chlorate gave a smaller fraction of the α anomer than NBS. The results with the iodonium salt and the fact that a prolonged reaction time increased the proportion of the α anomer suggest that the β anomer is a kinetic product that slowly equilibrates to the α anomer. When **2** was kept in a $CDCl_3$ solution, no equilibration could be detected by ^{1}H NMR even after one week. The phosphate group in **2** can be selectively deprotected by Pd/C-catalyzed hydrogenation in the presence of cyclohexylamine (2 equiv; MeOH, 1 h, room temperature). Further hydrogenation gave the cyclohexylammonium salt of glucose 1-phosphate.

Because we wished to develop practical synthetic routes to sugar nucleotides in general[17,18] and to UDP-GlcNAc in particular, we investigated the phosphorylation of 4-pentenyl glycosides derived from glucosamine. The *N*-phthalimidoglucosamine derivative **3** was obtained as described,[13] except that introduction of the 4-pentenyloxy chain was achieved more efficiently using the Hamada procedure[19] (Scheme II). Under the conditions of this scheme, **3** yielded exclusively the β-2-*N*-phthalimido-3,4,6-tri-*O*-acetylglucosamine 1-phosphate **4**. The β stereochemistry was established by ^{1}H NMR spectroscopy, on the basis of the coupling constants (J = 8.1 Hz and J_{HCOP} = 7.6 Hz).

On the basis of the examples provided by **2** and **4**, we believe that the Fraser-Reid methodology provides convenient access to protected glycosyl 1-phosphates. The generality of the method remains to be established through further examples.

Experimental Section

General. Reagents and solvents were reagent grade and used as received; CH_2Cl_2 and MeCN were distilled from CaH_2 and Et_2O from sodium benzoquinone ketyl. TLC analyses were performed on glass plates with UV fluorescent indicator (Merck, Silica gel 60 F254) and were stained with a mixture of *p*-anisaldehyde, acetic acid, sulfuric acid, and ethanol (5.5:32:7.5:2.00) or with the Dittmer–Lester reagent for phospho compounds.[16] Flash chromatography employed 40–63 μm of silica (Merck). ^{1}H NMR spectra were obtained at 300 and 500 MHz, ^{13}C at 75.45 MHz, and ^{31}P at 121.49 MHz. Molecular sieves (4 Å, Aldrich) were dried in an oven at 180 °C. **1** and **3** were prepared as described with slight modifications for **3** (see text).

