An Electrochemical and Spectrophotometric Study of the Reduction of Some 9-Substituted Fluorenes in Dimethylformamide[1]

Avinash Lagu and Harry B. Mark, Jr.*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

John R. Jezorek

Department of Chemistry, The University of North Carolina at Greensboro, Greensboro, North Carolina 27412

Received May 17, 1976

Electrochemical and spectrophotometric results for the electrode reduction in DMF of the nonalternant hydrocarbon fluorene substituted at one 9 position by a methyl, phenyl, or benzyl group indicate that the radical anion originally produced decomposes to the fluorenyl anion and hydrogen. In the presence of proton donor the parent species is regenerated. If the second 9 position is substituted by a benzyl group the radical anion again yields the fluorenyl carbanion, which, in the presence of proton donor, yields the singly substituted fluorene. Fluorene substituted at the 9 position by two phenyl groups, two methyl groups, or a phenyl and a methyl group does not cleave any of these substituents. Rather in at least one case it appears as if C_{11}–C_{12} bond cleavage occurs instead. In none of these cases does a normal ECE type mechanism seem to occur.

The electrochemical reduction of alternant aromatic hydrocarbons has been shown to proceed by the so-called electrochemical–chemical–electrochemical (ECE) mechanism in electrochemically inert protic media.[2–7] The anion radical produced at the electrode abstracts a proton from the donor, with the subsequent reduction of the neutral radical. Another chemical step then follows this second electrochemical reduction. In aprotic media the anion radical must abstract protons from solvent, supporting electrolyte, another hydrocarbon molecule, or impurity, or return to starting material. Polarographically, most alternant aromatic hydrocarbons display two one-electron waves in aprotic media, and one two-electron wave, at more positive reduction potentials, in the presence of proton donors.

However, the situation for nonalternant aromatic hydrocarbons is not so clear. A few systems have been studied, with varying results. The type of molecule which has received most attention is that in which a bridge methylene is present between two parts of a benzenoid system. The bridge methylene contributes to the aromaticity of the ring system through hyperconjugative effects, and hence these compounds are considered nonalternant. Further, the methylene hydrogens are found to be weakly acidic (pK_a = 20–25).[8–10] Janata et al. studied the electrochemical reduction of 4,5-methylenephenanthrene and found that the usual ECE process occurred in the presence of proton donors, and even to a small extend in aprotic media where self-protonation took place.[10] It was found that 9,10-dihydro-4,5-methylenephenanthrene was a product in both situations, and that 4,5-methylenephenanthrene behaved as a typical alternant aromatic hydrocarbon. For this system a second wave was observed at more negative potentials under both proton-donor and aprotic conditions. This was attributed to reduction of the 9,10-dihydro-4,5-methylenephenanthrene, a fluorene derivative. Study of the nonalternant hydrocarbon fluorene (RH_2) itself by Jezorek et al. revealed behavior quite different from that of 4,5-methylenephenanthrene or other alternant hydrocarbons. This was true under both aprotic and proton-donor conditions.[11,12] It was found that the reduction of the protonated radical ($RH_3\cdot$) did not occur. That is, after the initial electrochemical and chemical steps, the mechanism was different from those previously studied. In the presence of proton donors, in fact, both polarographic and constant-potential electrolysis yielded an n value of 3, rather than the usual 2. Jezorek et al. proposed a mechanism in which loss of a 9-hydrogen atom was a product-determining step. When similar experiments were done on fluoranthene these anomalous results were not obtained, thus implicating the 9 position in the mechanism of the three-electron reduction of fluorene.[12]

In order to better understand the electrochemical behavior of nonalternant hydrocarbons, a series of 9-substituted fluorenes was examined in this study under both proton-donor and aprotic conditions. The aprotic experiments were expected to answer the question of whether parent hydrocarbon participated in self-protonation of the radical anion, as was postulated for fluorene.[12] The 9-substituted fluorenes are expected to be more acidic than fluorene itself.[13] Some 9,9-disubstituted fluorenes were also studied, and for these, of course, there are no hydrogens in the 9 position and parent participation is not possible. These 9-substituted and 9,9-disubstituted fluorenes were also studied under proton-donor conditions to see if anomalous results such as were found for fluorene would be obtained.

The species included in this investigation are 9-methylfluorene (9-MF), 9-phenylfluorene (9-PF), 9-benzylfluorene (9-BF), 9,9-dibenzylfluorene (DBF), 9-phenyl-9-benzylfluorene (PBF), 9-benzyl-9-methylfluorene (BMF), 9,9-diphenylfluorene (DPF), 9-phenyl-9-methylfluorene (PMF), and 9,9-dimethylfluorene (DiMF).

