EtOAc (10 mmol). *n*-Decane (5 mmol) was added as an internal standard and the reaction mixture was oxidized with alkaline H_2O_2 by using the standard procedure.[16] The aqueous layer was saturated with potassium carbonate and the ether layer was analyzed on GC using a Carbowax 20M column. 1-Hexanol (92%) and 2-hexanol (8%) were present in 97% overall yield.

Synthesis of Ketones by the DCME Reaction of Dialkylborinates. The preparation of dicyclopentyl ketone is representative. Ethyl dicyclopentylborinate was prepared as described earlier from cyclopentene (20 mmol), $LiBH_4$ (10 mmol), and ethyl acetate (10 mmol) in the presence of *n*-dodecane (10 mmol) as an internal standard. The solvent was replaced by THF (20 mL). To the solution at 0 °C was added α,α-dichloromethyl methyl ether, DCME (2.0 mL, 24 mmol), followed by 20 mL of a 2.0 M solution of lithium triethylcarboxide. The reaction mixture was warmed to room temperature and then stirred for 0.5 h. To this was added ethanol (95%, 10 mL), followed by NaOH (1.6 g). H_2O_2 solution (30%, 6 mL) was then carefully added and the mixture was maintained at 65 °C for 1 h. The aqueous layer was then saturated with NaCl and the THF layer was analyzed by GC after drying over anhydrous $MgSO_4$. Dicyclopentyl ketone was formed in 85% yield.

Hydroboration of Alkynes. Isolation of Monovinylborinates. The synthesis of diethyl (*E*)-1-octenylboronate is illustrative. To $LiBH_4$ (30 mmol) in a 100-mL round-bottomed flask was added 1-octyne (22 mL, 150 mmol, excess), followed by ethyl acetate (2.95 mL, 30 mmol). After stirring at 25 °C for 3 h, EE was pumped off, and the residue was repeatedly extracted with pentane. The combined pentane extract, after solvent evaporation and distillation, gave 12.6 g of 1-octyne (from the excess amount) and 5.1 g of diethyl (*E*)-1-octenylboronate (80%), bp 68–69 °C (1 mm).

Synthesis of Vinyl Iodides. Preparation of (*E*)-1-iodo-2-cyclopentylethylene is representative.[8] EtOAc (30 mmol) was added to a mixture of $LiBH_4$ (30 mmol) and cyclopentylethyne (150 mmol) in EE. After stirring for 3 h, NaOH (20 mmol) was added, and the reaction mixture was cooled to 0 °C. A solution of iodine in EE (3.05 g in 20 mL, 12 mmol) was then slowly added. Stirring was continued for 1 h at 0 °C. After the usual workup, (*E*)-1-iodo-2-cyclopentylethylene was isolated in 78% yield: bp 55 °C (1 mm); n^{20}_D 1.4971.

Oxidation of Vinylboronates. Aldehyde Synthesis. The in situ oxidation of the vinylboronates with H_2O_2 at pH 8 (phosphate buffer) provided aldehydes in good yields. The following procedure is typical. 1-Octyne (50 mmol) was hydroborated with $LiBH_4$ (10 mmol) and ethyl acetate (10 mmol) in the presence of *n*-decane (5 mmol) as internal standard. After 3 h, hydrochloric acid (5 mL, 2 N) was added to break the "ate" complex formed, followed by 5 mL of phosphate buffer. Oxidation with H_2O_2 was then carried out as usual. GC analysis of the ether layer after saturating the aqueous layer with K_2CO_3 showed that 1-octanal was formed in 81% yield.

Formation of Divinylborinates. Diene Synthesis. The preparation of (3*Z*,5*E*)-4,5-diethyl-3,5-octadiene from 3-hexyne is illustrative.[9] 3-Hexyne (4.2 mL, 40 mmol) was hydroborated with $LiBH_4$ (20 mmol) and EtOAc (20 mmol) by using the general procedure. After 3 h, EE was replaced by THF (20 mL). NaOH (20 mL, 3 N) was then added and the reaction mixture was cooled to 0 °C. A solution of iodine (5.1 g, 20 mmol) in THF (20 mL) was then added. After the reaction mixture was stirred for 0.5 h, the excess iodine was destroyed by adding aqueous sodium thiosulfate. The diene was then extracted into pentane. Removal of the solvent after drying over anhydrous $MgSO_4$ followed by distillation gave 2.3 g of (3*Z*,5*E*)-4,5-diethyl-3,5-octadiene (70%). Comparison with an authentic sample showed that the compound is 98% pure.

Directive Effect in the Hydroboration of Internal Alkynes. The hydroboration of 1-phenyl-1-propyne is typical. 1-Phenyl-1-propyne (10 mmol) was hydroborated with $LiBH_4$ (10 mmol) and EtOAc (10 mmol). After 3 h, the reaction mixture was oxidized with alkaline H_2O_2 by the usual procedure. After the usual workup, 1.28 g of a mixture was obtained which contained propiophenone (76%) and phenylacetone (24%). The overall yield was 96%.

Synthesis of 1-Phenyl-1-iodoethylene. Phenylacetylene (50 mmol) was hydroborated with $LiBH_4$ (10 mmol) and EtOAc (10 mmol) in a flask protected from light. After 4 h, NaOH (6 mL, 3 N) was added and the contents were cooled to 0 °C. A solution of iodine (2.6 g) in ether (20 mL) was then added, and the mixture was stirred for 1 h at 0 °C. The ether layer was quickly worked up with minimum exposure to light. From the crude product, phenylacetylene was distilled off at reduced pressure (0.1 mm) at room temperature. Fractional distillation of the residue yielded 0.97 g of 96% pure 1-iodo-2-phenylethylene (bp 30 °C (0.05 mm)): NMR δ 7.20 (m, 5 H), 6.05 (d, 2 H).

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(16) Reference 15, p 15.