2,3,4,6-Tetra-*O*-benzylglucosyl Dibenzyl Phosphate (2). To a suspension of activated molecular sieves (0.2 g) in a solution of 4′-pentenyl tetrabenzylglucoside (120 mg, 0.19 mmol, 1 equiv) and dry acetonitrile (2 mL), were added successively dibenzyl phosphate (55 mg, 0.2 mmol, 1 equiv), and NBS (70 mg, 0.4 mmol, 2 equiv). The mixture was stirred under argon at room temperature for 8 h. The suspension was filtered to remove the molecular sieves, concentrated in vacuo, and chromatographed (silica; eluent, petroleum ether–ethyl acetate (8:2 to 7:3)). Compound **2** was obtained as a gum (110 mg, 72%, $\alpha/(\alpha + \beta)$ = 0.2). The same procedure was applied using iodonium dicollidine perchlorate with these quantities: 4′-pentenyl tetrabenzylglucoside (210 mg, 0.34 mmol, 1 equiv), acetonitrile (4 mL), dibenzyl phosphate (128 mg, 0.45 mmol, 1.15 equiv), iodonium dicollidine perchlorate (188 mg, 0.4 mmol, 1.18 equiv), and a reaction time of 10 h. Compound **2** (135 mg, 50%, $\alpha/\alpha + \beta$ = 0.15) was again isolated as gum: ^{1}H NMR ($CDCl_3$) δ 7.45–7.19 (m, 28 H), 7.19–7.08 (m, 2 H), 5.97 (dd, H1 α anomer, J = 6.7, 3.2 Hz), 5.24 (dd, H1 β-anomer, J = 6.7, 6.7 Hz), 5.10 (br d, 2 H, J = 6.9 Hz), 5.04 (t, 2 H, J = 6.7 Hz), 4.92–4.67 (m, 5 H), 4.58–4.44 (m, 3 H), 3.91–3.45 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 138.5–137.5 (m, Ph), 128.60, 128.53, 128.31, 128.09, 128.04, 127.98, 127.90, 127.82 (Ph); β anomer 99.31 (C1, d, J = 4.2 Hz), 84.55 (C3), 82.18 (C2, d, J = 6.7 Hz), 77.47 (C4), 75.82 (Bn), 75.71 (C5), 75.18 (Bn), 75.05 (Bn), 73.64 (Bn), 69.52 (BnOP, d, J = 3.5 Hz), 69.46 (BnOP, d, J = 3.5 Hz), 68.68 (C6); α anomer 95.93 (C1, d, J = 4.2 Hz), 81.34 (C3), 79.50 (C2, d, J = 6.7 Hz), 77.05 (C4), 75.80 (Bn), 75.25 (Bn), 73.69 (Bn), 73.24 (Bn), 72.73 (C5), 69.52 (BnOP, d, J = 3.5 Hz), 69.46 (BnOP, d, J = 3.5 Hz), 68.21 (C6); ^{31}P NMR ($CDCl_3$) δ −4.15. Anal. Calcd for $C_{48}H_{49}O_9P$: C, 72.02, H, 6.12. Found: C, 71.62, H, 6.28.

2-*N*-Phthalimido-3,4,6-tri-*O*-acetylglucosyl Dibenzyl Phosphate (4). To a suspension of activated molecular sieves in a solution containing 4′-pentenyl 2-*N*-phthalimido-3,4,6-tri-*O*-acetylglucoside (166 mg, 0.33 mmol, 1 equiv) in dry acetonitrile (4 mL) were successively added dibenzyl phosphate (101 mg, 0.36 mmol, 1.1 equiv) and NBS (118 mg, 0.66 mmol, 2 equiv). The mixture was stirred under argon at room temperature for 11 h. The suspension was then filtered to remove the molecular sieves, concentrated in vacuo, and chromatographed (silica; eluent, petroleum ether–ethyl acetate (7:3)). Compound **4** was obtained as a white solid (162 mg, 71%, β only): ^{1}H NMR ($CDCl_3$) δ 7.79–7.75 (m, 2 H), 7.70–7.66 (m, 2 H), 7.36–7.05 (m, 10 H), 6.13 (dd, H1 β-anomer, J = 8.1, 7.6 Hz), 5.88 (dd, H3, J = 10.2, 9.6 Hz), 5.21 (dd, H4, J = 10.1, 9.6 Hz), 5.02 and 4.97 (ABd, Bn, J = 12.0, 8.0 Hz), 4.82 and 4.72 (ABd, Bn, J = 12.0, 7.6 Hz), 4.45 (dd, H2, J = 10.2, 8.1 Hz), 4.32 (dd, H6 or 7, J = 12.8, 4.4 Hz), 4.14 (dd, H6 or 7, J = 12.8, 2.9 Hz), 4.00 (ddd, H5, J = 10.1, 4.4, 2.9 Hz), 2.75 (s, 3H), 2.03 (s, 3H), 1.85 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 134.63, 128.83, 128.78, 128.66, 128.16, 127.69, 123.96, 94.31 (C1, d, J = 3.5 Hz), 72.83, 70.41 (C3, C4), 70.01 (Bn, d, J = 2.9 Hz), 69.74 (Bn, d, J = 3.5 Hz), 68.59 (C5), 61.82 (C6), 55.13 (C2, d, J = 4.9 Hz), 20.95, 20.89, 20.69 (3 Ac); ^{31}P NMR ($CDCl_3$) δ −5.28. Anal. Calcd for $C_{34}H_{34}O_{13}NP$: C, 58.73; H, 4.89, N, 2.01. Found: C, 58.60, H, 5.01, N. 1.95.