Results and Discussion

This discussion will be broken into three parts because the nonalternant fluorene derivatives investigated in this study were found to display three distinct types of electrode reduction behavior. Those fluorenes substituted at only one of the two 9 positions exhibited one identifiable mechanism; those substituted at one 9 position by a benzyl group and at the other by some other moiety were found to have a second type of mechanism; and those disubstituted fluorenes in which neither 9 substituent was a benzyl group displayed yet a third type.

The Monosubstituted Fluorenes. A. Aprotic Conditions. All of the monosubstituted fluorenes exhibited a one-wave polarogram under aprotic conditions in dimethylformamide (DMF), and a diffusion limited current, i_d, linearly dependent on the square root of the height of the mercury column, $h^{1/2}$, suggesting a diffusion controlled process.[14] The quantity $E_{3/4} - E_{1/4}$ (the potential at $i = \frac{3}{4}i_d$ and $\frac{1}{4}i_d$, respectively) was determined for each polarogram and found to be 0.060 ± 0.005 V, suggesting a reversible one-electron process.[15] Cyclic voltammograms at about 0.2 and 2 V/s scan rates were taken for all three fluorene derivatives, with 9-MF showing an oxidation peak upon potential scan reversal at both scan rates, and 9-PF exhibiting evidence of an oxidation

Table I. Electrochemical and Spectral Data for the Substituted Fluorenes in DMF under Aprotic Conditions[a]

Substrate	$-E_{1/2}$, V[b]	CV oxidation wave[c]		λ_{max} for anion(s), nm[d]	Radical anion	Coulometric n value
		0.2 V/s	2.0 V/s			
9-BF	3.30	No	No	382	No	1
9-PF	3.16	No	Yes	372, 410 (sh), 490	No	1
9-MF	3.28	Yes	Yes	383	No	1
DBF	3.26	No	No	390–410, 490	No	2
PBF	3.09	No	No	390, 500	No	2
BMF	3.23	No	No	330, 350, 385	No	2
DPF	3.18	Yes	Yes		Yes, blue	
DiMF	3.39	Yes	Yes		Yes, blue	
PMF	3.22				Yes, blue	

[a] All substrates exhibited linear i_d vs. $h^{1/2}$, one wave polarograms with n values of 1, and an $E_{3/4} - E_{1/4}$ of 0.060 ± 0.005 V. [b] Vs. $Ag/AgClO_4$ (satd). [c] Cyclic voltammetric. [d] Produced coulometrically in special flow cell.

peak at the faster scan rate but not the slower. The 9-BF showed no evidence of an oxidation wave.

Controlled potential electrolysis at a mercury pool electrode in a specially designed flow cell allowed the UV–visible spectrum of the electrolysis products to be obtained during the reduction process.[16] Observed peaks were at 382 nm for 9-BF, 372, 410 (shoulder), and 490 nm for 9-PF, and at 383 nm for 9-MF (Table I). These peak positions correspond fairly closely to those reported by Bowden and Cockerill[13] in other solvents for the anions of the respective substrates. Addition of an excess of D_2O to the electrolysis solution produced a quantitative yield of the starting material 40–80% deuterated at the 9 position as determined by NMR spectroscopy. Constant potential electrolysis in an ordinary H-type cell carried out on the plateau of the polarographic wave gave an n value of about 1.0 for all three hydrocarbons as determined by integration of the current–time (i–t) curve. The same n value was obtained in the flow-cell experiments using 0.001 M substrate. The colored carbanion could be seen forming at the electrode for all three species. As these anions are sensitive to air,[12] conventional workup techniques could not be employed. At the conclusion of the electrolysis water was added to the electrolyzed solution and the product extracted with hexane. Evaporation of the hexane gave the 9-substituted substrate in quantitative yield. A summary of the electrochemical and spectral data for the three 9-substituted fluorenes is given in Table I.

B. Proton-Donor Conditions. The three monosubstituted fluorene derivatives exhibited similar behavior upon electrolysis in the presence of proton donor, just as they had under aprotic conditions. No change in $E_{1/2}$ was observed when polarograms were performed in hydroquinone media, but acute maxima were observed when the proton donor concentration was about 0.01 M and higher. The polarographic limiting current increased anywhere from 7- to 13-fold compared to the aprotic value and depending on the substrate used, when the proton donor concentration was increased from zero to about 0.1 M. The increase in i_d for these compounds was very small up to about 0.001 M hydroquinone. From this point up to the highest concentration of proton donor studied, 0.1 M, i_d increased rapidly in an exponential-like fashion. This description of the i_d vs. hydroquinone concentration curve holds for all the species reported in this study with only quantitative differences, the reasons for which are not clear.