Electrochemical Studies of the Reduction of 6,6-Dimethyldibenzofulvene Oxide and Tetraphenyloxirane

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The electrochemical reduction of 6,6-dimethyldibenzofulvene oxide (1) in dimethylformamide–0.1 M $(n\text{-Bu})_4NClO_4$ is an overall two-electron process that affords 9-fluorenyl anion and acetone in the absence of an added proton donor and 2-(9-fluorenyl)propanol (2) in the presence of diethyl malonate. The initial electroreduction of tetraphenyloxirane (3) is also a two-electron process and gives $Ph_2\bar{C}CPh_2(O^-)$ as an unobserved intermediate. This dianion reacts rapidly by abstracting a proton at either the benzhydryl carbon center (75%) or the oxygen center (25%) to give either $Ph_2CHCPh_2(O^-)$ or $Ph_2\bar{C}CPh_2(OH)$. The former anion then undergoes an elimination of Ph_2CH^- to afford $Ph_2C{=}O$ whereas $Ph_2\bar{C}CPh_2(OH)$ eliminates OH^- to give $Ph_2C{=}CPh_2$. $Ph_2C{=}O$ and $Ph_2C{=}CPh_2$ are then reduced at the applied potential to Ph_2CHOH and $(Ph_2CH)_2$, respectively. $Ph_2CHCPh_2(OH)$ (4) and 2 undergo electrochemically induced chain reactions in the potential range of interest with 4, affording equimolar amounts of $Ph_2C{=}O$ and Ph_2CH_2, whereas 2 gives equimolar amounts of fluorene and acetone. There is no evidence that carbene anion radicals are formed as transient intermediates in any of the electroreductions.

The preparation of a carbene ($R_2C{:}$) in solution or in the gas phase generally involves a precursor that fragments upon photolysis or thermolysis to give the desired carbene and a stable molecular species.[1] For example, photolysis

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Table I. Coulometric Data and Product Studies for the Controlled-Potential, Electrolytic Reduction of $\mathrm{Fl\overline{C(CH_3)_2O}}$ (1) and $\mathrm{FlHC(CH_3)_2OH}$ (2)[a]

no.	compd, (mM) concn	E_{applied} (V)	n	proton donor, concn (mM)	products, % yield: $\mathrm{FlC(CH_3)_2O}$ (mM)	$\mathrm{FlH_2}$	$\mathrm{FlHC(CH_3)_2OH}$	$\mathrm{(FlH)_2}$	Fl=O	$\mathrm{(CH_3)_2C{=}O}$
1	**1**, 2.24	−1.60	1.5(2.2)		32	60 (88)		1.3	1.8	63(93)
2	**1**, 1.78	−1.60	1.5(2.2)	DEM, 19	32	0.8	63 (93)			
3	**2**, 3.47	−1.90	0.2			101			1.4	91
4	**2**, 2.56[b]					98			2.5	52
5	**2**, 3.73[c]	−1.50				87			2.9	83
6	**2**, 1.49	−1.95	4.0	DEM, 16		8	79		5	trace

[a] Reductions effected at a platinum electrode in DMF–0.1 M $(n\text{-Bu})_4\mathrm{NClO_4}$. Yields in parentheses are calculated on the basis of starting material consumed. [b] 4.87 mM $\mathrm{(CH_3)_4NOH}$ added; no reduction. [c] 3.94 mM PhN=NPh added; 0.2 electron/molecule PhN=NPh added.

of $c\text{-}C_5H_4{=}N_2$ affords N_2 and $c\text{-}C_5H_4$:,[2] whereas photolysis of tetraphenyloxirane gives benzophenone and diphenylmethylene.[3] The goal of certain work in our laboratories is the preparation and study of several of the corresponding carbene anion radicals, $R_2C^{-}\cdot$.[4,5] One approach to the attempted preparation of these species involves the attachment of an electron to compounds which yield carbenes upon photolysis. Though this method has been used successfully to prepare $c\text{-}C_5H_4^{-}\cdot$ from $c\text{-}C_5H_4{=}N_2$ in the gas phase,[4] most claims[5-8] that carbene anion radicals have been prepared in the condensed phase by electroreductive elimination of N_2 from diazoalkanes have been either refuted or questioned.[9]

The present study involving oxiranes as potential carbene anion–radical precursors was undertaken in an attempt to circumvent certain difficulties that are attendant with many diazoalkanes, e.g., multiple pathways for the formation of the principal products.[5] Specifically, it was hoped that electroreduction of an oxirane might afford a short-lived anion radical which would decompose by a sequence involving cleavage of the carbon–oxygen bond to give the ring-opened anion radical, $R_2\dot{C}C(O^-)R_2$, followed by the elimination of $R_2C^{-}\cdot$. The compound which was studied most extensively, 6,6-dimethyldibenzofulvene oxide (**1**), was chosen in part because the ketone fragment $(CH_3)_2C{=}O$, if formed, would be electroinactive and in part because the electrochemical behavior of the expected product of fluorenylidene anion radical intermediacy, fluorene (FlH_2), has been well-characterized.[10]

Results

Reduction of 6,6-Dimethyldibenzofulvene Oxide (1). The redox behavior of **1** was examined at platinum and glassy carbon electrodes in dimethylformamide (DMF)–0.1 M $(n\text{-Bu})_4NClO_4$ as a function of temperature (−51 °C ≤ T ≤23 °C), cyclic voltammetric scan rate (0.05 V/s ≤ v ≤ 100 V/s), and added electroinactive proton donor (diethyl malonate (DEM) or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)). At −51 °C, only the cathodic peak ($E_{p,c}$ = −1.64 V) which is assigned to the reduction of **1** is observed on the first and all subsequent negative-going sweeps (Figure 1). Although the anion radical of **1** is too unstable to give a corresponding anodic peak for its reoxidation on the reverse, positive-going sweep at all scan rates up to and including 100 V/s, a product that arises from its decomposition is oxidized irreversibly at 0.04 V. No other readily discernible process is observed in the potential range from −2.4 V to 0.8 V.

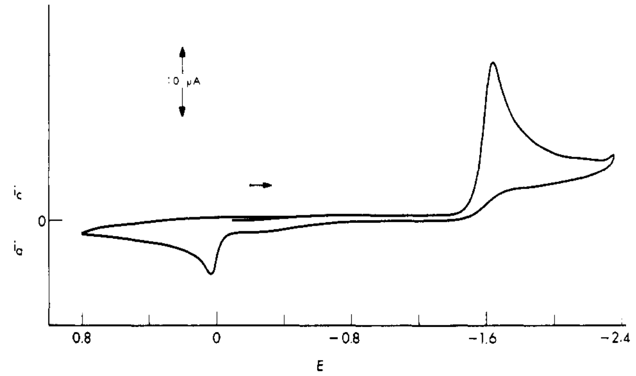

Figure 1. Cyclic voltammogram for the reduction of 3.69 m*M* solution of 6,6-dimethyldibenzofulvene oxide (**1**) in DMF–0.1 M $(n\text{-Bu})_4NClO_4$ at −51 °C. The scan rate at a spherical platinum electrode is 0.2 V/s.