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Registry No. 1, 134003-35-3; α-2, 82300-58-1; β-2, 38768-84-2; 3, 124771-17-1; 4, 88862-86-6.

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Effect of Substituents on the Electrochemistry of Substituted Tetraphenylethylenes

Jennifer L. Muzyka and Marye Anne Fox*

Department of Chemistry, University of Texas,
Austin, Texas 78712

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Mechanistic electrochemical studies[1,2] have shown that the tetraphenylethylene radical anion and radical cation, unlike other benzenoid hydrocarbons, tend to disproportionate efficiently,[4-12] with the position of the equilibrium depending on the ion-pairing ability of the solvent and

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Table I. Cyclic Voltammetry Half-Wave Redox Potentials[a] of Para-Substituted Tetraphenylethylenes 1

X	$E_{1/2}$ (V ± 30 mV) ($1 \rightarrow 1^{\bullet-}$)	$E_{1/2}$ (V ± 30 mV) ($1^{\bullet-} \rightarrow 1^{2-}$)	$E_{1/2}$ (V ± 30 mV) ($1 \rightarrow 1^{2+}$)
NO_2	-1.04^b	-1.44^b	
CF_3	-2.63^c		
Br	-2.46^c		
Cl	-2.46^c		
F	-2.31	-2.61	
H	-2.42		
Ph	-2.09		
Me	-2.48		
t-Bu	-2.50		
OMe	-2.83^b		0.77
NH_2	-3.07^b		0.03
NMe_2	-2.87^b		0.08

[a] Potentials vs SCE, sweep rate = 200 mV/s. Errors are calculated from the product of peak current and cell resistance. Electrochemistry performed in THF with 0.3 M TBAP at Pt. [b] The first and second waves for 1, X = NO_2, are probably two-electron reductions, generating respectively the dianion and tetranion.[12] [c] Irreversible, expressed as peak potential.

associated cations.[13-16] Solvation and ion-pairing effects, which stabilize the highly charged dianion more strongly than the neutral or singly reduced species, drive the disproportionation equilibrium from the monoanion toward the dianion, accounting for the small equilibrium constants observed in solution, particularly at the high ionic strengths usually encountered in electrochemical measurements.[17] Delocalization of charge in the dianion, as influenced by π-torsion, also strongly shifts disproportionation equilibria.[18]

This characteristic suggests the possible utility of tetraphenylethylene derivatives as catalysts for two-electron transfer, a reactivity that could be better exploited if a series of such compounds with varying redox potentials were available. Unfortunately, less is known about the magnitude of the separate electronic influences of substituents on the initial reduction potential and the radical anion dismutation. We describe here an electrochemical study of a series of para-substituted tetraphenylethylenes $(p\text{-}XC_6H_4)_2C{=}C(p\text{-}XC_6H_4)_2$ (1) in THF, which uses cyclic voltammetry and differential pulse voltammetry to determine the effect of substituents on both the redox potentials and the disproportionation equilibria of members of this family. These measurements were conducted in a common solvent (specifically, one that would be convenient for projected redox catalytic reactions) in order to probe whether two-electron catalytic reactivity might derive from possible charge-transfer (CT) complexes between members of this series.