Constant potential electrolysis in hydroquininone media did not produce an exponentially decreasing current. Instead a constant value much higher than background was observed. Extensive gas evolution at the cathode was obtained, and workup of the reaction mixture yielded only substrate as product. Constant potential electrolysis in the presence of hydroquinone of 9-PF and 9-BF deuterated at the 9 position was carried out under the same conditions as were used for the nondeuterated compounds. Again the only product was starting material in each case. Analysis of the products by NMR spectroscopy revealed that about 60% replacement of deuterium by proton had occurred. It should be pointed out that when 50% replacement of deuterium by proton has occurred, the probability of deuterated and nondeuterated fluorenes being reduced at the electrode is the same. Because the electrolysis current did not go to zero with time in 0.02 M hydroquinone media, an n value could not be calculated. It should be noted that results for both the macrocoulometry and flow-cell coulometry experiments were identical. While psuedo-first-order kinetics probably did not hold in the macrocoulometry situation as the hydroquinone excess over substrate was only twofold, a situation much closer to first order existed in the flow-cell experiments where a 20-fold or more excess of proton donor was used.

Based on the aprotic and hydroquinone media electrolysis experiments an overall mechanism for 9-BF, 9-PF, and 9-MF can be proposed.

$$\mathrm{ARH} + e^- \rightleftharpoons \mathrm{ARH}\cdot^- \qquad (1)$$

$$\mathrm{ARH}\cdot^- \rightarrow \mathrm{AR}^- + \tfrac{1}{2}H_2 \qquad (2)$$

where R = benzyl, phenyl, or methyl.
In the presence of proton donor:

$$\mathrm{AR}^- + \mathrm{HX} \rightarrow \mathrm{ARH} + \mathrm{X}^- \qquad (3)$$

The cyclic voltammetric experiments demonstrate that the radical anions are not especially stable, even though at faster scan rates, and for 9-MF, evidence of reversibility at the electrode is obtained. It would appear, however, that the anions are relatively stable compared to the radical anions, as the carbanions fulfill the $4n + 2$ rule of aromatic resonance stabilization.[17] The overall mechanism then appears to be one of cyclic regeneration of substrate, rather than the possible ECE pathway, that is, reactions 2 and 3 rather than 4.

$$\mathrm{ARH}\cdot^- \xrightarrow{\mathrm{HX}} \text{neutral radical} \rightarrow \text{further reduction} \qquad (4)$$

The first of the two possible pathways for decomposition of the radical anions, 2 and 3, catalytic hydrogen reduction, apparently predominates for all three singly substituted fluorenes under the conditions of this study.

9,9-Disubstituted Fluorenes Containing the Benzyl Group. A. Aprotic Conditions. Just as for the singly substituted fluorenes described above the doubly substituted, benzyl-containing fluorenes were found to have one-wave polarograms under aprotic conditions in DMF. In addition, they exhibited an i_d linearly dependent on $h^{1/2}$, and an $E_{3/4} - E_{1/4}$ of 0.060 ± 0.005 V. Cyclic voltammograms at scan rates of about 0.2 and 2 V/s showed no evidence of an oxidation wave with potential reversal. This indicates an overall irreversible process, at least under these experimental conditions. Constant potential electrolysis on the plateau of the polarographic wave, performed in the special flow cell, produced colored reaction products with broad absorption spectra. These spectra appeared to be a composite of a mixture of product species, one of which may have been the benzyl anion,[18-20] another the anion of the fluorene fragment. In addition there may have been present some species produced by reaction of these carbanions with traces of oxygen.[12] The electrochemical and spectrophotometric data are summarized in Table I. When water was added to the electrolyzed solution in either the flow cell or regular H cell, the mixture extracted with hexane, and the hexane evaporated, only singly substituted fluorene was obtained; a benzyl group was lost in all three cases. Integration of the *i–t* curve under aprotic conditions in both the coulometric–spectrophotometric and massive electrolysis experiments yielded an *n* value of approximately 2 for each of the three doubly substituted, benzyl-containing fluorenes. This result was unexpected because the polarographic limiting current was about the same as that for fluorene itself, a known one-electron reduction. As the diffusion coefficients for these substituted fluorenes are expected to be about the same as for fluorene, it follows that reduction of the substituted fluorenes should also be a one-electron process. It is a fact, however, that constant potential electrolysis at a mercury pool, where reaction products can accumulate and where the solution is stirred, is a different experiment than polarography, where the dropping-mercury electrode is being constantly renewed with fresh mercury and the solution is unstirred.[14]