The addition of excess diethyl malonate (DEM; [DEM]/[**1**] = 11) had no effect upon the cathodic peak height ($i_{p,c,1}$) for the reduction of **1**. However, DEM did cause the anodic peak which was present near 0.04 V in aprotic media to disappear and a second, large cathodic peak ($i_{p,c,2}/i_{p,c,1}$ = 1.2) to appear near −2.0 V. On the basis of product and cyclic voltammetric studies which will be described below, the species that is reduced at the potential of the second cathodic wave is the alcohol $FlHC(CH_3)_2OH$ (**2**).

The number of electrons, n, consumed in the overall reduction of one molecule of **1** was ascertained by single-potential-step chronoamperometry. In this technique, the potential is stepped from a value (−1.00 V) which is insufficiently negative to cause any reduction of **1** to a value (−1.90 V) which is sufficiently negative such that the concentration of **1** is rendered effectively zero at the electrode surface. The experimental quantity of interest, $it^{1/2}/C = 59 \pm 3\ \mu A\ s^{1/2}/mM$, is diffusion controlled in the time range 10 ms ⩽ t ⩽ 8 s and is proportional to $D^{1/2}n$, where D is the diffusion coefficient. However, since D is not known for **1** under our reaction conditions, the value

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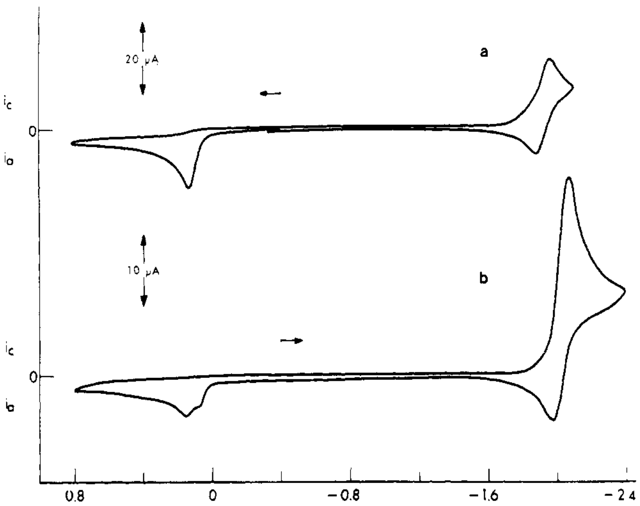

Figure 2. (a) Cyclic voltammogram for the oxidation of $\mathrm{FlH^-}$ resulting from the coulometric reduction of 2.98 m*M* solution of $\mathrm{FlH_2}$ in DMF–0.1 M $(n\text{-Bu})_4\mathrm{NClO_4}$ at −51 °C. The scan rate at a spherical platinum electrode is 0.2 V/s. (b) cyclic voltammogram for the reduction of 4.31 m*M* solution of $\mathrm{FlHC(CH_3)_2OH}$ (2) in DMF–0.1 *M* $(n\text{-Bu})_4\mathrm{NClO_4}$ at −51 °C. The scan rate at a spherical platinum electrode is 0.2 V/s.

of n must be estimated from a comparison of the $it^{1/2}/C$ value for 1 with that for an electroactive species of similar size and known n value. Fluorenone, which is reduced to its stable anion radical in a diffusion-controlled, one-electron process, afforded $it^{1/2}/C = 35 \pm 3\ \mu\mathrm{A\ s^{1/2}/m}M$ in the same time range. Thus, when the ratio of $it^{1/2}/C$ values for 1 and fluorenone is adjusted for fluorenone's larger diffusion coefficient, an n value of 2 is obtained for the reduction of 1.

A nominal n value of 2 is also obtained for the coulometric reduction of 1 in both the absence and the presence of an added proton donor (Table I). In the absence of an added proton donor (entry 1), arbitrary termination of the electrolysis after the addition of 1.5 electrons/molecule of 1 resulted in the consumption of 68% of the starting material and the formation of fluorene ($\mathrm{FlH_2}$) and acetone as the principal reduction products. If allowance is made for the amount of 1 that remains unreacted, the experimental coulometric n value is 2.2 and the yields of $\mathrm{FlH_2}$ and acetone are 88% and 93%, respectively. In contrast, the addition of an excess of DEM as an electroinactive proton donor (entry 2) results in the interdiction of the $\mathrm{FlH_2}$ and acetone product-forming channels and the formation of $\mathrm{FlHC(CH_3)_2OH}$ (2) in 93% yield. The coulometric n value, based again upon the fraction of 1 consumed, is not affected by the addition of DEM.

Redox Behaviors of $\mathbf{FlHC(CH_3)_2OH}$ and $\mathbf{FlH_2}$. The cyclic voltammetric reduction of 1 in the absence of an added proton donor was shown above to give a product that is oxidized irreversibly at 0.04 V. Although neither 2 nor $\mathrm{FlH_2}$ can be oxidized in the potential range from −2.0 to 1.6 V, previous studies[10,11] from this laboratory suggest that the conjugate bases of these species, $\mathrm{^-FlC(CH_3)_2OH}$ and $\mathrm{FlH^-}$, should be oxidized in the potential range from −0.1 to 0.2 V. In order to identify the electroactive anion that gives rise to the anodic peak at 0.04 V, the redox behaviors of 2 and $\mathrm{FlH_2}$ were examined at −51 °C. Electroreduction of $\mathrm{FlH_2}$ ($E_{\mathrm{p,c}} = -1.90$ V) in DMF–0.1 M $(n\text{-Bu})_4\mathrm{NClO_4}$ has been shown previously to afford a relatively stable anion radical that decomposes slowly by $\mathrm{C_9}$–H bond cleavage to give $\mathrm{FlH^-}$ as the principal product.[10] As shown in Figure 2a, $\mathrm{FlH^-}$ is then oxidized irreversibly at 0.13 V under these conditions ($E_{\mathrm{p,a}} = 0.08$ V when $T = 23$ °C). Though the reduction of 2 ($E_{\mathrm{p,c}} = -1.97$ V) also affords a relatively stable anion radical that reacts slowly on the cyclic voltammetric time scale (Figure 2b), decomposition of $2^{-}\cdot$ gives rise to two products which appear to be partially kinetically linked and which are oxidized irreversibly on the reverse positive-going sweep near 0.04 and 0.13 V. Cyclic voltammetric scan-rate studies demonstrate that the magnitude of the anodic peak at 0.13 V, which is assigned to the oxidation of $\mathrm{FlH^-}$, decreases at the expense of the anodic peak at 0.04 V as the scan rate is increased in the range $1\ \mathrm{V/s} \leqslant v \leqslant 10\ \mathrm{V/s}$. A more extensive study of the relationship between these species is not possible, however, because at scan rates in excess of about 10 V/s, the rate of $2^{-}\cdot$ decomposition was too slow to produce discernible amounts of these materials. However, since controlled-potential electrolysis of 2 give $\mathrm{FlH_2}$ as the only product that contains the fluorene moiety (entry 3, Table I), the species which is oxidized at 0.04 V must be a 9-substituted fluorenyl anion that lies in the $\mathrm{FlH^-}$ product-forming channel. This anion must be $\mathrm{^-FlC(CH_3)_2OH}$.