The observed half-wave potentials for the oxidation and reduction of 1 are shown in Table I. Cyclic voltammetric (CV) behavior depends significantly on X: the electroreductions of 1, X = Ph, H, CH_3, *t*-Bu, Figure 1a, show one reversible wave, which was shown by coulometry measurements to involve two sequential one-electron transfers separated by less than 0.1 V. In contrast, the cyclic voltammograms (CVs) of 1, X = Br, Cl, CF_3, show irregularly shaped waves consistent with the known tendency of aryl halides to undergo irreversible reduction,[19,20] although fluoro-substituted 1 exhibits two quasi-reversible CV waves which were shown by coulometry to represent one-electron-reduction steps, Figure 1b. Two separate reduction steps are also observed for 1, X = NO_2, but with better reversibility, Figure 1c. Analogous observations in DMF and acetonitrile have been rationalized with each wave representing a two-electron reduction, with the mono-, di-, tri-, and tetraanions all existing as stable species.[12] The CVs for 1 bearing electron-donating groups (X = OMe, NH_2, and NMe_2) reveal one irreversible reduction wave in THF, as is typified by 1, X = NH_2, Figure 1d.

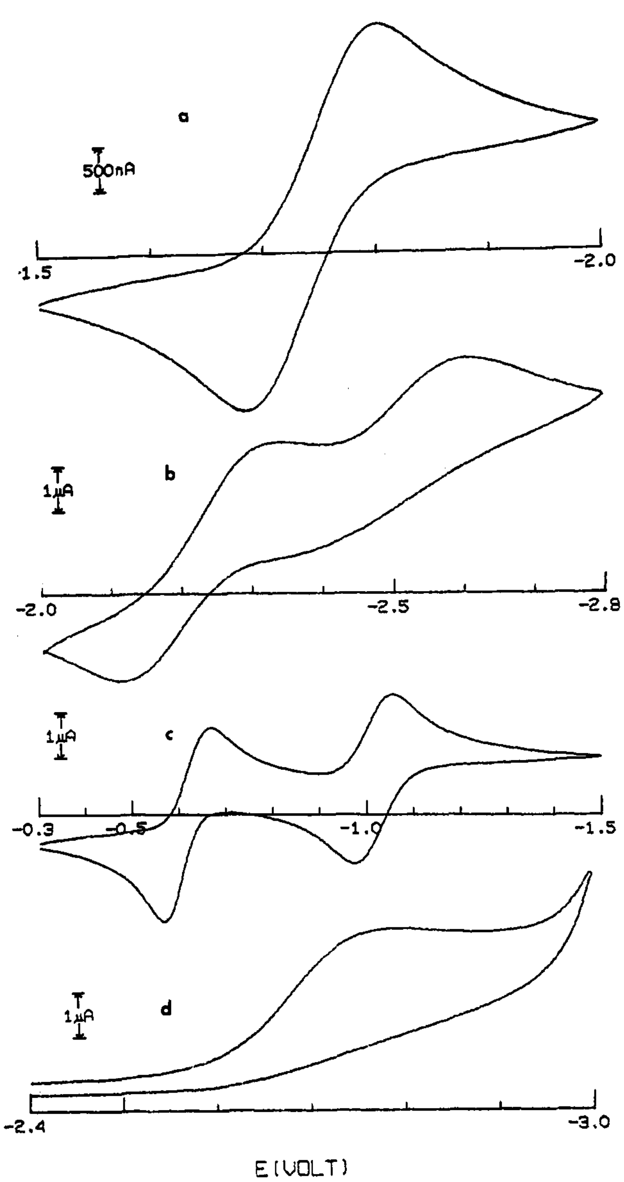

Figure 1. Cyclic voltammograms of 1 on Pt in THF containing 0.3 M TBAP: (a) X = Ph; (b) X = F; (c) X = NO_2; (d) X = NH_2. [1] = 3 mM; scan rate = 200 mV/s, potential vs Ag wire quasi-reference electrode.