B. Proton Donor Conditions. Polarography performed on the disubstituted, benzyl-containing fluorenes in the presence of varying concentrations of hydroquinone was not accompanied by a significant shift in $E_{1/2}$ with increased proton donor concentration as required for an ECE type mechanism. However, i_d was threefold higher for DBF and ninefold for PBF and BMF at 0.1 M hydroquinone as compared to the aprotic values. Constant potential electrolysis in the presence of hydroquinone showed behavior for DBF similar to that of 9-BF; for PBF similar to 9-PF; and for BMF similar to 9-MF. Extraction of the electrolyzed mixture with hexane yielded only the monosubstituted fluorene species mentioned above, a benzyl group having been lost in each case. Based upon the *n* value obtained coulometrically and the monosubstituted products recovered from the hexane extraction, it would appear that cleavage of a benzyl radical occurs upon addition of one electron to the disubstituted, benzyl-containing fluorenes, but that this cleavage is sufficiently slow or otherwise different so as to not influence the polarographic behavior. Indications are that even in the presence of proton donor the rate of cleavage is fast compared to protonation (ECE pathway) or that even if protonation does occur, the neutral radical is not further reduced and subsequent cleavage still occurs. Coulometric *n* values in the presence of hydroquinone were impossible to calculate as, after a time, the current leveled out at a value much higher than background.

As the monosubstituted fluorene fragment was recovered in all cases there is no question that benzyl-group cleavage occurs. In order to explain the *n* value of 2 it would seem reasonable to postulate that the benzyl fragment is further reduced to the anion,[21] and reacts with solvent and/or impurities to form toluene. However, attempts to identify toluene in the reaction mixture were not fruitful, nor were efforts to identify bibenzyl (formation of which, however, cannot explain an *n* value of 2). Therefore, the total mechanistic picture remains unclear. Benzyl cleavage is certain, however, as is formation of the monosubstituted fluorene fragment *via* protonation of the carbanion.

It should be noted that the monosubstituted fluorene fragment is itself electroactive, and at the higher proton donor concentrations, i_d increases markedly, as was seen for the three monosubstituted fluorenes discussed earlier. Therefore, the electrolysis current, leveling off at a value much higher than background in the presence of proton donor, can be considered to be a composite of the reduction of the disubstituted fluorenes, and monosubstituted fluorene fragment, and possibly of the benzyl fragment. The fluorene fragment facilitates catalytic hydrogen ion reduction, as explained in the section on monosubstituted fluorenes, and results in large current increases as the proton donor concentration is increased.

That it is a benzyl radical that splits off the parent fluorene molecule rather than a phenyl or methyl group can be ascribed to the fact that the benzyl radical is resonance stabilized to a greater extent than either the $CH_2\cdot$ or $C_6H_5\cdot$ radicals. Kerr[22] and Benson[23] have shown that the homolytic dissociation energy of the H_3C–H bond in methane and the C_6H_5–H bond in benzene is about 104 kcal/mol for both but for the $C_6H_5CH_2$–H bond of toluene is only about 85 kcal/mol. It thus appears as if the benzyl radical is about 19 kcal/mol more stable than the methyl and phenyl radicals.

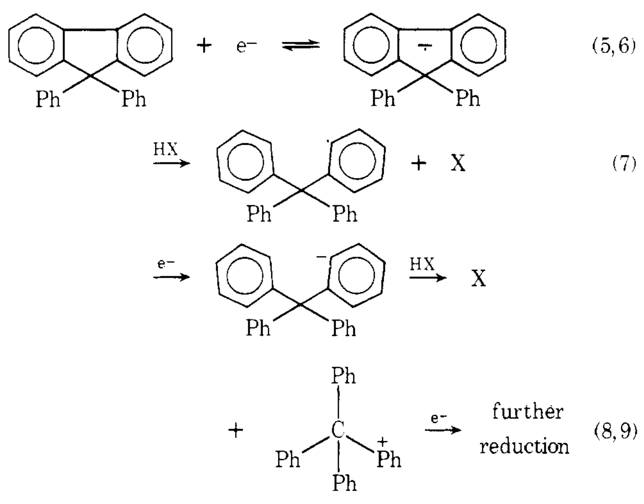
It is interesting to note that while carbon–carbon bond cleavage is not uncommon for alkali metal reduction of disubstituted fluorenes[24,25] or for electrochemical oxidations,[26] it is a very unusual process for electrochemical reductions. It is possible that the very stable cyclopentadienyl-type structure of the fluorene anion makes it a good leaving group, not unlike a halide-anion leaving group in the electrochemical reduction of organic halogen compounds.[27]

Disubstituted Fluorenes Not Containing a Benzyl Group. A. Aprotic Conditions. Just as for the six fluorenes described previously, DPF, PMF, and DiMF gave one-wave polarograms under aprotic conditions in DMF solvent, and exhibited an i_d linearly dependent on $h^{1/2}$ and an $E_{3/4} - E_{1/4}$ of 0.060 ± 0.005 V. Cyclic voltammograms of DPF and DiMF at scan rates of about 0.2 and 2.0 V/s possessed oxidation peaks in all cases, and potential differences between the cathodic and anodic peaks of 56 and 60 mV, respectively. This is close to the Nernstian value of 59 mV expected for a reversible one-electron process. The electrochemical and spectral data are summarized in Table I.