The second major product of the controlled-potential electrolysis of 2 is acetone. As demonstrated by the results associated with entries 3–5, the transformation of 2 into $\mathrm{FlH_2}$ and acetone can be initiated by electron transfer to 2 (entry 3), by the abstraction of a proton from 2 by an added base (entry 4), or by the abstraction of a proton from 2 by an electrogenerated base (entry 5). In the first method, electrolysis at a potential of −1.90 V was terminated arbitrarily after only 0.2 electron/molecule of 2 had been added. Examination of the solution at this point revealed that all 2 was consumed and that $\mathrm{FlH_2}$ and acetone were formed in high yields. The nonintegral n value that is significantly less than 1 requires the transformation to occur by a chain process. A smaller n value might have sufficed to effect the reaction, but the lack of a method to distinguish rapidly on-line between the reactant, 2, and product, $\mathrm{FlH_2}$, precludes the ready determination of n_{min}.

In the method involving the electrogenerated base, the working electrode potential is adjusted to a value ($E = -1.60$ V) that is sufficiently negative to reduce PhN=NPh ($E_{\mathrm{p,c,1}} = -0.62$ V and $E_{\mathrm{p,c,2}} = -1.39$ V at −51 °C) to $\mathrm{PhN{=}NPh^{2-}}$ but insufficiently negative to reduce 2 ($E_{\mathrm{p,c}} = -1.97$ V). $\mathrm{PhN{=}NPh^{2-}}$, which is a strong base that is capable of abstracting either the $\mathrm{C_9}$ proton from $\mathrm{FlH_2}$ or the hydroxylic proton from 9-fluorenol,[11] then reacts with 2 to give $\mathrm{FlHC(CH_3)_2O^-}$ and/or $\mathrm{^-FlC(CH_3)_2OH}$. The remaining reactions in the chain process would then be the same as in the electroinitiated chain reaction. Again, because there is no rapid method to determine when the consumption of 2 is complete, the electrolysis was terminated arbitrarily after the addition of 0.70 C to a DMF–0.1 M $(n\text{-Bu})_4\mathrm{NClO_4}$ solution containing 107 μmol of 2 and 37 μmol of PhN=NPh ($n = 0.2$). Examination of the electrolyzed solution after it had been quenched by the addition of an excess of DEM showed that the transformation of 2 into $\mathrm{FlH_2}$ and acetone was nearly complete (entry 5).

Mode of $\mathbf{FlHC(CH_3)_2OH^{-}\cdot}$ Decomposition. The cyclic voltammetric results demonstrate that $\mathrm{^-FlC(CH_3)_2OH}$ is formed as a transient intermediate in the electroreduction of 2 and require that homolytic $\mathrm{C_9}$–H bond cleavage be one mode of $2^{-}\cdot$ decomposition. In order to confirm this interpretation, electrolysis of 2 was effected in the presence of a large excess of electroinactive DEM. If $\mathrm{^-FlC(CH_3)_2OH}$ is formed from $\mathrm{FlHC(CH_3)_2OH^{-}\cdot}$ by $\mathrm{C_9}$–H bond cleavage, then the addition of DEM should cause $\mathrm{^-FlC(CH_3)_2OH}$ to

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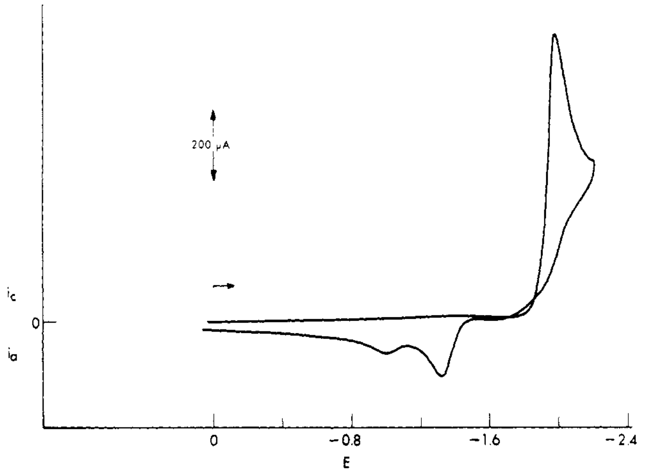

Figure 3. Cyclic voltammogram for the reduction of 2.88 m*M* solution of tetraphenyloxirane (3) in DMF–0.1 *M* (n-Bu)$_4$NClO$_4$ at 23 °C. The scan rate at a planar platinum electrode is 0.2 V/s.

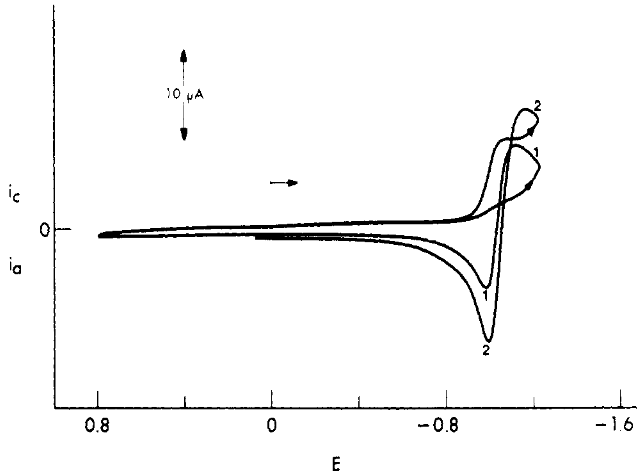

Figure 4. Cyclic voltammogram for the reduction of 1.42 m*M* solution of Ph$_2$CHCPh$_2$OH (4) in DMF–0.1 M (n-Bu)$_4$NClO$_4$ at 23 °C. The scan rate at a spherical platinum electrode is 0.2 V/s.

