon electrochemical or chemical reduction may react in several ways, although the chemical reducing agent may induce over-reduction in some cases. In **2** and **3a**, compounds which lack acetyl substituents on the phenyl at C_1 and C_2 of the central double bond, rapid dimerization to a pinacol occurs. This coupling appears to be more rapid for **2** than for **3a**, since with **2** no other product is observed, but with **3a** other products are also formed. The electrochemical studies suggest that these reductions are one-electron processes, and the coupled product **6** is structurally analogous to that obtained in the one-electron reduction of acetophenone. The formal charge distributions in $\mathbf{2}^{\bullet -}$ and $\mathbf{3a}^{\bullet -}$, Table 2, suggest that these reactions can be regarded as carbonyl group reductions in which the radical anion is likely to combine with a second radical anion to afford the expected pinacol via interaction of the singly occupied molecular orbital of each anion. Further reduction to the dianions of **3a** and **3b** localizes more negative charge on the olefinic carbons, producing **7a** and **7b**, respectively. Thus, upon reduction, **2** dimerizes rapidly to afford only the pinacol, but when **3a** is reduced, both the tetraarylethane product **7** and the dimerization product **6** are formed, indicating that either the rate of dimerization has decreased or over-reduction is easier in this compound than in **2**.

For **3b**, **3c**, **4**, and **5** (and **3a**, to a minor extent), disproportionation followed by protonation produces the related tetraarylethane, in parallel to reactivity previously reported for electrochemically[15] or chemically[11] reduced **1**. Figure 13 shows the evolution of the molecular orbitals as **3b** is reduced by one and two electrons. In the radical anion, the symmetry of the HOMO and LUMO is broken but is reestablished upon further reduction. Extensive delocalization in the HOMO of $\mathbf{3b}^{2-}$ is expected to contribute to the stability of the dianion, enabling facile double reduction. Once a dianion is formed, however, the driving force for coupling decreases since this would require the interaction of molecular orbitals that are now completely filled. Protonation to the reduced products **7b** and **7c** takes place with **3b** and **4**, although in the absence of a proton source, the dianions of **3b**, **3c**, **4**, and **5** appear to be quite stable. The stabilizing effect of delocalization is consistent with the two-electron reduction processes that are indicated by the quasi-reversible electrochemistry of **1**, **3b**, **3c**, **4**, and **5**. We are unable to distinguish experimentally between a reaction pathway involving disproportionation, followed by protonation by solvent, and one proceeding by protonation of the radical anion by solvent, followed by reduction and a second protonation step. We can conclude, however, that one-electron reductions of acetylated tetraphenylethylenes lead to coupled products (pinacols) and two-electron reductions lead to reduction of the olefin.

Conclusions

The successive substitution of tetraphenylethylene by acetyl groups results in significant changes in the electronic structure of the compounds. These changes are manifested in both the electronic spectra and the electrochemistry of **2**−**5**. The dramatic differences in both the electrochemical behaviors and the reduction product distributions observed for **3a** and **3b**, both diacetylated derivatives of the parent compound, show that the reactivity of the reduced compounds is very sensitive to substitution. Ultimately, our goal is the preparation of two-electron transfer catalysts with varying redox potentials and reactivity. This work demonstrates that by using substituents such as the acetyl group, these attributes can easily be tuned.

Acknowledgment. This work was supported by the National Science Foundation and the Robert A. Welch Foundation. M.O.W. gratefully acknowledges a postdoctoral fellowship from the Natural Sciences and Engineering Research Council of Canada. We thank Scott Reese for assistance with the bulk electrolysis experiment.

Supporting Information Available: Copies of ^{13}C NMR spectra (6 pages). This material is contained in 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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