Constant potential electrolysis on the plateau of the polarographic wave produced the blue anion radicals of the substrates for all three fluorene compounds. No breakdown of these anion radicals to the yellow-red carbanions could be detected even after several hours standing under the nitrogen atmosphere. It appears that the anion radicals of these three species are much more stable than those discussed earlier.

Addition of water to the electrolyzed DPF solution, extraction with hexane, and evaporation of the hexane yielded a white solid with three components as shown by thin layer chromatography on alumina, with hexane developer. However, 9-PF was not one of the products as may have been suggested by the reactions of the disubstituted fluorenes discussed earlier or by the metalation studies of Janzen and coworkers.[25] For PMF and DiMF a similar extraction procedure yielded a colorless oil as product. Gas chromatographic analysis of the oil from DiMF on a Carbowax 20M column at 180 °C showed four components, none of which was 9-MF. Thin layer chromatographic analysis, with hexane developer, of the oil from PMF electrolysis showed no 9-PF or 9-MF. None of the products were identified further as these analyses and the long-term stability of the radical anions indicates that the cleavage of 9 substituents observed for the benzyl-substituted fluorenes does not occur in these three cases.

B. Proton Donor Conditions. Polarography of these three disubstituted fluorenes in the presence of increasing concentrations of hydroquinone resulted in an increase of i_d and a positive shift in $E_{1/2}$, as expected for an ECE mechanism. In 0.10 M hydroquinone the i_d was about 12, 6, and 6 times larger than under aprotic conditions for DPF, DiMF, and PMF, respectively. Shifts in $E_{1/2}$ were about 9, 7, and 8 mV respectively, quite small compared to the usual ECE situation of perhaps 50–100-mV shifts. Also, acute maxima were observed at proton donor concentrations above 5×10^{-2} *M*. Extraction with hexane of the solutions from exhaustive electrolysis of the three fluorene derivatives gave the same products as are discussed above. Again, in the presence of proton donor, it appears as if loss of a 9 substituent does not occur. Apparently only the 9-benzyl group, of the series of substituents studied, is a good leaving group. Reaction products were not identified individually because it was clear that cleavage at the 9 position did not occur. An exception to this was the solid product resulting from DPF electrolysis. This solid had a very high melting point, about 230 °C, and its UV spectrum exhibited a peak near 222 nm and a broad, less intense, band centered around 270 nm, virtually identical with the spectrum of tetraphenylmethane.[28] The mass spectrum exhibited two peaks of roughly equivalent intensity with *m/e* values of 322 and 320. A possible mechanism can be postulated as follows. The radical anion of DPF can undergo a reaction with proton donor at C_{11} or C_{12} (equivalent positions) resulting in cleavage of the C_{11}–C_{12} bond and the production of tetraphenylmethane (mol wt 320). Subsequent reduction and protonation of a double bond would result in a product of molecular weight 322. Major peaks for both of these species were observed in the mass spectrum, as indicated above.



This mechanism is still speculative, as not enough corroborating evidence is on hand, but it does appear as if C_{11}–C_{12} bond cleavage occurs, unlike the situation for the other fluorene derivatives studied.

Conclusions

Of the fluorene derivatives reported in this investigation the singly substituted species most resemble fluorene itself in mechanism. Both fluorene and the singly substituted derivatives are thought to release a hydrogen atom after the first reduction step[12] rather than being protonated and further reduced as in a normal ECE sequence. Also, the three carbanions produced all react with oxygen, as does fluorenyl carbanion, to produce fluorenone.[12]

The doubly substituted derivatives, of course, cannot release a hydrogen atom, but do either cleave a benzyl group from the 9 position or apparently undergo cleavage of the five-membered ring system itself. For some reason, not understood at this time, these nonalternant hydrocarbons do not follow the usual ECE reaction pathway to a dihydro reduction product, but rather shed 9-position substituents or (apparently) cleave the C_{11}–C_{12} bond. Continued investigations are underway in our laboratory to attempt to understand the reasons for this unusual behavior.

Experimental Section

Instrumental. All electrochemical measuremnts were carried out using a Princeton Applied Research Model 173 potentiostat, Model 176 current-to-voltage converter with digital readout, and Model 178 electrometer probe. Reproducibility of potential settings was about ±2 mV. The ramp voltage for polarography was generated using a circuit described by Means.[29] An Exact Model 126b VCF sweep generator was used to obtain triangular waves of the desired frequency for cyclic voltammetry. Recording of some of the electrochemical experiments was done on an Electro Instruments Model 500 X-Y recorder. Cyclic voltammograms were recorded and stored on a Tektronix Model 5103N oscilloscope, and photographs taken with a C-5 oscilloscope camera. Cyclic voltammetry experiments utilized a Metrohm Model E 410 hanging-mercury-drop electrode.