Differential pulse voltammetry (DPV) can be used to study the potential difference between the first and second reduction steps[21] even when $\Delta E_{1/2}$ is less than 100 mV, i.e., in the range in which cyclic voltammetry cannot resolve

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Table II. Differential Pulse Voltammetry[a] for the Reduction and Oxidation of Para-Substituted Tetraphenylethylenes 1

X	width (mV)[b]	K_{disp}[c]
	Reduction Waves ($1^{\bullet-}$)	
NO_2	83 (first wave)	0.35
	125 (second wave)	0.11
F	244[d]	7.3×10^{-5}
H	83	0.35
Ph	120	0.11
Me	103	0.17
t-Bu	98	0.19
	Oxidation Waves ($1^{\bullet+}$)	
OMe	86	0.30
NH_2	117	0.11
NMe_2	59	2.18

[a] Potentials vs SCE. Electrochemistry performed in THF with 0.3 M TBAP at Pt. [b] Peak width at half-height. [c] Disproportionation equilibrium constant calculated from eq 1. Errors ±10%. Difference between first and second half-wave potentials calculated from the working curve in ref 21. [d] Separation between first and second peaks used to calculate ΔE.

separate peaks.[22] As might be expected from the cyclic voltammetry results, a DPV for 1, X = H, CH_3, *t*-Bu, Ph, Figure 2a, shows a single symmetrical scan. Those for 1, X = Cl, Br, CF_3, were irregularly shaped and unsymmetrical, as would be expected with substrates undergoing rapid, irreversible secondary reaction, and again the fluoro- and nitro-substituted compounds display two symmetrical DPV waves, parts b and c, respectively, of Figure 2. Despite the absence of a reverse wave in the CVs for 1 bearing electron-donating substituents (X = OMe, NH_2, NMe_2), the DPVs for such compounds (Figure 2d, 1, X = NMe_2) are symmetrical.

From the DPV peak width or peak separation, the disproportionation equilibrium constants were calculated, eq 1. The measured DPV peak widths and calculated

$$K_{disp} = \exp(\Delta E_{1/2} n_1 n_2 F/RT) \qquad (1)$$

disproportionation equilibrium constants for 1 are listed in Table II. Reductions that were irreversible were excluded from this analysis.

No oxidation waves could be observed for the parent, the alkyl-substituted, or the electron-withdrawing-substituted compounds within the THF redox window. Cyclic voltammetric oxidation of the compounds bearing strong electron-donating substituents (1, X = OMe, NH_2, NMe_2), however, proceeds in THF via a single two-electron reversible wave, Table I. These waves show the expected solvent shifts as described previously for oxidations of 1, X = OMe and NMe_2, in methylene chloride and acetonitrile.[11,23-25] From the observed peak widths in their differential pulse voltammograms or peak separations, the oxidative disproportionation equilibrium constants are calculated, Table II.

The absorption spectra of 1:1 mixtures of the easily oxidized 1 (X = OMe, NH_2, and NMe_2) with the easily reduced 1 (X = NO_2, Br, Cl, F, H, Ph, Me, *t*-Bu) represented exact superimpositions of the spectra of the individual components: neither spectral shifts, new bands, nor changes in intensity could be observed. Charge-transfer complexes could be observed, however, upon mixing 1 (X = H, Me, and OMe) with tetracyanoethylene (TCNE).

