could not specify participation of 3d orbitals in the sulfur atom clearly.

**Supplementary Material Available:** NMR parameters of $PhSO_nFl$-H in THF (Table VIII), the electronic absorption spectrum of sodium $PhSO_2Fl^-$ carbanion in THF (Figure 7), a plot of $\nu_{max}$ and $1/r_C$ for the alkali metal $PhSO_2Fl^-$ carbanions (Figure 8), correlation between $\sigma_I$ and chemical shifts of the protons in the sodium $PhSO_nFl^-$ carbanions (Figure 9), correlation between $\sigma_I$ and $E_{ox}$ of $PhSO_nFl^-$ carbanions (Figure 10), an oscilloscope trace of the decay of $AQ^-\cdot\|Li^+$ at 545 nm (Figure 11), and the kinetics of reaction 5 (Figure 12) (7 pages). Ordering information is given on any current masthead page.

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# Electrochemistry of the Carbon–Halogen Bond. 9-Fluorenyl and Benzhydryl Halides in Dimethylformamide, at Platinum and Vitreous Carbon Electrodes

**F. M. Triebe, K. J. Borhani, and M. D. Hawley***

*Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506.*

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**Abstract:** Electrochemical reductive dehalogenations of 9-fluorenyl and benzhydryl bromides and chlorides at platinum and vitreous carbon electrodes in dimethylformamide initially require two electrons/molecule and afford the corresponding carbanions as short-lived intermediates. The electrogenerated carbanions may be protonated by diethyl malonate to give their corresponding hydrocarbons or, in the absence of added proton donor, react with their starting halides by either proton transfer or displacement of halide ion. Reaction by the first of the latter two pathways leads to the corresponding olefin via an electroactive monohaloethane, whereas reaction involving the displacement of halide ion gives an electroinactive nonhalogenated ethane; the pathway which is followed appears to be determined by the ease with which halide ion is displaced. Reaction by either channel is rapid: the rate constants obtained for the displacement of bromide ion from 9-bromofluorene and benzhydryl bromide are $1 \times 10^5$ and $8 \times 10^4\ M^{-1}\ s^{-1}$, respectively, while the rate constant for proton transfer from 9-chlorofluorene to 9-fluorenyl anion is $8 \times 10^3\ M^{-1}\ s^{-1}$. All starting halides give multiple reduction waves on platinum because of either adsorption of halide ion or electrocatalysis from electrode products and adventitious impurities. No specific surface effects are observed with vitreous carbon electrodes.

## Introduction

During our recent studies of the electroreduction of diphenyldiazomethane[1] and diazofluorene,[2] anodic waves were observed in the rapid scan cyclic voltammograms which we felt might be due to either carbanion or carbene radical anion intermediates. In order to study the electrochemical behavior of the 9-fluorenyl and diphenylmethyl carbanions and their possible role in the reduction of diazoalkanes, we have attempted to generate these species in situ from alternate precursors, viz., by the electrolytic reductive dehalogenation of

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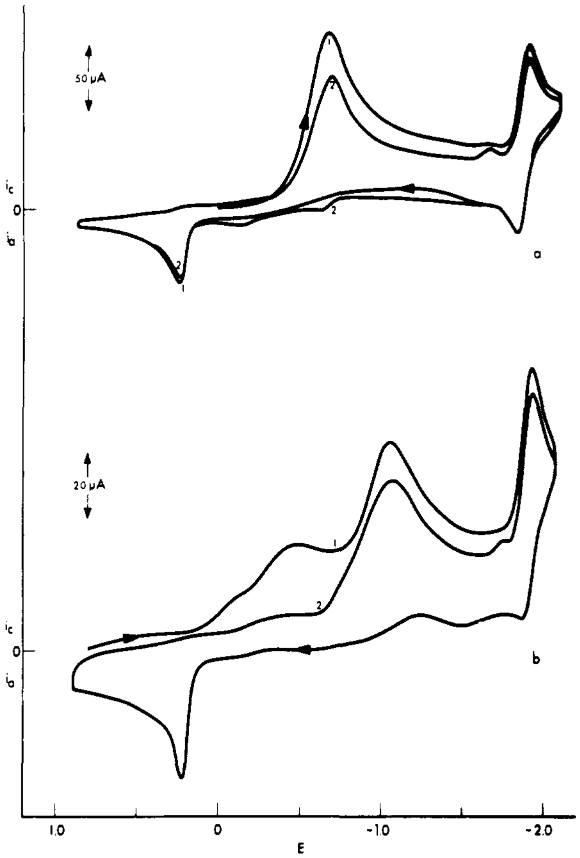


Figure 1. Cyclic voltammograms in 0.1 M TBAP-DMF at a scan rate of 0.2 V/s: (a) 2.18 × $10^{-3}$ M 9-chlorofluorene on a planar vitreous carbon electrode, (b) 1.62 × $10^{-3}$ M 9-chlorofluorene on a planar platinum electrode.

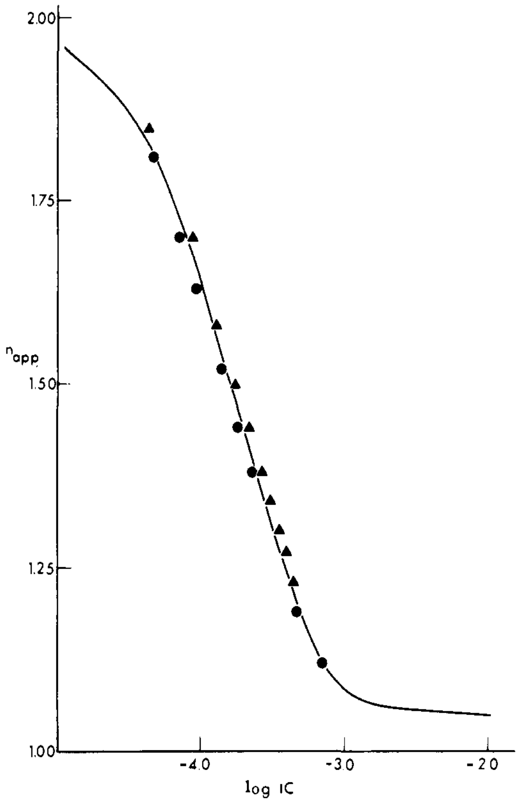


Figure 2. Single potential step chronoamperometric data for the reduction of 9-chlorofluorene on a planar platinum electrode. The solid curve was obtained by the digital simulation of eq 1 and 2 with the second-order rate constant $k$ specified as 8 × $10^3$ $M^{-1}$ $s^{-1}$. Concentrations (M) of 9-chlorofluorene in 0.1 M TBAP-DMF are (●) 2.34 × $10^{-3}$ and (▲) 4.44 × $10^{-3}$.

the 9-fluorenyl and benzhydryl halides. The redox behavior of these monohalo compounds also merits study in its own right. First, despite the large number of polarographic studies of the carbon–halogen bond, few product and $n$ value determinations of this process have actually been conducted.[3] Second, if the reductive cleavage of the carbon–halogen bond is initially a two-electron process, then the difference in basicity, and hence stability, between 9-fluorenyl anion and diphenylmethyl anion might be expected to affect the distribution between monomeric and dimeric products. Third, the study of the redox behavior of the corresponding *gem*-dihalo compounds cannot be understood until the behavior of the monohalo compounds has been elucidated first. An understanding of the redox behavior of the *gem*-dihalo compounds is important since they have also been suggested to be precursors to carbenes[4,5] and carbene radical anions.[6] The latter class of species is of particular interest to us since we have postulated their intermediacy in the reductive elimination of nitrogen from diazoalkanes.[1,2]

## Results and Discussion

The reductions of 9-chlorofluorene (FlHCl), 9-bromofluorene (FlHBr), benzhydryl chloride, and benzhydryl bromide have been studied electrochemically at platinum and vitreous carbon electrodes in solvent-electrolyte systems composed of DMF and tetraalkylammonium salts. The redox behavior of the several halides is basically similar and is generally affected by the nature of the electrode surface, the presence of proton donors and adventitious electroactive substances, and the mass transfer rate. Since all of these effects are observed in the electroreduction of 9-chlorofluorene, the basic reduction pathway is formulated with this chemical system.