be protonated, 2 to be continuously regenerated, and the chain reaction to be shut down. Indeed, after the arbitrary termination of a controlled-potential electrolytic reduction of 2 in the presence of DEM at the point $n = 4$, 2 was recovered in 79% yield (entry 6). However, it must be pointed out that, although DEM is electroinactive, the addition of DEM causes the cathodic peak height for the electroreduction of 2 to be increased by a factor of approximately 3. This cyclic voltammetric behavior is attributed to homogeneous electron transfer from $2^{-}\cdot$ to DEM[10] and is the principal mode of $2^{-}\cdot$ decomposition under these reaction conditions. In addition, since DEM was shown above to protonate all $^{-}$FlC(CH$_3$)$_2$OH formed in the electroreduction of 1 (entry 2, Table I), the formation of FlH$_2$ and Fl=O (FlH$_2$ + adventitious O$_2$ → Fl=O + H$_2$O)[10] in a combined yield of 13% requires that $2^{-}\cdot$ decomposes in part by C$_9$–C bond cleavage. Unfortunately, we are not able to determine the ratio of C$_9$–H to C$_9$–C bond cleavage because was have no ready way to ascertain what fraction of $2^{-}\cdot$ reacts by electron transfer.

Redox Behavior of Tetraphenyloxirane (3). The cyclic voltammetric reduction of 3 in DMF–0.1 M (n-Bu)$_4$NClO$_4$ affords a single cathodic peak ($E_{p,c} = -2.00$ V) near the cathodic potential limit on the first negative-going scan (Figure 3). Although $3^{-}\cdot$ is too unstable to give an anodic peak for its reoxidation on the reverse, positive-going sweep, anodic peaks for the oxidation of products that arise from the decomposition of $3^{-}\cdot$ are seen near −1.32 and −1.00 V. By comparison with authentic samples, the more negative anodic process is assigned to the reversible oxidation of Ph$_2$C=CPh$_2^{-}\cdot$ to Ph$_2$C=CPh$_2$ whereas the more positive anodic process is assigned to the reversible oxidation of Ph$_2$C=O$^{-}\cdot$ to Ph$_2$C=O. The formation of Ph$_2$C=O in the electroreduction of 3 is also believed to account for the relatively unusual crossing of the cyclic voltammetric current–potential curves in the vicinity of −1.86 V (Figure 3). Such crossing of the negative- and positive-going curves would be possible if a reduction product of 3 were more readily reduced than 3 and if the 3 reduction products were regenerated continuously.[12] A reaction scheme which involves reduction of Ph$_2$C=O$^{-}\cdot$ to Ph$_2$C=O^{2-} ($E_{p,c} = -1.84$ V) and the subsequent electrocatalyzed reduction of 3 by Ph$_2$C=O^{2-} is proposed in the Discussion Section to account for this phenomenon.

A controlled-potential electrolytic reduction ($E = -2.10$ V) of 3 which was terminated arbitrarily at the point n = 4 afforded Ph$_2$CHOH, 12%; Ph$_2$C=O, 0.6%; Ph$_2$CH$_2$, 15%; (Ph$_2$CH)$_2$, 44%; and Ph$_2$C=CPh$_2$, 3%; along with 29% unreacted 3. A theoretical n value of 4 is predicted for the reduction of 3 if both Ph$_2$C=O and Ph$_2$C=CPh$_2$, the electroactive products which arise initially from the reduction of 3, are reduced to Ph$_2$CHOH and (Ph$_2$CH)$_2$, respectively, at the applied potential. The fact that approximately 5.6 electrons are consumed for each molecule of 3 reduced is due to the close proximity of the cathodic background ($E_{c,\mathrm{limit}} = -2.2$ V) and the inadvertent reduction of one or more components of the solvent–electrolyte system.

Reduction of Ph$_2$CHCPh$_2$OH (4). The formation of 2 from $^{-}$FlC(CH$_3$)$_2$OH occurred only when the electroreduction of 1 was effected in the presence of an added proton donor (entry 2, Table I). However, the greater basicity of a benzhydryl anion (pK_a of Ph$_2$CH$_2$ is 32.1 in MeSO[13b]) than a 9-fluorenyl anion (pK_a of FlH$_2$ is 22.6 in MeSO[13a]) suggests that 4 might be a plausible intermediate or product in the electroreduction of 3 under both protic and aprotic conditions. Although 4 was not expected to be electroactive in the accessible potential range, significant cathodic current begins to flow as soon as the electrode potential is made more negative than approximately −1.1 V (Figure 4). Moreover, when the direction of the potential scan is reversed at −1.2 V, the current, instead of decreasing as expected on the reverse, positive-going sweep, continues to increase as the electrode potential is scanned from −1.2 to −1.1 V. This behavior, along with the abrupt switch from a cathodic current at −1.1 V to the peak cathodic current at −1.0 V, is indicative of an electrochemically induced chain reaction.[12] The electroactive component ($E = -1.04$ V) that is formed from 4 could be readily identified on the basis of its cyclic voltammetric behavior as benzophenone. Controlled-potential electrolysis of 4, which was complete after the passage of less than 0.05 electrons/molecule of 4, afforded Ph$_2$CH$_2$ and Ph$_2$C=O quantitatively in equimolar amounts.

Discussion

Reduction Pathway for 6,6-Dimethyldibenzofulvene Oxide (1). The absence of an anodic wave (Figure 1) near −1.6 V for the reoxidation of $1^{-}\cdot$ at all scan

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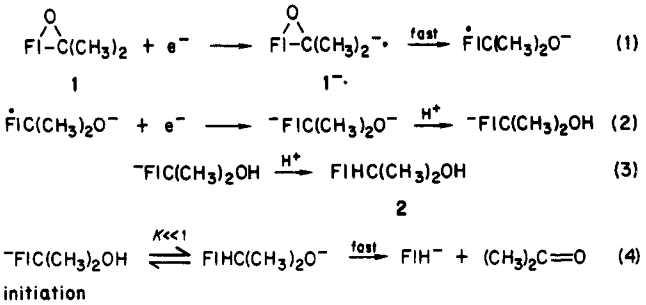
Scheme I. Electroreduction of 6,6-Dimethyldibenzofulvene Oxide