Exhaustive, controlled potential, massive electrolysis experiments were carried out using a conventional H-type cell equipped with a fine-porosity, sintered-glass frit separating cathode and anode compartments. The mercury-pool cathode was continuously stirred by a magnetic stirrer to expose fresh metal surface during electrolysis. Simultaneous coulometric–spectrophotometric experiments were carried out using a special flow cell designed by Janata and Mark.[16] This cell, designed for the cell compartment of the Cary 14 spectrophotometer, allowed the spectra of electrode reaction products to be observed during the electrolysis.

The reference electrode used was constructed from two 2-cm lengths of 4-mm glass tubing separated by a 2-cm length of Corning Glass Works porous cane (thirsty glass). All three pieces were then covered by heat-shrinkable polyethylene tubing. A second piece of polyethylene tubing was sealed to one of the pieces of glass tubing, and this compartment filled with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) in DMF, and the end closed off with a 1 cm piece of porous cane. This compartment served as the salt bridge. The top compartment contained a saturated solution of $AgClO_4$ in 0.1 M TBAP–DMF solution. A length of polished silver wire was immersed in this solution as the electrical contact element. This electrode was equilibrated for at least 24 h before use, and all air bubbles were removed. These electrodes were found to be stable for several weeks.

Chemicals and Solutions. TBAP (G. F. Smith) was dissolved in a minimum of acetone and the solution filtered; it was then precipitated by adding distilled water, filtered, and washed twice with distilled water. This product was dissolved again in acetone, precipitated with ethyl ether, filtered, washed three times with ethyl ether, and dried in a vauum oven at 100 °C for 6 h. This procedure completely removed iodide impurity. DMF (Burdick and Jackson, Distilled in Glass) was dried by the method of Moe.[30] Dimethylamine impurity produced was removed by degassing under vacuum for 2 h. Purified solvent was stored over activated Linde Type 5A molecular sieves for at least 72 h before use. The D_2O used was the usual high purity, commercially available grade. If Karl Fischer titration showed the water content of the stock DMF to be less than 0.015%, the solvent was used directly without purification after storing over sieves as above. Background currents of all solvent–0.1 M TBAP solutions were less than about 0.2 μA at the point of solvent breakdown, about −3.6 V.

All electrochemical solutions were 0.1 M in TBAP. The concentration of electroactive species was about 0.001 M for polarographic, cyclic voltammetric, and coulometric–spectrophotometric experiments, and 0.01 M for exhaustive electrolysis studies. Solutions for protic electrolysis were about 0.02 M in hydroquinone.

Polarographic and cyclic voltammetric solutions were deoxygenated by bubbling nitrogen (high purity, Delta Products) for at least 15 min and solutions for controlled potential electrolysis for at least 30 min before reaction; and a nitrogen atmosphere was maintained over the solutions during the course of the measurement. The nitrogen was dried and deoxygenated as described previously.[12]

Extraction of controlled potential electrolysis solutions was done with reagent grade hexane. The solution from the cathode compartment was pipetted into a separatory funnel containing 100 ml each of hexane and water. The hexane extracts were combined and backwashed with three 100-ml portions of water to remove DMF. The hexane layer was then run through several layers of filter paper to remove water and the solvent removed on a rotary evaporator.

Syntheses. 9-MF. The method of preparation was essentially that of Scherf and Brown[31] and Murphy and Hauser[32] using 1,2-dimethoxyethane solvent, phenyllithium (Alpha Products, 1.4 M in 70:30 benzene–ether) as the proton-abstracting agent, and methyl iodide. Benzene extraction and $CaCl_2$ drying produced a yellow oil, which was chromatographed on neutral alumina. The 9-MF (first fraction off) was decolorized with charcoal. Prior to electrolysis the 9-MF was dissolved in benzene and filtered through a short column of alumina. The filtrate was evaporated to dryness under nitrogen giving a product of mp 44–45 °C (lit.[33] 45 °C).

9-BF. Essentially the same method as given by Scherf and Brown[31] and Murphy and Hauser[32] was used here, employing 1,2-dimethoxyethane, phenyllithium, and benzyl chloride, followed by ether extraction and $CaCl_2$ drying. The crude product was recrystallized from methanol giving a species melting at 135 °C (lit.[33] 134–135 °C).

9-PF. The procedure of Kovache[34] and Mathieu[35] was followed for this species, yielding a product with mp 145 °C (lit.[33] 145 °C).

DBF. The method of Scherf and Brown[31] was utilized, yielding a product melting at 147–148 °C (lit.[31] 146 °C).

DiMF. A procedure essentially the same as that for DBF was used.[31] The product exhibited a mp of 95–96 °C (lit.[33] 95–96 °C). Alumina filtration of a benzene solution of DiMF was performed prior to electrochemical use, as noted above for 9-MF.