**Cyclic Voltammetric Reduction of FlHCl on Carbon.** The cyclic voltammetric reduction of 9-chlorofluorene at a vitreous carbon electrode is seen in Figure 1a to occur near −0.58 V. Although the 9-chlorofluorene radical anion is too unstable to give a corresponding anodic wave on the reverse sweep, numerous kinetically controlled, electroactive products result from its decomposition. The reversible couple which arises near −1.92 V is readily identified[7] by electrochemical and chromatographic methods as being due to fluorene and its stable radical anion. The relatively large anodic wave which appears near 0.20 V is kinetically linked to the appearance of fluorene and is attributed to the oxidation of 9-chlorofluorenyl anion, $FlCl^-$. The oxidation of $FlCl^-$ occurs approximately 0.12 V more positive than the oxidation of 9-fluorenyl anion (0.08 V)[7] and, like $FlH^-$, is irreversible at $v \leq 100$ V/s. In addition to these principal electrode reactions, several minor processes which are due to dimeric species are discernible on the second and subsequent cycles. The small peak at −1.68 V is assigned to the irreversible reduction of bifluorenyl to fluorene and bifluorenyl anion[7] while the anodic waves near −0.64 and −0.18 V arise from the stepwise reversible oxidation of bifluorenylidene dianion to bifluorenylidene. Both bifluorenyl and bifluorenylidene are found among the products of the electrolytic reduction of FlHCl (see coulometry results below).

**Chronoamperometry.** In this experiment the current is recorded as a function of time (1 ms $\leq t \leq$ 10 s) after the electrode potential has been stepped abruptly from a value where no electrode reaction occurs to a value sufficiently negative that the concentration of FlHCl is rendered zero at the electrode surface ($E = -1.4$ V). Since the number of electrons in the electroreduction is proportional to the current, each experimental current-time curve may be used to calculate a corresponding curve of the apparent $n$ value, $n_{app}$, vs. time, $t$. Data

**Table I.** Representative Data for the Coulometric Reduction of 9-Fluorenyl and Benzhydryl Halides and Related Compounds

| entry no. | compd | concn, mM | $E_{\text{applied}}$, V | $n$ | supporting electrolyte | products, yields |
|---|---|---|---|---|---|---|
| 1 | 9-chlorofluorene | 6.83 | −1.2 | 0.5 | TBAP | 9-chlorofluorene, 58%; fluorene, 19%; 9-chlorobifluorenyl, 8%; bifluorenyl, 13%; bifluorenylidene, 2%; fluorenone, 1% |
| 2 | 9-chlorofluorene | 7.06 | −1.3 | 1.0 | TBAP | 9-chlorofluorene, 35%; fluorene, 37%; 9-chlorobifluorenyl, 3%; bifluorenyl, 21%; bifluorenylidene, 0.6%; fluorenone, 0.4%. |
| 3 | 9-chlorofluorene | 5.57 | −1.3 | 1.86 | TBAP | fluorene, 82%; bifluorenyl, 17% |
| 4 | 9-chlorofluorene[a] | 1.65 | −1.3 | 2.42 | $\mathrm{TBAPF_6}$ | fluorene, 93% |
| 5 | 9-chlorobifluorenyl | 6.66 | −0.8 | 2.18 | TBAP | bifluorenyl, 77%; bifluorenylidene, 21%; tributylamine, 46% |
| 6 | 9-bromofluorene | 3.44 | −0.4 | 1.50 | TBAP | fluorene, 17%; bifluorenyl, 83%; bifluorenylidene, 1% |
| 7 | 9-bromofluorene[b] | 1.24 | −0.5 | 1.30 | $\mathrm{TBAPF_6}$ | fluorene, 59%; bifluorenyl, 37% |
| 8 | benzhydryl chloride | 6.73 | −1.0 | 0.75 | TBAP | benzhydryl chloride, 46%; diphenylmethane, 26%; tetraphenylethane, 14%; tetraphenylethene, 8%; 1-chlorotetraphenylethane, trace; benzophenone, 0.4% |
| 9 | benzhydryl chloride | 6.28 | −1.0 | 0.75 | $\mathrm{TMAPF_6}$ | benzhydryl chloride, 48%; diphenylmethane, 28%; tetraphenylethane, 6%; tetraphenylethene, 5%; 1-chlorotetraphenylethane, 4%; benzophenone, 0.3% |
| 10 | benzhydryl chloride | 3.93 | −1.6 | 1.69 | $\mathrm{TMAPF_6}$ | diphenylmethane, 74%; tetraphenylethane, 14%; tetraphenylethene, 10%; benzophenone, 1% |
| 11 | benzhydryl bromide | 13.19 | −0.6 | 1.00 | TEAP | benzhydryl bromide, 30%; diphenylmethane, 36%; tetraphenylethane, 32% |
| 12 | benzhydryl bromide | 7.31 | −0.80 | 0.75 | $\mathrm{TMAPF_6}$ | diphenylmethane, 20%; tetraphenylethane, 44%; benzhydryl bromide, 21% |
| 13 | benzhydryl bromide | 6.70 | −1.20 | 1.74 | $\mathrm{TMAPF_6}$ | diphenylmethane, 52%; tetraphenylethane, 48% |
| 14 | benzhydryl bromide[c] | 6.22 | −1.20 | 2.00 | $\mathrm{TBAPF_6}$ | diphenylmethane, 89%; tetraphenylethane. 8% |

[a] Reduction was effected in the presence of 14.75 mM diethyl malonate. [b] Reduction was effected in the presence of 12.08 mM diethyl malonate. [c] Reduction was effected in the presence of 16.15 mM diethyl malonate.

from these experiments show that the reduction of FlHCl in the presence of a large excess of the electroinactive proton donor diethyl malonate is a diffusion-controlled, two-electron process. However, in the absence of the added proton donor, the $n$ value is dependent upon both time and concentration of FlHCl, decreasing smoothly from an upper limit of 2.0 for $tC < 10^{-5}$ M s to a lower limit of 1.0 for $tC > 10^{-3}$ M s (Figure 2).