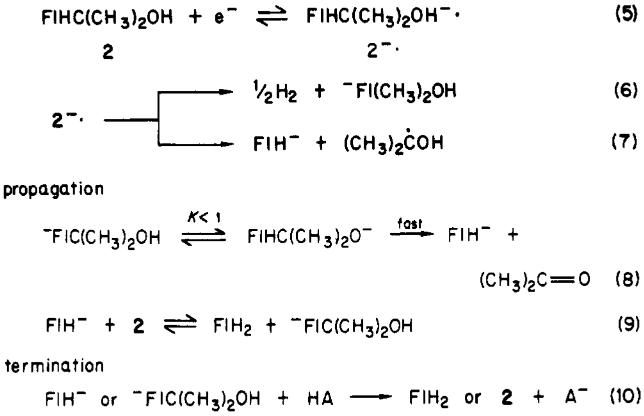
rates up to 100 V/s establishes a maximum half life of 10^{-3} s for this species. Since the reduction of 1 in the presence of an excess of electroinactive DEM affords the alcohol $\text{FlHC(CH}_3)_2\text{OH}$ (2), $1^-\cdot$ must decompose by rapid cleavage of the C_9–O bond to give the ring-opened anion radical, $\dot{\text{F}}\text{lC(CH}_3)_2\text{O}^-$, as an unobserved intermediate (Scheme I eq 1). Cleavage of the C_9–O bond has been reported previously for the anion radicals of FlHOH and FlHOCH_3; the proposal that the oxygen in $\dot{\text{F}}\text{lC(CH}_3)_2\text{O}^-$ has a greater electron affinity than the C_9 carbon is based upon the observation that FlH^- is oxidized at 0.13 V whereas FlHO^- cannot be oxidized in the accessible potential range ($E <$ 1.2 V).[11]

In order to obtain the chronoamperometric and coulometric n value of 2 for the reduction of 1 to product in both aprotic (eq 1, 2, and 4) and protic (eq 1–3) media, $\dot{\text{F}}\text{lC(CH}_3)_2\text{O}^-$ must either be reduced to the corresponding dianion or the solvent-derived radical which is formed when $\dot{\text{F}}\text{lC(CH}_3)_2\text{O}^-$ abstracts H· must be reduced in a one-electron process. The former pathway (eq 2) is favored because (1) 9-fluorenyl radicals, which are reduced in the general vicinity of 0.1 V[10,11] would be electroactive at the potential at which 1 ($E_{\text{p,c}} = -1.64$ V) is reduced; (2) there is no precedent in related work involving 9-fluorenyl radicals that H· abstraction from DMF–0.1 M $(n\text{-Bu})_4\text{NClO}_4$ will give an electroactive, solvent-derived radical;[10] and (3) the product of H· abstraction, $\text{FlHC(CH}_3)_2\text{O}^-$, should either afford, as does FlHO^-, a cathodic wave near −2.1 V for its reduction to an unstable dianion radical and no anodic wave for its oxidation,[11] or afford FlH^- ($E_{\text{p,a}} = 0.13$ V at −51 °C) via an elimination reaction. None of these expectations for $\text{FlHC(CH}_3)_2\text{O}^-$ intermediacy is in accord with the experimental results.

$^-\text{FlC(CH}_3)_2\text{O}^-$, the unobserved dianion which would be formed if $\cdot\text{FlC(CH}_3)_2\text{O}^-$ were reduced, is proposed to be rapidly protonated on oxygen to give $^-\text{FlC(CH}_3)_2\text{OH}$ (eq 2). Protonation on this site is consistent with the reported pK_a's of fluorene (22.6[13a]) and 2-propanol (30.25[13b]) in $(\text{CH}_3)_2\text{SO}$ and the redox and chemical behavior expected for $^-\text{FlC(CH}_3)_2\text{OH}$ but not for $\text{FlHC(CH}_3)_2\text{O}^-$ (vide ante).

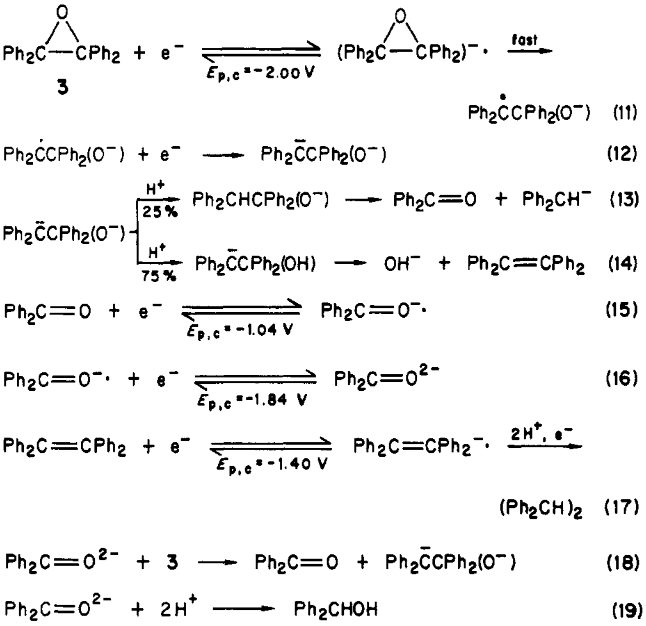
Reduction Pathway for $\text{FlHC(CH}_3)_2\text{OH}$. A nonintegral coulometric n value for the reduction of 2 that is significantly less than 1 and the determination that FlH_2 and acetone are formed as products in high yields require a chain reaction. If the chain reaction (Scheme II, eq 5–10) is initiated electrochemically, then $2^-\cdot$ is proposed to undergo parallel decomposition pathways involving cleavages of the C_9–H (eq 6) and the C_9–C (eq 7) bonds to give $^-\text{FlC(CH}_3)_2\text{OH}$ and FlH^-, respectively. The C_9–C bond energy in 2 is unknown, but the fact that C_9–H bond cleavage is the principal reaction channel in the decomposition of $2^-\cdot$ suggests that the value must be in excess of that for the C_9–H bond (~81 kcal/mol).[14]

Scheme II. Reduction of $\text{FlHC(CH}_3)_2\text{OH}^a$



^{a} HA = component of the solvent-electrolyte system or an adventitious proton donor.