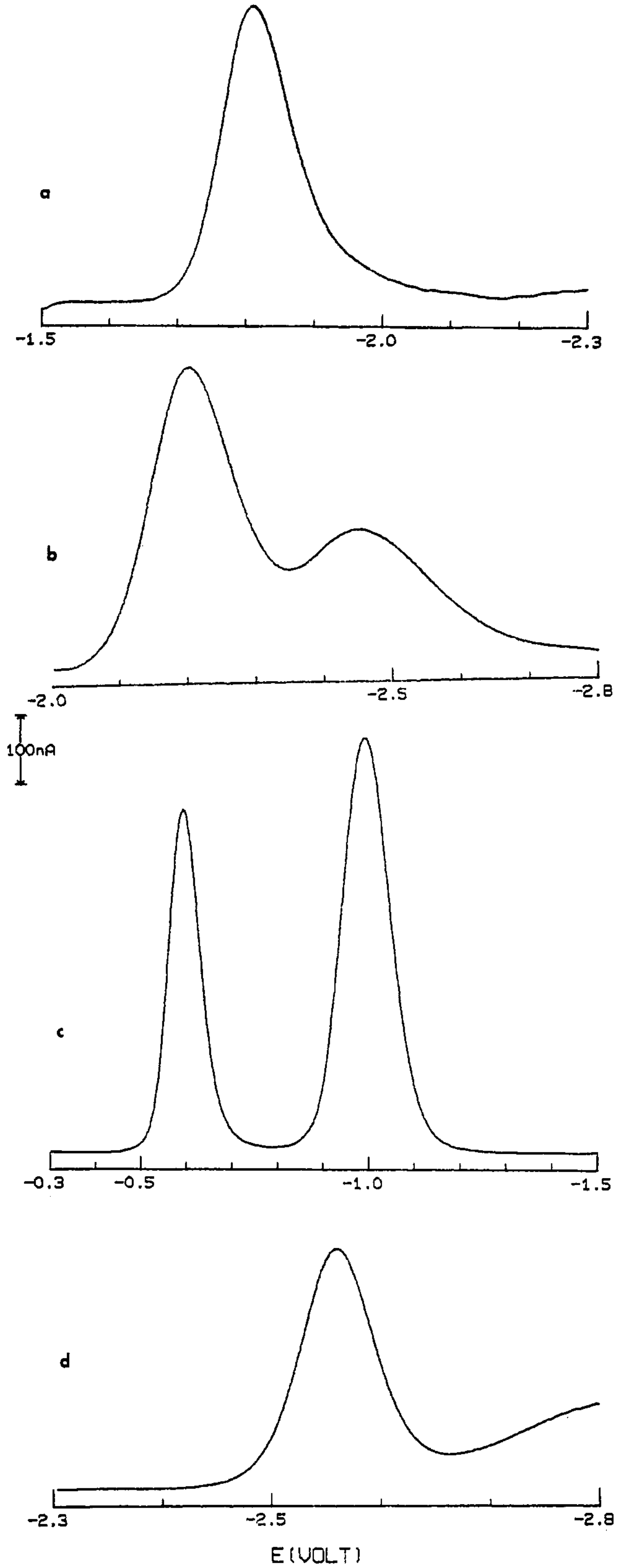

Figure 2. Differential pulse voltammogram of 1: (a) X = Ph; (b) X = F; (c) X = NO_2; (d) X = NMe_2. Conditions as in Figure 1.

A linear correlation ($E_{1/2} = 0.29\sum\sigma^- - 2.44$, $R^\infty = 0.97$) was observed between the observed reduction potentials of substituted 1, Table I, with $\sum\sigma^-$.[26] Poorer correlation

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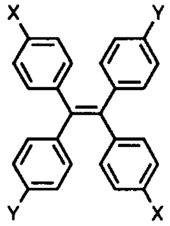
($R^2 = 0.85$) was found with $\sum\sigma$. This is as expected, since the reduction builds up negative charge at sites directly in resonance with the ring substituents. This plot also accommodates, with high correlation coefficients, the reduction potentials for 1 (X = CN) and merostabilized tetraphenylethylenes 2 (X = H, Y = Me; X = H, Y = OMe; X = H, Y = CN; and X = OMe, Y = CN) and their geometric isomers in acetonitrile which were previously reported by Leigh and Arnold.[27]



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The observed anion radical disproportionation equilibrium constants for 1 (Table II), however, are much less sensitive to the substituent, with an anomalously large difference being observed for only 1, X = F. The near invariability of the equilibrium constants for most members of this series indicates that although the electronic effect of the substituents greatly perturbs the reduction potentials, their effect on the disproportionation of the electrogenerated anion is negligible. This suggests that the substituents studied here have minor effects on ion pairing relative to the effects of solvent and counterion.

The cation disproportionation constants determined here (Table II), like the anion dismutations, fail to show strong substituent dependence, but rather exhibit appreciable solvent sensitivity. Thus, the strong solvent and ion-pairing effects observed in the disproportionation of radical anions seem to affect the radical cations similarly.