The variation of $n_{\text{app}}$ with both time and the concentration of FlHCl is consistent with the kinetically controlled appearances of fluorene and 9-chlorofluorenyl anion in the cyclic voltammograms of FlHCl and suggests that the rate-determining solution reaction involves proton transfer from unreacted starting material to 9-fluorenyl anion. The reaction sequence described by eq 1 and 2 was digitally simulated using Feldberg's procedures for the single-potential-step chronoamperometric method.[8] A dimensionless working curve was then constructed from the values of $n_{\text{app}}$ which were calculated for numerous values assigned arbitrarily to $ktC$, where $C$ is the concentration of the species being reduced. The curve was then fitted to the experimental data points (Figure 2) by shifting the simulated curve along the abscissa until the best visual agreement with the data was obtained. The results of these experiments give a value of $8 \times 10^3$ M$^{-1}$ s$^{-1}$ for the rate constant for proton transfer in eq 2.

$$\mathrm{FlHCl} + 2e^- \rightarrow \mathrm{FlH}^- + \mathrm{Cl}^- \tag{1}$$

$$\mathrm{FlH}^- + \mathrm{FlHCl} \xrightarrow{k} \mathrm{FlH_2} + \mathrm{FlCl}^- \tag{2}$$

**Coulometry.** Data for the controlled-potential electrolysis of 9-chlorofluorene and the other halides at platinum cathodes are summarized in Table I. In the presence of a large excess of the proton donor diethyl malonate, reductive dehalogenation of 9-chlorofluorene gives an $n$ value of 2.42 and affords fluorene in nearly quantitative yield (entry 4). In the absence of the added proton donor, the product distribution is dependent upon the relative rates of mass transfer and solution chemical reactions. For example, when electrolysis is effected as rapidly and as completely as possible (entry 3), the ratio of monomeric to dimeric products is approximately 5:1. However, if electrolysis is interrupted well before electrolysis is complete, as in entry number 1, the ratio of monomeric to dimeric products is nearly one. These results are consistent with the relatively rapid proton transfer from unreacted starting material to 9-fluorenyl anion which was observed in the cyclic voltammetric and chronoamperometric studies of FlHCl above and the comparatively slow, follow-up reactions of the 9-chlorofluorenyl anion with both FlHCl and components of the solvent–electrolyte system (see Scheme I). The slowness of these latter reactions accounts for the observation that the rate of electrolysis decreases markedly after one electron per molecule of FlHCl has been passed.

**Intermediates in Reduction of FlHCl.** Product studies of the partially electrolyzed solutions of FlHCl show the presence of two electroactive dimeric species, 9-chlorobifluorenyl and bifluorenylidene (entries 1 and 2, Table I). Since a plausible pathway to the olefin involves dehydrohalogenation of 9-chlorobifluorenyl by bases which are generated in situ during the electrolytic reductions,[9] the cyclic voltammetric and coulometric reductions of 9-chlorobifluorenyl and bifluorenylidene were examined at a platinum cathode.

At a scan rate of 0.2 V/s, the principal cathodic wave (Figure 3) for the reduction of 9-chlorobifluorenyl ($E_{\text{p,c}} = -0.7$ V) is followed at more negative potential (−1.8 V) by a small reduction peak due to bifluorenyl.[7] Although both of these cathodic processes are irreversible at our maximum scan rate of 100 V/s, anodic waves which are ascribed to the oxidation of bifluorenylidene dianion, bifluorenylidene radical anion, and 9-bifluorenyl anion are seen on the reverse, anodic sweep at −0.66, −0.19, and 0.10 V, respectively. The second cathodic sweep includes the previously observed reduction processes as well as peaks due to the stepwise reduction of bifluorenylidene to its dianion.

The controlled-potential electrolysis of 9-chlorobifluorenyl at a potential of −0.80 V yields bifluorenyl (77%) and bifluorenylidene (21%) as the major and minor product, respectively (entry 5, Table I). Fluorene, the product which would be expected if 9-chlorobifluorenyl radical anion had undergone

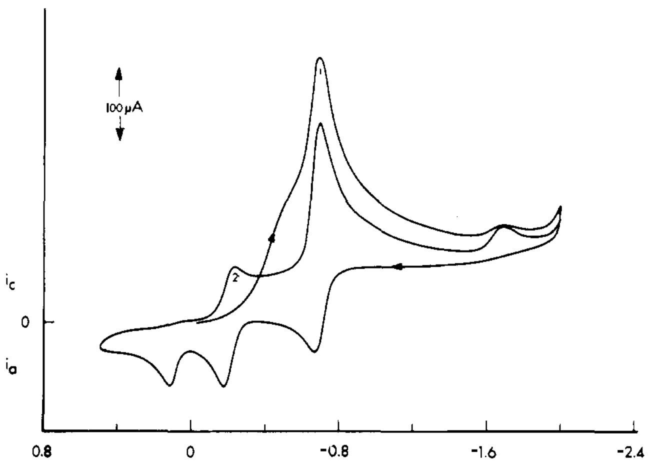


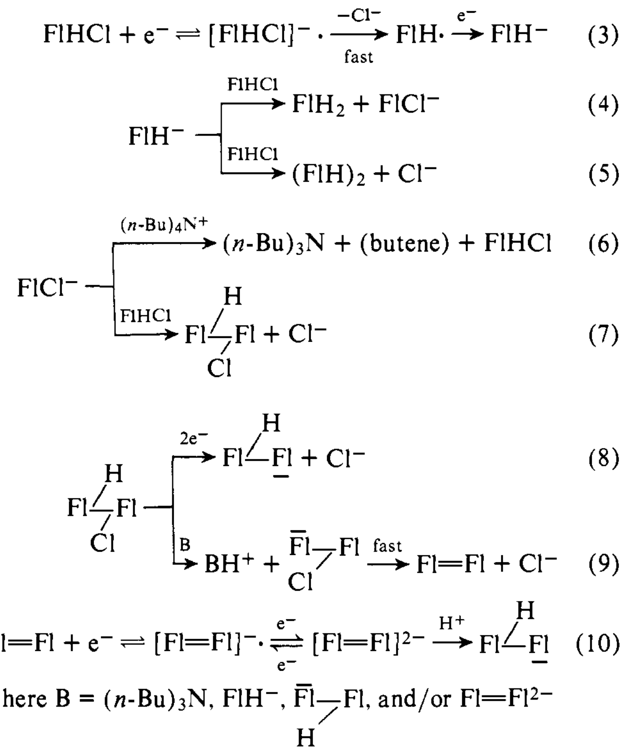
Figure 3. Cyclic voltammogram of $2.92 \times 10^{-3}$ M 9-chloro-9,9′-bifluorenyl in 0.1 M TBAP-DMF on a planar platinum electrode. The scan rate was 0.2 V/s.

carbon–carbon bond cleavage, was not found among the products.

The cyclic voltammetric reduction of bifluorenylidene to its dianion occurs in two successive one-electron steps ($E_{p,c,1} = -0.25$ V and $E_{p,c,2} = -0.72$ V). Although no decomposition of the dianion is noted on the time scale of the cyclic voltammetric and chronoamperometric experiments ($t < 20$ s), appreciable decomposition of the dianion occurs during the period required to perform an exhaustive, controlled-potential electrolysis ($t \sim 20$ min). For example, in the double-potential-step coulometric electrolysis of bifluorenylidene at −1.30 and 0.80 V, the $n$ value for reoxidation of the bifluorenylidene dianion ($n_a = 1.34$) is significantly smaller than the $n$ value required to produce the dianion from the starting compound ($n_c = 2.0$). Product studies after reoxidation show that bifluorenylidene and bifluorenyl are present in 82 and 20% yield, respectively. Since tributylamine is also found in 67% yield, decomposition of the dianion by a pathway which involves the abstraction of a proton from the cation of the supporting electrolyte to give the conjugate base of bifluorenyl is indicated. It should also be noted that anodic oxidation of 9-bifluorenyl anion ($E_{p,a} = 0.10$ V) occurs at the applied potential of 0.80 V and affords bifluorenylidene as one product.[7] The olefin presumably results when the one-electron oxidation product, bifluorenyl radical, abstracts a hydrogen atom from 9-bifluorenyl anion to form bifluorenyl and bifluorenylidene radical anion. The latter species would then be oxidized at the applied potential to the olefin.