Scheme III. Electroreduction of Tetraphenyloxirane



The first step in the propagation cycle (eq 8) formally involves transfer of the hydroxylic proton in $^-\text{FlC(CH}_3)_2\text{OH}$ to the C_9 carbon. On the basis of the pK_a values cited above for fluorene and 2-propanol, a value of log $K = -7.6$ can be estimated for the ratio of the $\text{FlHC(CH}_3)_2\text{O}^-$ isomer to the $^-\text{FlC(CH}_3)_2\text{OH}$ isomer. As evidenced by the combined results of the cyclic voltammetric and coulometric reduction experiments involving 1, the transformation of $^-\text{FlC(CH}_3)_2\text{OH}$ into FlH^- and acetone is slow on the cyclic voltammetric time scale at −51 °C but rapid on the coulometric time scale. $\text{FlHC(CH}_3)_2\text{O}^-$ is a presumed intermediate in the reaction, but the absence of a discernible cathodic peak for its reduction in the vicinity of −2.1 V requires it to be short-lived.

Reduction Pathway for Tetraphenyloxirane (3). As in the case of $1^-\cdot$, $3^-\cdot$ is too unstable to give an anodic wave for its reoxidation under all reaction conditions. However, whereas decomposition of $1^-\cdot$ ultimately yields only the products of a carbanion elimination reaction, FlH^- and acetone, decomposition of $3^-\cdot$ gives both carbanion ($\text{Ph}_2\text{=O}$, eq 13) and hydroxide ($\text{Ph}_2\text{C=CPh}_2$, eq 14) elimination products (Scheme III). In order to account for the final product distribution of 15% Ph_2CH_2 and 47% combined yields of $\text{Ph}_2\text{C=CPh}_2$ and $(\text{Ph}_2\text{CH})_2$, protona-

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Scheme IV. Reaction of $Ph_2CHCPh_2OH^a$

initiation

$$Ph_2C{=}O + e^- \rightleftharpoons Ph_2C{=}O^-\cdot \qquad (20)$$

$$Ph_2C{=}O^-\cdot + Ph_2CHCPh_2OH \rightarrow Ph_2\dot{C}OH + Ph_2CHCPh_2O^- \qquad (21)$$

propagation

$$Ph_2CHCPh_2O^- \longrightarrow Ph_2CH^- + Ph_2C{=}O \qquad (22)$$

$$Ph_2CH^- + Ph_2CHCPh_2OH \longrightarrow Ph_2CH_2 + Ph_2CHCPh_2O^- \qquad (23)$$

termination

$$Ph_2CH^- + HA \longrightarrow Ph_2CH_2 + A^- \qquad (24)$$

[a] HA = component of the solvent–electrolyte system.

tion of the presumed, but unobserved, $Ph_2\bar{C}CPh_2(O^-)$ intermediate occurs approximately 75% on the oxygen center and 25% on the benzhydryl carbon center (eq 13 and 14). Concomitant protonation of $Ph_2\bar{C}CPh_2O^-$ at both the oxygen and carbon sites is expected since the pK_a's of the corresponding acids should be similar and approximately 30.5 ± 1 in this solvent system.[13b] The electroactive products of these reactions, $Ph_2C{=}O$ and $Ph_2C{=}CPh_2$, are then reduced at the applied potential to Ph_2CHOH and $(Ph_2CH)_2$, respectively (eq 15–17 and 19). As predicted by the stoichiometry for this reaction scheme, the sum of the $Ph_2C{=}O$ and Ph_2CHOH yields (13%) equals the Ph_2CH_2 yield (15%) within experimental error.

The crossing of the positive- and negative-going cyclic voltammetric curves at −1.86 V (Figure 3) is attributed to the electrocatalytic reduction of **3** by $Ph_2C{=}O^{2-}$. In the range $-1.84\ V > E > -1.96\ V$, the potential is sufficiently negative to reduce $Ph_2C{=}O^-\cdot$ to $Ph_2C{=}O^{2-}$ but insufficiently negative to cause the direct reduction of **3** to $3^-\cdot$ at the electrode surface. However, because **3** undergoes rapid, irreversible ring opening (eq 11), a significant rate of homogeneous electron transfer from $Ph_2C{=}O^{2-}$ to **3** is permitted (eq 18).[15] The substantial cathodic current at −1.86 V on the reverse, positive-going sweep arises when $Ph_2C{=}O$ is reduced at the electrode surface and the subsequent solution reactions (eq 15–18) cause $Ph_2C{=}O$ to be continuously regenerated.

Scheme for the Reaction of Ph_2CHCPh_2OH (Scheme IV). The rapid transformation of **4** into equimolar amounts of Ph_2CH_2 and $Ph_2C{=}O$ was shown by cyclic voltammetry to occur by an electrochemically induced chain reaction.

Because the chain reaction can also be initiated by the addition of a strong base to a solution of **4**, the propagation cycle is probably analogous to that for the reaction of **2** (eq 8 and 9) and involves proton transfer followed by elimination of $Ph_2C{=}O$ from the intermediate anion. However, in contrast to **2**, the chain reaction involving **4** can be induced at potentials that are considerably more positive than the cathodic peak potential for the reduction of the corresponding oxirane ($E_{p,c} = -2.00$ V for **3**). As demonstrated in Figure 4, signficant cathodic current first starts to flow in the apparent reduction of **4** in the vicinity of −1.0 V. Because this value corresponds closely to the peak cathodic potential for the reduction of the expected reaction product $Ph_2C{=}O$ ($E_{p,c} = -1.03$ V), we believe that the chain reaction is initiated by the electroreduction of a trace amount of $Ph_2C{=}O$ which is present as an impurity, followed by the abstraction of a proton from **4** by $Ph_2C{=}O^-\cdot$ (eq 20 and 21). Termination is presumed to involve the abstraction of a proton from a component of the solvent–electrolyte system by Ph_2CH^-.

Relationship of This Work to Previous Studies. The difficulty with which oxiranes are reduced has limited the number of electrochemical studies of this functional group. Although this is apparently the first study involving the redox behavior of **1**, the electroreduction of **3** has been reported by Boujlel and Simonet to give Ph_2CHOH, 37%; Ph_2CH_2, 58%; and $(Ph_2CH)_2$, 5%.[16] These workers also report that **4** is detected as an intermediate in the electroreduction of **3**, that **4** is reduced by cleavage of the carbon–carbon bond to give Ph_2CHOH and Ph_2CH_2, and that a ketone is not formed as an intermediate in the electroreduction of **3**. In contrast, our results show that the reduction of **3** affords $Ph_2C{=}O$ as a discernible electroactive intermediate, that the product distribution is a function of the relative rates of protonation of $Ph_2\bar{C}CPh_2(O^-)$ at the benzhydryl carbon and the oxygen sites, and that alcohol **4**, if it were formed, would rapidly undergo an electrochemically induced chain reaction to give $Ph_2C{=}O$ and Ph_2CH_2.