The oxidation and reduction potentials for pairs of electron-rich and -poor 1, Tables I and II, indicate that complete ground-state equilibration to form a dication–dianion pair would be endothermic, as is consistent with the absence of CT bands. Although this contrasting behavior is at least partially thermodynamic, it may also in fact derive from the kinetic retardation for electron transfer in these systems imposed by a requisite geometry change[18,28] encountered in either the two-electron oxidation or reduction or the difficulty of permitting strong electronic interaction between two substrates twisted from planarity in their ionic states. No evidence for ground-state charge-transfer complexation between electron-rich and -poor members of the series could be detected.

Experimental Section

Instrumentation. Absorption spectra were obtained on a Hewlett-Packard 8451A diode-array spectrophotometer. The cyclic voltammetric and differential pulse voltammetric experiments were performed on a Bioanalytical Systems BAS-100 electrochemical analyzer. The solvent (ca. 3 mL) was cryostatically distilled into the electrochemical cell, which had been held under vacuum for at least 1 h. The cell, which had a silver wire quasi-reference electrode (−0.38 V with respect to SCE) in a compartment separated by a pin hole, contained flame-dried basic alumina and approximately 300 mg of tetrabutylammonium perchlorate (TBAP), producing a final electrolyte concentration of approximately 0.3 M. The working electrode was a Pt disk electrode, and a Pt foil served as the counter electrode. Ferrocene was added to the solution after the measurements as an internal potential calibration. The substituted tetraphenylethylene was added as a solid via a side arm after checking the electroactivity of the background. Coulometry was conducted on a Princeton Applied Research (PAR) electrochemical apparatus (Model 173 potentiostat, Model 176 universal programmer, Model 179 coulometer, and Houston Instruments Model 2000 x-y-t recorder).

Materials. Tetrahydrofuran was distilled from sodium before being stored over $LiAlH_4$ under vacuum until use. Tetrabutylammonium perchlorate (TBAP, Aldrich) was recrystallized from acetone–ether and dried under vacuum before use.

Tetraphenylethylene (Aldrich) was used as received, and the substituted 1 were prepared by literature methods, often by titanium-induced reductive coupling of the substituted benzophenones as the key step:[29] tetra-4-biphenylylethylene (1, X = Ph),[29] tetra-4-tolylethylene (1, X = CH_3),[30] tetrakis(4-*tert*-butylphenyl)ethylene (1, X = *t*-Bu),[31] tetrakis(4-nitrophenyl)ethylene (1, X = NO_2),[32] tetrakis(4-fluorophenyl)ethylene (1, X = F),[33] tetrakis(4-bromophenyl)ethylene (1, X = Br),[34] tetrakis(4-chlorophenyl)ethylene (1, X = Cl),[29] tetrakis[4-(trifluoromethyl)phenyl]ethylene (1, X = CF_3),[35] tetrakis(4-anisylphenyl)ethylene (1, X = OMe),[29,36] tetrakis(4-aminophenyl)ethylene (1, X = NH_2),[32] and tetrakis[4-(*N*,*N*,-dimethylamino)phenyl]ethylene (1, X = NMe_2).[37]

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Improved Method for the Preparation of Enantiomerically Pure Sulfinate Esters

James K. Whitesell* and Man-Shing Wong

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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Applications of chiral sulfoxides[1] have been examined extensively since the pioneering studies of Phillips[2] and Gilman[3] that provided access to these materials in enantiomerically pure form. Their method, based on the separation of diastereomeric sulfinate esters of menthol and subsequent reaction with Grignard reagents, has remained, with some improvements,[4] the most practical technique for the preparation of enantiomerically pure sulfoxides.[5] The technique provides ready access to only one enantiomeric series because only one of the diastereomers of the intermediate menthol sulfinate esters is generally crystalline.[6]

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