**Reduction Pathways for 9-Chlorofluorene.** The reaction pathways which are proposed for the reduction of 9-chlorofluorene are described by Scheme I. The initial $n$ value of 2 which is observed in the chronoamperometric reduction requires that the 9-chlorofluorene radical anion undergo rapid carbon–chlorine bond cleavage to give the 9-fluorenyl radical, FlH·. Since reduction is being effected at a potential considerably more negative than the potential at which 9-fluorenyl anion is oxidized to the radical ($E_{p,a} = 0.08$ V),[7] FlH· is reduced rapidly, either at the electrode surface or in the bulk of solution by undecomposed 9-chlorofluorene radical anion (eq 3). Kinetic control of the chronoamperometric $n$ value in the absence of added proton donor results when 9-fluorenyl anion abstracts a proton from unreacted starting material to form fluorene and 9-chlorofluorenyl anion (eq 4), neither of which is electroactive at the applied potential. Proton transfer from the halide to the electrogenerated base is also observed in the reduction of benzhydryl chloride (vide infra) and has been reported to occur by Baizer and Chruma[9] in the electrolytic reduction of ethyl bromoacetate. Subsequent reactions of the 9-chlorofluorenyl anion occur too slowly on the chronoamperometric time scale to have any appreciable effect on the $n$ value.

**Scheme I**



$$\mathrm{FlHCl} + e^- \rightleftharpoons [\mathrm{FlHCl}]^-\cdot \xrightarrow[\text{fast}]{-\mathrm{Cl}^-} \mathrm{FlH}\cdot \xrightarrow{e^-} \mathrm{FlH}^- \quad (3)$$

$$\mathrm{FlH}^- \xrightarrow{\mathrm{FlHCl}} \mathrm{FlH_2} + \mathrm{FlCl}^- \quad (4)$$

$$\mathrm{FlH}^- \xrightarrow{\mathrm{FlHCl}} (\mathrm{FlH})_2 + \mathrm{Cl}^- \quad (5)$$

$$\mathrm{FlCl}^- \xrightarrow{(n\text{-Bu})_4\mathrm{N}^+} (n\text{-Bu})_3\mathrm{N} + (\text{butene}) + \mathrm{FlHCl} \quad (6)$$

$$\mathrm{FlCl}^- \xrightarrow{\mathrm{FlHCl}} \mathrm{Fl}\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{\angle}}\mathrm{Fl} + \mathrm{Cl}^- \quad (7)$$

$$\mathrm{Fl}\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{\angle}}\mathrm{Fl} \xrightarrow{2e^-} \mathrm{Fl}\overset{\mathrm{H}}{\angle}\underset{-}{\mathrm{Fl}} + \mathrm{Cl}^- \quad (8)$$

$$\mathrm{Fl}\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{\angle}}\mathrm{Fl} \xrightarrow{\mathrm{B}} \mathrm{BH}^+ + \overline{\mathrm{Fl}}\underset{\mathrm{Cl}}{\angle}\mathrm{Fl} \xrightarrow{\text{fast}} \mathrm{Fl{=}Fl} + \mathrm{Cl}^- \quad (9)$$

$$\mathrm{Fl{=}Fl} + e^- \rightleftharpoons [\mathrm{Fl{=}Fl}]^-\cdot \underset{e^-}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Fl{=}Fl}]^{2-} \xrightarrow{\mathrm{H}^+} \mathrm{Fl}\overset{\mathrm{H}}{\angle}\underset{-}{\mathrm{Fl}} \quad (10)$$

where B = $(n\text{-Bu})_3\mathrm{N}$, $\mathrm{FlH}^-$, $\overline{\mathrm{Fl}}\underset{\mathrm{H}}{\angle}\mathrm{Fl}$, and/or $\mathrm{Fl{=}Fl}^{2-}$

The product distribution between fluorene and dimeric species is then dependent upon the relative rates of electrolytic reduction of 9-chlorofluorene and nucleophilic displacement of chloride ion from 9-chlorofluorene by 9-chlorofluorenyl anion (eq 5). If the electrode reaction is permitted to predominate, fluorene is the major product. Since no starting material remains in exhaustively electrolyzed solutions, the inclusion of the pathway by which 9-chlorofluorenyl anion abstracts a proton from the cation of the supporting electrolyte to regenerate starting material is required (eq 6). Tributylamine is observed as a product of these reductions, but no attempt was made to quantitate this component.

If the chloride displacement reaction is permitted to predominate (eq 7), as in the case when electrolysis is terminated before the concentration of 9-chlorofluorene is rendered zero, 9-chlorobifluorenyl results.[10] Since both this species and bifluorenylidene are electroactive at the applied potential, bifluorenyl is ultimately formed by the sequence of reactions described by 8–10. Dehydrohalogenation of the monohalo dimer intermediate (eq 9) is expected to occur readily by any of the several electrogenerated bases, including $\mathrm{FlH}^-$, $\mathrm{Fl{=}Fl}^{2-}$, $\mathrm{FlH{-}Fl}^-$, and $(n\text{-Bu})_3\mathrm{N}$.[9,11] Although thermally induced dehydrohalogenation was not observed at room temperature, conversion of the monohalo dimer to olefin occurred rapidly when analysis of the electrolyzed solutions was attempted by gas chromatography.

Although the formation of bifluorenylidene in the electrochemical reduction of 9,9-dichlorofluorene has been suggested to occur by dimerization of fluorenylidene, Fl:,[5] the formation and subsequent redox behavior of 9-chlorobifluorenyl obviate any need here for invoking the intermediacy of the carbene in the pathway leading to the olefin. In addition, the possibility that fluorene could be formed from $\mathrm{FlCl}^-$ via the carbene seems small. Since 9-chlorofluorenyl anion is reasonably long lived, decomposition of the anion by loss of chloride ion would

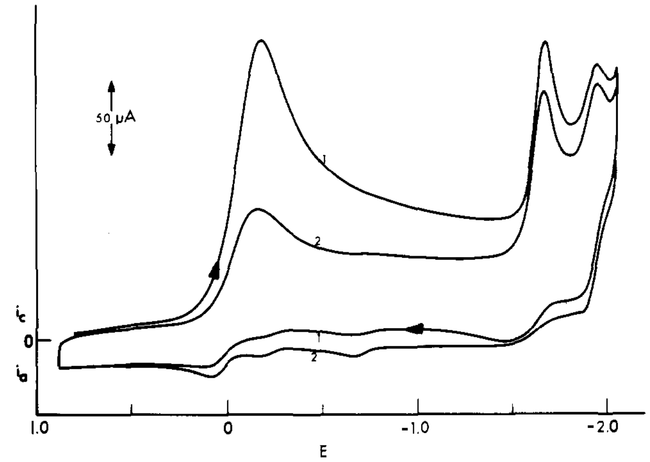


Figure 4. Cyclic voltammogram of $3.72 \times 10^{-3}$ M 9-bromofluorene in 0.1 M TBAP-DMF on a planar vitreous carbon electrode. The scan rate was 0.2 V/s.

necessarily occur in the bulk of solution. The resulting carbene would be expected to be short lived and to decompose rapidly to give fluorene by repeated hydrogen atom abstraction from components of the solvent system.[2] If fluorene were to be formed by this pathway, an $n$ value of one would be predicted for the reduction of 9-chlorofluorene. In fact, the experimental $n$ value of 1.86 is in almost perfect agreement with the proposed reaction pathways (Scheme I) and the observed product distribution (entry 3, Table I): $n = 2$ (fraction fluorene) + fraction bifluorenyl = 2(0.86) + 0.17 = 1.89.