DPF. Attempts to use the procedure of Gilman[36] and Gorsich were unsuccessful, and a modified procedure had to be developed. 2-Phenylbenzoic acid (25 g) was dissolved in 300 ml of methanol and 2 ml of concentrated H_2SO_4 was added. This mixture was then refluxed for 18 h. The methanol was stripped off with a rotary evaporator and the residue washed with water until rinsings were neutral. The product was dissolved in ether, dried with $CaCl_2$, placed in a 300-ml three-neck flask, and purged several times with nitrogen. Phenyllithium (0.25 mol) was added slowly over a period of 60–75 min. The mixture was cooled and stirred for 12 h under nitrogen. Then 10% (v/v) HCl in methanol was added until the solution was acid to litmus. The solution was then extracted with water several times until the extracts were neutral to litmus. The ether layer was shaken with $CaCl_2$ and evaporated on a rotary evaporator, and 200 ml of acetic acid was added to the residue. This solution was refluxed for 15 min, at which time DPF crystallized out. This was recrystallized from methanol to give a product with mp 223 °C (lit.[37] 222 °C).

Anal. Calcd for $C_{25}H_{18}$: C, 94.32; H, 5.68, mol wt, 318. Found: C, 94.22; H, 5.68, mol wt, 318.

BMF. 9-Benzylfluorene (5 g, 0.02 mol) was added to 50 ml of dioxane in a three-neck, 300-ml flask which was purged with nitrogen several times. Potassium (0.78 g, 0.02 mol) was added with nitrogen flowing. The flask was again purged. The solution was refluxed for 2 h and cooled, and 5 ml of methyl iodide (slight excess) was added with a syringe. The solution was stirred for 2 h under nitrogen, 40 ml of water containing 4 ml of HCl was added, and the solution was repeatedly extracted with benzene. The benzene extracts were backwashed with water to remove dioxane, dried with $CaCl_2$, and evaporated to dryness. The crude BMF was recrystallized three times from hexane to give a product with mp 99 °C.

Anal. Calcd for $C_{21}H_{18}$: C, 93.33; H, 6.67, mol wt, 270. Found: C, 93.31; H, 6.70, mol wt, 270.

PBF and PMF. 9-PF (50 g, 0.02 mol) was dissolved in 50 ml of 1,2-dimethoxyethane in a 300 ml, three-neck flask. After thorough purging with nitrogen 0.02 mol of phenyllithium was added with a syringe. The mixture was refluxed for 2 h, cooled to room temperature, and 3.0 g of benzyl chloride slowly added from a syringe. The solution was stirred for 2 h under nitrogen and 40 ml of water containing 4 ml of concentrated HCl was added. The reaction mixture was extracted several times with benzene and the extracts were combined and backwashed with water to remove the solvent. The benzene extracts were then dried with $CaCl_2$, filtered, and evaporated to dryness. The crude PBF was recrystallized from ethanol to give a product with mp 141 °C (lit.[33] 140 °C).

Anal. Calcd for $C_{20}H_{16}$: C, 93.97; H, 6.03. Found: C, 93.85; H, 6.05.

PMF was prepared similarly except that methyl iodide was, of course, used instead of benzyl chloride. The pure PMF had mp 84 °C (lit.[33] 85 °C).

Prior to electrolysis these species were filtered through alumina, as explained above.

9-Phenyl-9-deuteriofluorene. As above, the anion of 9-PF was prepared by dissolving 3.0 g of 9-PF in 40 ml of dioxane in a three-neck flask, purging with nitrogen, adding 0.015 mol of phenyllithium, and refluxing for 2 h under nitrogen. The red anion was clearly seen. After cooling to room temperature, 5 ml of 99+% D_2O (an excess) was added by syringe. This solution was stirred for 2 h under nitrogen, and then 40 ml of water containing 4 ml of HCl was added. Benzene extraction, water backwashing, $CaCl_2$ drying, and evaporation to dryness then followed. Crude, deuterated 9-PF was dissolved in benzene, the solution filtered through a small column of neutral alumina, and the filtrate evaporated under a stream of nitrogen followed by vacuum drying for 2 h. The NMR of 9-PF exhibits a peak for the 9 proton at δ 5.05,[35] while the deuterated material prepared as above had no detectable absorption in the range δ 4.75–5.25, indicating complete deuteration of the 9 position.

9-Benzyl-9-deuteriofluorene. This material was prepared in essentially the same manner as the deuterated 9-PF. To 2.50 g (0.01 mol) of 9-BF in 40 ml of dioxane was added 0.012 mol of phenyllithium. After refluxing, 5 ml of D_2O was added, then the H_2O–HCl mixture, followed by benzene extraction. The benzene extracts were water backwashed, dried with $CaCl_2$, and evaporated to dryness. Methanol was used to recrystallize the product. Alumina filtration was also used prior to electrochemical experiments. The NMR of 9-BF[35] exhibits a doublet centered at δ 3.10 due to the benzyl protons, and a triplet due to the 9-position proton centered at δ 4.20. The deuterated product prepared as described above exhibited only a singlet with integrated area corresponding to two protons at δ 3.10, but no signal at δ 4.20, indicating complete deuterium substitution at the 9 position.