Question Concerning Carbene Anion Radical Intermediacy. One of the purposes of this study was to determine the feasibility of preparing carbene anion radicals from oxiranes. Although our results indicate that the oxirane anion radicals undergo the prerequisite carbon–oxygen bond cleavage, the subsequent rate of reduction of the ring-opened anion radicals to their corresponding dianions is much more rapid than the desired elimination of the carbene anion radical. Accordingly, these oxiranes do not appear to be viable precursors for carbene anion radicals in the condensed phase.

Experimental Section

Instrumentation. Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential loss between the reference and working electrodes.[17,18] Control of the potentiostat and the acquisition and processing of the rapid-scan cyclic voltammetric and chronoamperometric data were performed with a laboratory digital computer (ADAC Model 2000, LSI 11/2). The three-electrode potentiostat which was used for the controlled-potential electrolyses has been described previously.[19]

Cell, Electrodes, and Electrolysis Procedures. All electrochemical experiments were performed on an all-glass vacuum line. The solvent dimethylformamide (DMF) was transferred into the cell by trap-to-trap distillation. Traces of oxygen, if present, were removed by several freeze–pump–thaw cycles. Helium was used to bring the cell up to atmospheric pressure. A positive pressure of helium was maintained when the reference electrode and compounds were transferred into the cell. Slush baths, which were prepared from liquid nitrogen and the appropriate liquid,[20] were used to maintain the cell at constant, subambient temperature.

Several platinum and vitreous carbon electrodes were used for the cyclic voltammetric experiments. All chronoamperometric experiments were performed with a planar platinum electrode which had a geometric area of 0.20 cm^2. All potentials listed were measured with respect to a cadmium amalgam which is in contact with a DMF solution that is saturated with both sodium chloride and cadmium chloride (Type A-III).[21] The potential of this electrode is −0.75 V vs. SCE. Dual reference electrodes were used in all rapid-scan cyclic voltammetric and chronoamperometric experiments.[22] The second reference electrode, which was a

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platinum wire in series with a 0.1 μF capacitor, was placed in parallel with the cadmium amalgam electrode.

The progress of a large-scale electrolysis was monitored periodically by cyclic voltammetry. At the conclusion of an electrolysis, the mixture was protonated in a dry helium atmosphere with an appropriate proton donor (e.g., acetic acid or diethyl malonate). The solution was then analyzed by high-performance liquid chromatography (HPLC).

Chromatography. The products of the electrolyzed solutions were separated by HPLC using a 6.35-mm diameter by 25-cm length stainless steel column packed with either LiChrosorb RP-8 or Alltech C_{18}, 10-μm mean particle size. The eluting solvent was a mixture of methanol and water; the solvent ratio was optimized for each product composition. The flow rate of the eluting solvent was 1 mL/min. The wavelengths used in the analyses were 270 nm for acetone and 254 nm for the remainder of the products. Calibration curves were constructed daily.

Chemicals. DMF (Burdick and Jackson) was purified by passage thrugh a column of alumina (80–200 mesh, Brockman activity 1, activated at 600 °C overnight) and was collected over a mixture of Davison 4-Å molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag.

6,6-Dimethyldibenzofulvene oxide (1),[23] 2-(9-fluorenyl)propanol (2)[24] and tetraphenyloxirane (3)[25] were synthesized according to literature procedures; all other compounds were commercially available. The purities of all compounds were checked by melting point, HPLC, and/or cyclic voltammetry.

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Registry No. 1, 81277-93-2; 2, 56954-90-6; 3, 470-35-9; 4, 981-24-8.

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Electrochemical–Kinetic Study of the Oxidative Cyclization of 2,5-Dihydroxyphenylalanine, 2,5-Dihydroxyphenylethylamine, and α-Methyl-2,5-dihydroxyphenylethylamine

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The anodic oxidation reactions of 2,5-dihydroxyphenylethylamine (**1a**, DHPA), α-methyl-2,5-dihydroxyphenylethylamine (**1b**, α-MeDHPA), and 2,5-dihydroxyphenylalanine (**1c**, 2,5-dopa) were studied at the carbon-paste electrode in 1 M $HClO_4$ and in McIlvaine buffers of varying pH at 15, 20, 25, and 30 °C. Cyclic voltammetry showed that, within the pH range 6.5–7.5, each of the three compounds was oxidized via an EC mechanism involving an initial two-electron oxidation to a *p*-quinone (**2a,b,c**), which after deprotonation to the free amine **3a,b,c**, rapidly cyclized to the relatively stable 5-oxoindoline quinone imine **4a,b,c**. The indoline quinone imines **4a,b** underwent further, much slower tautomerization to the corresponding 5-hydroxyindoles **6a,b**, which could be isolated following constant potential electrolysis experiments. The indoline quinone imine **4c** from 2,5-dopa (**1c**) underwent decarboxylative rearrangement to yield 5-hydroxyindole (**6a**). Double potential step chronoamperometry of **1a**, **1b**, and **1c** afforded first-order rate constants for cyclizations of the *p*-quinonylethylamines **3** to the corresponding 5-oxoindoline quinone imines **4**. At 25 °C the transient *p*-quinonylethylamines **3a,b,c** had half-lives of 50, 5, and 7 ms, respectively. Authentic 5-hydroxyindoline (**5a**), the reduction product of **4a**, was synthesized independently by debenzylation of 5-(benzyloxy)indoline hydrochloride.

In earlier articles we reported detailed electrochemical–kinetic studies of the oxidative cyclizations of the melanin precursor 3,4-dihydroxyphenylalanine (dopa)[1] and of several related catecholamines, including dopamine,[3] α-methyldopa,[2] α-methyldopamine, and α-methylnorepinephrine.[3] The isomer of dopa, 2,5-dihydroxyphenylalanine (**1c**, 2,5-dopa) is also of some physiological significance and has shown antibiotic activity[4,5] as well as utility as a cardiac stimulant.[6] This hydroquinone amine **1c** had been suggested early[7] as a metabolic intermediate in the conversion of tyrosine to homogentisic acid in alkaptonurics but only recently has been demonstrated to play such a role in the metabolism of tyrosine by several strains of Aspergillus.[8]

As an alternative to oxidative degradation of the side chain leading to homogentisic acid, nuclear oxidation of 2,5-dopa (**1c**) should produce the corresponding *p*-quinone **2c**, a species of as yet unknown stability, which can cyclize to indolic products, paralleling the behavior of dopa quinone. For this reason it was of interest to conduct a

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