**Proton Transfer vs. Nucleophilic Substitution.** Whereas 9-fluorenyl anion reacts with FlHCl principally by proton transfer, attack of $FlH^-$ on FlHBr leads mainly to loss of bromide ion and the formation of bifluorenyl (eq 5). As evidenced in the cyclic voltammogram (Figure 4), the reduction of FlHBr occurs irreversibly at −0.19 V and affords bifluorenyl ($E_{p,c} = -1.68$ V) as its principal product. The reduction of the $(FlH)_2$ also occurs irreversibly by carbon-carbon bond cleavage to regenerate 9-fluorenyl anion. The small wave at more negative potential ($E_{p,c} = -1.96$ V) is due to fluorene, which most probably arises by the abstraction of a proton from unreacted 9-bromofluorene (eq 4). Involvement of this second pathway is minor, however, as evidenced by the magnitudes of the fluorene and bifluorenylidene peaks relative to that of the bifluorenyl wave.

In order for bifluorenyl to be the principal product of 9-bromofluorene reduction, the rate constant for the displacement of bromide ion must be appreciably larger than $1 \times 10^4$ $M^{-1}$ $s^{-1}$, the approximate rate constant for proton transfer from FlHBr to $FlH^-$. Since the reactants which lead to dimer formation and proton transfer are identical, the model which was used for the digital simulation of proton transfer in the 9-chlorofluorene system is also appropriate for the present study of the displacement of bromide ion. In order to measure the rate constant, the electrode potential in the single-potential-step chronoamperometric experiment was made sufficiently negative so as to reduce the concentration of FlHBr at the electrode surface to zero, but not so negative as to cause the reduction of bifluorenyl, the principal product of the solution reaction. The rate constant was then obtained from the best visual fit of the experimental curve of $n_{app}$ vs. log $tC$ and the dimensionless, simulated curve of $n_{app}$ vs. log $ktC$ (Figure 5). Although the kinetic behavior is occurring near the limit of our instrumental capabilities, the predicted dependence of $n_{app}$ on both time and concentration of FlHBr is adequate. The value of $1 \times 10^5$ $M^{-1}$ $s^{-1}$ which is obtained for the overall rate constant is approximately an order of magnitude larger than the estimated rate constant for proton transfer and is consistent with the observation that bifluorenyl is the principal product of FlHBr reduction (entry 6, Table I).

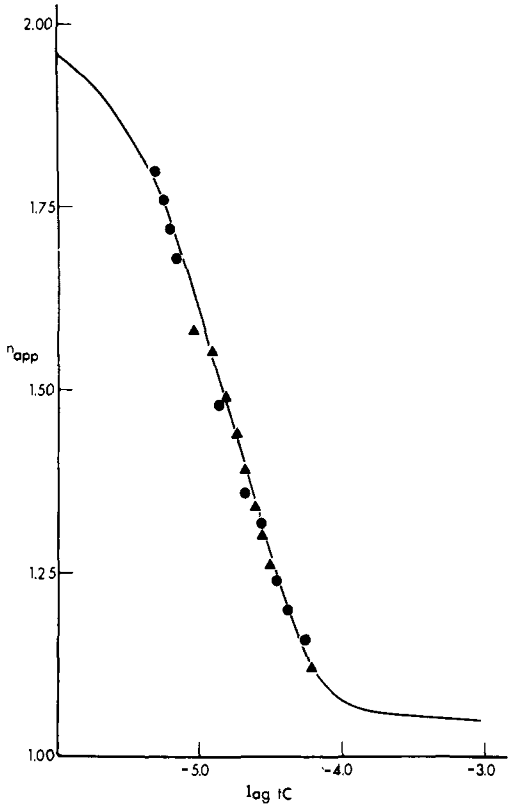


Figure 5. Single potential step chronoamperometric data for the reduction of 9-bromofluorene on a planar platinum electrode. The solid curve was obtained by digital simulation for rate-determining displacement of bromide ion from 9-bromofluorene by 9-fluorenyl anion with $k = 1 \times 10^5$ $M^{-1}$ $s^{-1}$. Concentrations (M) of the 9-bromofluorene in 0.1 M TBAP-DMF are (●) $0.68 \times 10^{-3}$ and (▲) $3.00 \times 10^{-3}$.

**Effect of Electrode Material.** In contrast to the single reduction wave which was observed for 9-chlorofluorene on vitreous carbon (Figure 1a), the redox behavior of FlHCl on platinum is strongly influenced by the condition of the platinum surface (Figure 1b). Although occasional cyclic voltammograms are obtained in which a single irreversible cathodic wave is observed near −1.13 V, the majority also have a relatively broad, irreversible prepeak near −0.64 V. The ratio of the magnitudes of the prepeak to the main wave decreases with increasing scan rate and is enhanced by the addition of tetramethylammonium chloride to the solution. Similar electrode surface effects are also observed for 9-bromofluorene and benzhydryl bromide: a single, irreversible peak is seen for each compound on vitreous carbon while one or more prepeaks of unpredictable magnitude and location usually occur on platinum.

The prepeak on platinum surfaces has been observed in these and other laboratories for numerous chloro and bromo compounds and nearly all iodine-containing compounds.[12-14] Bard[12] has suggested that the prepeaks at platinum represent electron transfer assisted by absorbed halide ion whereas the normal wave results from the ordinary electron transfer through the metal-solution interface to a molecule in solution. Normal reduction of these compounds on vitreous carbon is presumably the result of no specific interaction of products and reactants with the electrode material.[15]

**Electrocatalytic Reduction of Benzhydryl Chloride by Benzophenone.** The cyclic voltammetric reduction of benzhydryl chloride in DMF-$(n\text{-}Bu)_4NClO_4$ at either platinum or vitreous carbon electrodes consists of two cathodic

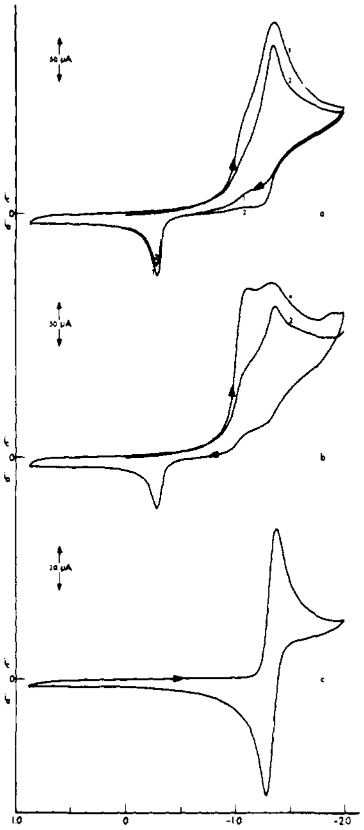


**Figure 6.** Cyclic voltammograms in 0.1 M TBAP-DMF on a planar platinum electrode at a scan rate of 0.2 V/s: (a) $4.77 \times 10^{-3}$ M benzhydryl chloride; (b) same as (a) but with addition of benzophenone, [benzophenone]/[benzhydryl chloride] = 0.028; (c) $3.58 \times 10^{-3}$ M 1,1,2,2-tetraphenylethene.

processes ($E = -1.03$ and $-1.38$ V), both of which are kinetically controlled (Figure 6a). The less negative process (either a shoulder or a peak, depending upon concentration and scan rate) is located at the same potential as that for the reversible reduction of benzophenone to its radical anion and is increased, at the expense of the second wave, by a decrease in scan rate. As shown in Figure 6b, the addition of a small amount of benzophenone to the solution of benzhydryl chloride ($[Ph_2CO]/[Ph_2CHCl] = 0.028$) causes the normal reduction wave for benzhydryl chloride to be nearly eliminated while the magnitude of the benzophenone wave is markedly enhanced.