Acknowledgments. This research was supported in part by the National Science Foundation, Grant NSF MPS 720514-A02.

Registry No.—9-BF, 1572-46-9; 9-PF, 789-24-2; 9-MF, 2523-37-7; DBF, 4709-64-2; PBF, 35377-96-9; BMF, 61076-90-2; DPF, 20302-14-1; DiMF, 4569-45-3; PMF, 56849-83-3; 2-phenylbenzoic acid, 947-84-2; phenyllithium, 591-51-5; methyl iodide, 74-88-4; benzyl chloride, 100-44-7; 9-phenyl-9-deuteriofluorene, 61076-91-3; D_2O, 7789-20-0; 9-benzyl-9-deuteriofluorene, 15480-52-1.

References and Notes

(1) Taken in part from the Ph.D. Thesis of A. L. Lagu, The University of Cincinnati, May 1974.

(2) G. J. Hoijtink, J. Van Shooten, E. de Boer, and W. J. Aalbersbert, *Recl. Trav. Chim. Pays-Bas*, **73**, 355 (1954).

(3) G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **73**, 895 (1954).

(4) P. S. Given and M. E. Peover, *J. Chem. Soc.* 385 (1960); *Collect. Czech. Chem. Commun.*, **25**, 3195 (1960).

(5) G. J. Hoijtink and J. Van Shooten, *Recl. Trav. Chim. Pays-Bas*, **71**, 1089 (1952).

(6) J. Janata and H. B. Mark, Jr., *J. Phys. Chem.*, **72**, 3616 (1968).

(7) (a) N. H. Velthorst and G. J. Hoijtink, *J. Am. Chem. Soc.*, **87**, 4529 (1965); (b) *ibid.*, *89*, 209 (1967).

(8) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721 (1967).

(9) A. Streitwieser, Jr., "Molecular Orbital Theory," Wiley, New York, N.Y., 1962, pp 414–415.

(10) J. Janata, J. Gendell, R. G. Lawton, and H. B. Mark, Jr., *J. Am. Chem. Soc.*, **90**, 5226 (1968).

(11) J. R. Jezorek and H. B. Mark, Jr., *Anal. Lett.*, **3**, 515 (1970).

(12) J. R. Jezorek, A. Lagu, T. Siegel, and H. B. Mark, Jr., *J. Org. Chem.*, **38**, 788 (1973).

(13) K. Bowden and A. F. Cockerill, *J. Chem. Soc. B*, 173 (1970).

(14) J. Herovsky and J. Kuta, "Principles of Polarography", Academic Press, New York, N.Y., 1966, pp 73–115.

(15) J. Tomes, *Collect. Czech. Chem. Commun.*, **9**, 12 (1937).

(16) J. Janata and H. B. Mark, Jr., *Anal. Chem.*, **39**, 1876 (1967).

(17) A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968).

(18) G. Hafelinger and A. Streitwieser, Jr., *Chem. Ber.*, **101**, 672 (1968).

(19) R. Asami, M. Levy, and M. Szwarc, *J. Chem. Soc.*, 361 (1962).

(20) R. Waack and M. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

(21) C. K. Mann, J. L. Webb, and H. M. Walborsky, *Tetrahedron Lett.*, 2249, (1966).

(22) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(23) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(24) G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **39**, 1388 (1961).

(25) E. G. Janzen, W. B. Harrison, and J. B. Pickett, *J. Organomet. Chem.*, **16**, 48 (1969).

(26) R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969.

(27) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970, pp 201–243.

(28) L. R. LaPaglia, *J. Mol. Spectrosc.*, **6**, 427 (1961).

(29) D. K. Means, Ph.D. Thesis, University of Michigan, 1970.

(30) N. S. Moe, *Acta Chem. Scand.*, **21**, 1389 (1967).

(31) G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 697 (1960).

(32) W. S. Murphy and C. R. Hauser, *J. Org. Chem.*, **31**, 85 (1966).

(33) G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **39**, 1388 (1961).

(34) A. Kovache, *Ann. Chim. (Paris)*, **10**, 205 (1918).

(35) A. Mathieu, *Bull. Soc. Chim. Fr.*, 1526 (1971).

(36) H. Gilman and R. Gorsich, *J. Org. Chem.*, **23**, 550 (1958).

(37) R. G. Clarkson and M. Gomberg, *J. Am. Chem. Soc.*, **52**, 2881 (1930).