The effect of the benzophenone is to cause the indirect reduction of benzhydryl chloride in the bulk of solution; a similar phenomenon has been observed in the electrolytic reduction of other alkyl halides, activated olefins, and aryl azides.[16] Observance of this behavior requires (1) a species which is reduced to a stable, lower oxidation state at a potential more positive than that of the substance, e.g., benzophenone/benzophenone$^{-}\cdot$, (2) electron transfer from the electrolytically generated reducing agent to the substrate, and (3) rapid, irreversible decomposition of the reduced substrate, e.g., loss of chloride ion from the radical anion of benzhydryl chloride. Since the chemical reducing agent is continually regenerated at the electrode surface, the concentration of the reversibly reduced species need not be large in order for it to exert a profound effect upon the electrode behavior (eq 11-13).

$$Ph_2C{=}O + e^- \rightleftharpoons Ph_2C{=}O^-\cdot \qquad (11)$$

$$Ph_2C{=}O^-\cdot + Ph_2CHCl \rightarrow Ph_2C{=}O + [Ph_2CHCl]^-\cdot \qquad (12)$$

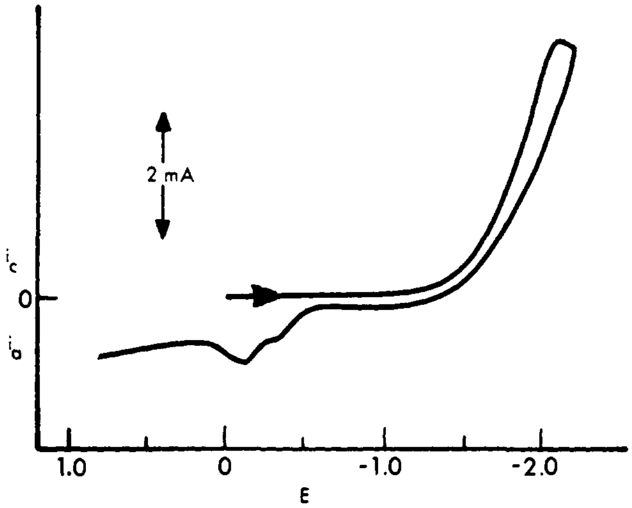


**Figure 7.** Cyclic voltammogram of $5.00 \times 10^{-3}$ M benzhydryl chloride in 0.1 M TBAP-DMF on a planar platinum electrode at a scan rate of 50 V/s.

$$[Ph_2CHCl]^-\cdot \xrightarrow[\text{fast}]{-Cl^-} Ph_2CH\cdot \xrightarrow{Ph_2C{=}O^-\cdot} Ph_2CH^- \qquad (13)$$

In this example of electrocatalysis the concentration of benzophenone in the original solution of benzhydryl chloride must be small, as evidenced by the fact that no wave is seen in the cyclic voltammogram near $-1.8$ V for the reduction of the benzophenone radical anion to its dianion. Since the carefully purified starting material was determined to contain less than 0.1% benzophenone, the major portion of the benzophenone which is present in the electrolyzed solutions (0.1-1%: entries 8-10, Table I) is probably formed in situ by attack of either adventitious oxygen on the intermediate diphenylmethyl anion or superoxide ion on benzhydryl chloride. Superoxide ion, which would be formed by the electrolytic reduction of oxygen at the applied potential,[17] is known to cause displacement of halide ion from alkyl halides.[18]

Electrocatalysis and surface effects both serve to complicate the interpretation of the redox behavior of these and other halogenated compounds. Although vitreous carbon appears to minimize certain problems arising from the nature and condition of the electrode surface, the occurrence of electrocatalysis may be difficult to eliminate. In the case of 9-chlorobifluorenyl (vide supra), both thermal decomposition and electroreduction afford bifluorenylidene, a species which is reduced stepwise to its stable dianion at potentials of $-0.26$ and $-0.72$ V. Although the difference in reduction potential between bifluorenylidene/bifluorenylidene radical anion and 9-chlorobifluorenyl is too large for homogeneous electron transfer to occur at a significant rate, the rate of reduction of 9-chlorobifluorenyl by electrogenerated bifluorenylidene dianion is so rapid at pen and ink recording speeds that a cathodic peak for 9-chlorobifluorenyl appears at the same potential as that for the reduction of bifluorenylidene radical anion (Figure 3). Electrocatalysis is detected in this case by the appearance of a more negative peak ($E_{p,c} = -0.9$ V) at scan rates in excess of 5 V/s. The scan rate required to detect electrocatalysis in other systems is obviously related to the rate of electron transfer and should increase rapidly as the potential difference between the electrogenerated reductant and the substrate decreases.[19]

**Other Kinetically Controlled Processes in the Reduction of Benzhydryl Chloride.** In addition to electrocatalysis by benzophenone, other processes are kinetically controlled on the time scale of the cyclic voltammetric and chronoamperometric experiments. As the cyclic voltammetric scan rate is increased, the anodic wave assigned to the irreversible oxidation of chlorodiphenylmethyl anion shifts in the positive direction and decreases in relative magnitude (Figure 7). Concomitantly, a second anodic wave which is kinetically linked to the chlorodiphenylmethyl anion oxidation wave appears at slightly more negative potential ($E_{p,a} = -0.36$ V at $v = 50$ V/s). This peak is due to the oxidation of the primary electrode product, benzhydryl anion, to its radical. No reversibility is seen for this process at our maximum scan rate of 100 V/s.

Chronoamperometric $it^{1/2}/C$ values obtained on platinum at a potential more negative than the normal reduction wave for benzhydryl chloride correspond to a diffusion-controlled two-electron process for $t$ less than approximately 30 ms. At longer $t$, the $n$ value first decreases smoothly to approximately 1.2, and then increases slowly. As in the previous halide systems, the initial $n$ value of two corresponds to the reductive dechlorination of benzhydryl chloride to give benzhydryl anion. Kinetic control of the $n$ value results when this anion abstracts a proton from starting material. Since the products of partial electrolysis of benzhydryl chloride include both the olefin and 1-chlorotetraphenylethane (entries 8-10, Table I), subsequent reactions of chlorodiphenylmethyl anion are analogous to those which were observed above in the 9-chlorofluorene system (Scheme I). The redox behavior of benzhydryl chloride differs from that of 9-chlorofluorene, however, since the rate of dimer formation is significantly more rapid in the former system. Reduction of the olefin occurs reversibly at the same potential ($E_{p,c} = -1.37$ V, Figure 6c) as that for the uncatalyzed reduction of benzhydryl chloride and accounts for the facts that (1) the lower limit for $n$ in the chronoamperometric kinetics studies is nonintegral and (2) the magnitude of the more negative wave in the cyclic voltammogram of benzhydryl chloride increases on subsequent cycles relative to that of the first wave (Figure 6a).

**Comparison of Electrochemical and Chemical Reduction Pathways for Benzhydryl Chloride.** The reduction of benzhydryl chloride in THF by the dropwise addition of sodium naphthalene has been shown to give tetraphenylethane and diphenylmethane in yields of 85 and 11%, respectively, in the absence of *t*-BuOH and 2.5 and 100%, respectively, in the presence of *t*-BuOH; inverse addition of the reagents affords the ethane and diphenylmethane in yields of 21 and 63%, respectively.[20,21] Lee and Closson[20] suggest that their results require the intermediacy of the diphenylmethyl anion and that tetraphenylethane most probably arises by a process involving electron transfer from diphenylmethyl anion to benzhydryl chloride, followed by coupling of the caged benzhydryl radicals (eq 14). In addition, since the ethane is formed even under the conditions of inverse addition, these workers argue that the carbanion must compete effectively with the excess naphthalene radical anion for unreacted starting material.

$$\mathrm{Ph_2CH^- + Ph_2CHCl \rightarrow [Ph_2\dot{C}H \cdots Ph_2\dot{C}H \cdots Cl^-] \rightarrow (Ph_2CH)_2 + Cl^-} \quad (14)$$

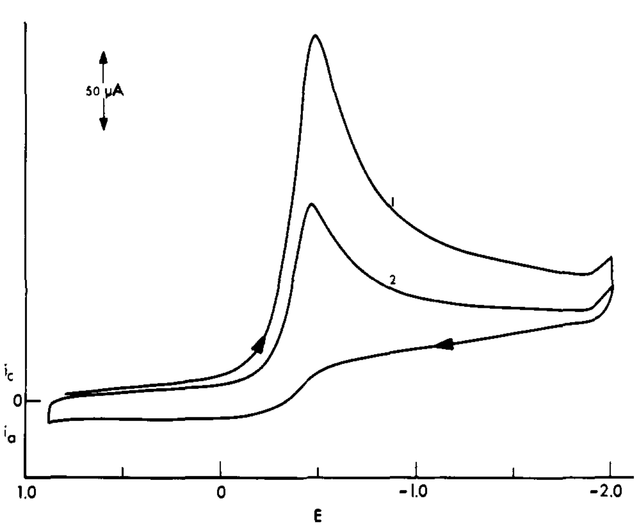


**Figure 8.** Cyclic voltammogram of $4.15 \times 10^{-3}$ M benzhydryl bromide in 0.1 M TBAP-DMF on a planar vitreous carbon electrode at a scan rate of 0.2 V/s.

In contrast, our results indicate that diphenylmethyl anion reacts with benzhydryl chloride principally by proton transfer. Although the electrochemical and chemical reduction pathways may be dissimilar because of the effect of cation and/or solvent, it should be noted that our proposed scheme is very similar to the reaction sequence reported by Hoeg and Lusk[22] for the attack of *n*-butyllithium on benzyl chloride in THF: proton transfer from benzyl chloride to carbanion, monohaloethane formation, and finally dehydrochlorination to give the olefin. Moreover, our electrochemical data indicate that electron transfer would be extremely unlikely in the reaction of mono- and polyphenylmethyl anions with benzylic chlorides. The oxidation of chlorodiphenylmethyl anion and other mono- and polyphenylmethyl anions[23] occurs in the range from −0.3 to −0.4 V vs. Cd(Hg). Although the peak potentials observed here for the reduction of benzhydryl chloride ($E_{p,c} = -1.37$ V) and the oxidation of benzhydryl anion ($E_{p,a} = -0.36$ V) have no exact significance because of the effect of follow-up chemical reactions, the equilibrium constants for electron transfer from phenylmethyl anions to benzhydryl chloride nevertheless can be quickly estimated as being smaller than $10^{-15}$. Even if one allows for diffusion-controlled electron transfer in the reverse direction, the rate of electron transfer in the forward direction should be several orders of magnitude too small to account for the observed kinetic behavior in the cyclic voltammetric and chronoamperometric experiments:

$$\mathrm{Ph_2CH^- + Ph_2CHCl \overset{K < 10^{-15}}{\rightleftharpoons} Ph_2CH\cdot + Ph_2CHCl^-\cdot} \quad (15)$$

Since the basic redox processes would not be expected to change appreciably as one goes from DMF to THF, it seems improbable that diphenylmethyl anion could compete effectively with any strong chemical reductant in the transfer of an electron to unreacted benzylic halides.[24]

**Redox Behavior of Benzhydryl Bromide.** The absence of a redox couple in the cyclic voltammogram near −1.38 V (Figure 8) clearly demonstrates that the olefin, tetraphenylethene, is not formed in the electroreduction of benzhydryl bromide on vitreous carbon. Chronoamperometric $n$ values on platinum are kinetically controlled for $tC < 10^{-3.5}$ M s, but become diffusion controlled and approximately equal to one for $tC > 10^{-3.5}$ M s (Figure 9). Since LC analysis of the electrolyzed solutions also shows no evidence of olefin (entries 11-14, Table I), we conclude on the basis of the chronoamperometric results that diphenylmethyl anion must rapidly displace bromide ion from starting material ($k = 8 \times 10^4$ M$^{-1}$ s$^{-1}$) to form tetraphenylethane.

It should be noted that coulometric reduction of benzhydryl bromide at a platinum surface affords diphenylmethane as a second major product (entries 11-13, Table I). Although the formation of this product is not expected on the basis of our short-term chronoamperometric experiments, variations in the product distribution are frequently observed in electrochemical studies when the time scale of the experiment and the degree of electrolysis are altered markedly. The most ready but unproven explanation of this behavior is that continued electrolysis eventually leads to attack of the solvent-supporting electrolyte system by the strongly basic electrogenerated anions. The observed formation of trialkylamine, the expected Hofmann degradation product of the supporting electrolyte cation, is consistent with this suggestion.

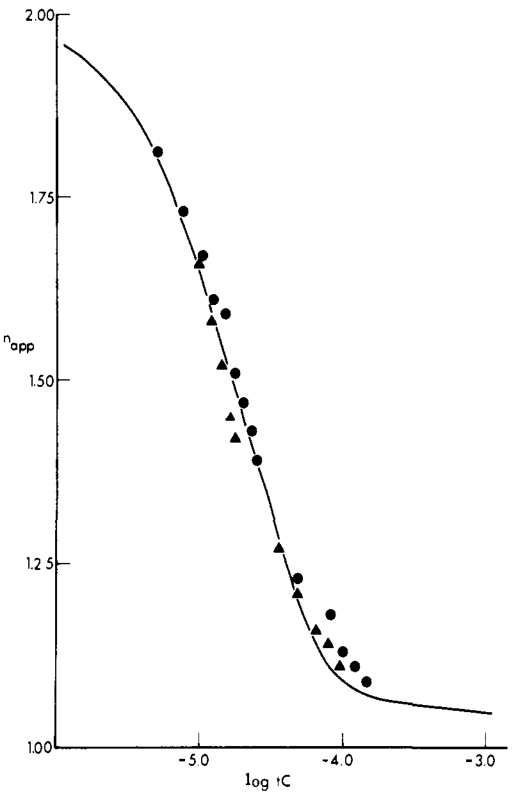


**Figure 9.** Single potential step chronoamperometric data for the reduction of benzhydryl bromide on a planar platinum electrode. The solid curve was obtained by digital simulation for rate-determining displacement of bromide ion from benzhydryl bromide by diphenylmethyl anion with $k = 8 \times 10^4$ $M^{-1}$ $s^{-1}$. Concentrations (M) of the benzhydryl bromide in 0.1 M TBAP-DMF are (●) $2.59 \times 10^{-3}$ and (▲) $1.68 \times 10^{-3}$.

## Conclusions

Our results demonstrate that electrogenerated 9-fluorenyl and benzhydryl anions may react with their starting halides by either proton transfer or displacement of halide ion. Reaction by the former pathway leads to the corresponding olefin via the monohaloethane, whereas the latter pathway gives the ethane; the factor which apparently determines the reaction channel is the ease by which halide ion is lost from the starting material. Reaction by either channel is rapid, as evidenced by rate constants of $1 \times 10^5$ and $8 \times 10^4$ $M^{-1}$ $s^{-1}$ for the displacement of bromide ion from 9-bromofluorene and benzhydryl bromide, respectively, and of $8 \times 10^3$ $M^{-1}$ $s^{-1}$ for proton transfer from 9-chlorofluorene to 9-fluorenyl anion. These data clearly indicate that the 9-fluorenyl and diphenylmethyl anions are potent nucleophiles, reacting several orders of magnitude more rapidly than either "naked" azide, thiocyanate, and halide ions with benzyl tosylate in acetonitrile[25] or superoxide ion with alkyl bromides in $Me_2SO$.[18]

## Experimental Section

**Instrumentation.** Cyclic voltammetry and chronoamperometry were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential loss between the reference and working electrodes.[26] Control of the potentiostat and the acquisition and processing of data in the chronoamperometric studies were performed with a laboratory digital computer (LAB 8/e, Digital Equipment Corp.). The three-electrode potentiostat-coulometer which was used for the exhaustive, controlled-potential experiments has been described recently.[27] Unlike the other potentiostats, this instrument has no provision for electronic correction of ohmic potential losses between the reference and working electrodes.

**Chromatography.** Direct analysis of the electrolyzed mixtures was performed with temperature-programmed gas chromatographs (Hewlett-Packard Model 700) which were equipped with flame ionization detectors. Most of the separations were effected on a 0.25-in. 2-ft stainless steel column of 3% Dexil 300 GC (Olin Corp.) on 80/100 Chromosorb W. To separate more polar components (e.g., 9-chlorofluorene and 9-fluorenone), a 0.25-in., 6-ft stainless steel column of 3% FFAP on 80/100 Chromosorb W-HP was used. The flow rate of purified nitrogen carrier gas was 30 mL/min. Calibration curves for the standards were constructed daily.

Since 9-chloro-9,9′-bifluorenyl and 1-chloro-1,1,2,2-tetraphenylethane rapidly dehydrochlorinate at elevated temperatures, solutions which were suspected to contain these monohalogenated dimers were also analyzed by LC. The basic instrument consisted of a Waters Associates Model 6000A pump and a Schoeffel Instrument Corp. Model SF 770 UV-vis variable wavelength detector. The electrolyzed 9-chlorofluorene mixtures were separated on a 0.25-in., 25-cm stainless steel column of LiChrosorb RP18, 10-$\mu$m mean particle size. The flow rate of the eluting solvent (85/15 methanol-water) was 1 mL/min. To separate the electrolyzed benzhydryl chloride mixtures, a 0.25-in., 25-cm stainless steel column of LiChrosorb RP8, 10-$\mu$m mean particle size, was used. The eluting solvent was 80/20 methanol-water; the flow rate was 1 mL/min. Calibration curves for the standards were constructed daily.

**Chemicals.** With the exceptions of 9-chloro-9,9′-bifluorenyl,[28] 9-bromofluorene,[29] 1-chloro-1,1,2,2-tetraphenylethane,[30] tetrabutylammonium hexafluorophosphate,[31] and bifluorenylidene,[32] all chemicals were commercially available. Each commercial sample was further purified by established procedures and its final purity checked by a melting point determination and/or by chromatography. Heat- and light-sensitive reagents were stored at 0 °C in well-sealed brown glass bottles. With the exception of solvents, all reagents were stored in a vacuum desiccator over phosphorus pentoxide. *N,N*-Dimethylformamide (Burdick and Jackson) was purified by passage through a column of alumina, 80–200 mesh, of Brockman activity 1 activated at 600 °C overnight, and was collected over a mixture of activated Davison 4A molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. The transfer of the solvent to the vacuum line and the subsequent handling of the solvent and supporting electrolyte have been described previously.[33]

**Cells, Electrodes, and Electrolysis Procedure.** All electrochemical experiments were performed on an all-glass vacuum line. The solvent was transferred into the cell on the vacuum line by trap-to-trap distillation. All potentials are with respect to cadmium amalgam which is in contact with an anhydrous dimethylformamide solution that is saturated with both cadmium chloride and sodium chloride. This electrode is reported to have a potential of −0.75 V vs. the aqueous saturated calomel electrode.[3] The platinum working electrodes, cell designs, and general electrolysis procedures have been described previously.[34] All chronoamperometric experiments were performed on a planar platinum button electrode with a geometric area of 0.25 $cm^2$. Cyclic voltammetric experiments were performed with both this electrode and a planar vitreous carbon electrode.[35]

The extent of large-scale electrolyses was monitored periodically by cyclic voltammetry. At the conclusion of the experiment, the electrolysis mixture was either oxidized at a potential which would oxidize all anions or anion radicals that had been produced or protonated in a dry helium atmosphere with diethyl malonate. The mixtures were then analyzed directly by gas chromatography and/or high-pressure liquid chromatography.

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(35) We thank Professor D. E. Bartak, The University of North Dakota, for a gift of this electrode.

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# Reappraisal of the Stereochemistry of Electrophilic Additions to 3-Norcarenes. X-ray and $^1$H NMR Analysis of Norcarene Epoxide Conformation. The Role of Magnetic Anisotropic Contributions of Epoxide Rings

**Leo A. Paquette,* William E. Fristad,[1] Cliff A. Schuman, Mark A. Beno, and Gary G. Christoph***

*Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.*
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**Abstract:** The stereochemical outcome of the addition of singlet oxygen, Br$^+$, and peracid to four structurally varied 3-norcarenes has been investigated to obtain direct insight into prevailing product-determining steric effects in these systems. The various end products have been interconverted chemically to elucidate relative configuration. The stereochemical assignments have been established by reference to two 7,7-dibromo epoxides, the structures of which were elucidated by three-dimensional X-ray methods. Approach of an electrophile anti to the cyclopropane ring was seen to be preferred in each of the cases examined, although the product ratios did vary with the particular substitution plan. The preferred conformations of the 3-norcarene epoxides have been assessed by $^1$H NMR spectroscopy through analysis of vicinal coupling constants. Finally, the question of epoxide ring anisotropy effects is addressed.

Recently, several papers from this laboratory described impressively stereocontrolled photooxygenation reactions of 3-norcarenes and norcaradienes which were interpreted in terms of effective quenching by proximate hydrazide functionality.[2-4] The electronic relaxation of $^1\Delta_g$ singlet oxygen was thought to arise when the ionization potentials of $^1O_2$, the hydrazide moiety, and the olefinic center, as well as the frontier orbital relationship between them, were properly ordered. Structural assignments to the individual products were made on the basis of their respective $^1$H NMR spectra, supportive Eu(fod)$_3$ pseudocontact shifting in selected cases, and chemical interconversions where suitable.

In view of the important implications of these conclusions, we felt compelled to further substantiate these observations and test the scope of the phenomenon by more extensive experimentation. Unfortunately, we have not found it possible to duplicate certain fundamental experimental data reported earlier,[5] and have, in fact, shown that various hydrazides are not truly effective in their ability to quench the reactivity of singlet oxygen.[6] Subsequently, we concluded that some of the original stereochemical assignments were likely in error, despite the large number of experiments addressed previously to this question. Additional work of a totally unequivocal nature was obviously required and recourse has now been made to complementary three-dimensional X-ray crystallographic analysis.

The present paper addresses the general question of electrophilic additions (including $^1O_2$) to variously substituted 3-norcarene systems and analyzes those complications frequently associated with interpretation of the $^1$H NMR spectra of epoxides. The ensuing paper[7] describes new results which show stereoelectronic control of singlet oxygen reactivity by hydrazides to be a myth.

## Electrophilic Additions

**3-Norcarene.** Early $^1$H NMR studies of the alicyclic methylene proton region of **1**, readily available from the Simmons–Smith cyclopropanation of 1,4-dihydrobenzene,[8]

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