# ELECTROCHEMICAL STUDIES OF WEAK CARBON AND NITROGEN ACIDS: FLUORENE AND *p*-CYANOANILINE IN DIMETHYLFORMAMIDE

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### ABSTRACT

The electrochemical reduction of fluorene and *p*-cyanoaniline in DMF at a platinum electrode is initially a one-electron process which affords the corresponding readical anions. In the absence of an added proton donor, decomposition of the radical anions occurs by carbonhydrogen bond cleavage to give the conjugate bases of the starting materials, the anions subsequently slowly abstract a proton from the tetraalkylammonium cation of the supporting electrolyte to regenerate the original electroactive species. In the presence of dimethylmalonate, both radical anions rapidly electron transfer to the added proton donor. Neither self-protonation nor protonation by the added donor was observed for either radical anion. In addition to proton abstraction, 9-fluorenyl anion reacts with oxygen to give fluorene and hydroxide ion. Abstraction of a proton from fluorene by the latter species then effects a chain reaction in which 9-fluorenyl anion is the chain-carrying species. Reduction of bifluorenyl occurs with carbon-carbon bond cleavage to give 9-fluorenyl anion as the initial product. Subsequent proton transfer from bifluorenyl to 9-fluorenyl anion then yields the final products, 9-bifluorenyl anion and fluorene, in equimolar amounts.

### INTRODUCTION

Recent studies from our laboratory have been concerned with the identification of the reaction pathways of transient carbene  $(R_2C^{-})$  [1,2] and nitrene  $(RN^{-})$  radical anions. During the course of those studies, kinetically controlled anodic waves were observed which we felt might be due to either these species or their corresponding hydrogen atom abstraction products,  $R_2CH^{-}$  and  $RNH^{-}$ . In order to distinguish between the two types of anionic species, we have prepared the diamagnetic anions by an independent electrochemical method based on the reductive elimination of hydrogen from their corresponding conjugate acids.

The weak carbon and nitrogen acids of interest to us include fluorene and p-cyanoaniline. Although the redox behavior of these species has been examined previously [3-5], the principal decomposition pathway of the corresponding radical anions in an aprotic medium, viz., loss of hydrogen, has not been reported. In addition, we have examined briefly the effects of added oxygen and electroinactive proton donors on the electrolytic reduction of fluorene and the redox behavior of bifluorenyl. The latter species is included in this report since it also affords 9-fluorenyl anion upon electroreduction.

## EXPERIMENTAL

#### Instrumentation

Cyclic voltammetry and chronoamperometry experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential loss between the reference and working electrodes [6]. Control of the potential and the acquisition and processing of data in the chronoamperometric studies were performed with a laboratory digital computer (LAB 8/e, Digital Equipment Corporation). The three-electrode potentiostat-coulometer which was used for the exhaustive, controlled-potential experiments has been described recently [7].

# Chromatography

Direct analysis of the electrolyzed mixtures was performed on temperatureprogrammed gas chromatographs (Hewlett-Packard, Model 700) which were equipped with flame-ionization detectors. Most of the separations were performed on either a 7-mm, 60-cm stainless steel column of 3% Dexil 300 gc (Olin Corp.) on 80/100 Chromosorb W or on a 7-mm, 60-cm stainless steel column of 3% FFAP on 80/100 Chromosorb W-HP. Calibration curves for the standards were constructed daily.

## Chemicals

With the exceptions of tetrabutylammonium perchlorate [8], tetrabutylammonium hexafluorophosphate [9], and bifluorenylidene [10], all chemicals were commercially available. The purity of each compound was checked by a melting point determination and/or by chromatographic methods. Heat- and light-sensitive reagents were stored at  $0^{\circ}$ C in well-sealed brown glass bottles. With the exception of the solvents, all reagents were stored in a vacuum desiccator (desiccant: phosphorus pentoxide). N,N-Dimethylformamide (Burdick and Jackson) was purified by passing through a column of alumina, 80–200 mesh of Brockman Activity 1, and was collected over activated Davison 4A Molecular Sieves. This procedure was carried out in a dry nitrogen-filled glove bag.

## Cells, electrodes, and electrolysis procedure

All electrochemical experiments were performed on an all-glass vacuum line. The solvent was distilled into the cell on the vacuum line with any traces of oxygen, if present, being removed by freeze-pump-thaw cycles. All potentials are in reference to cadmium amalgam in contact with an anhydrous dimethylformamide solution which 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 [11]. The platinum working electrodes and general cell design have been described previously [12].

The extent of electrolysis was monitored periodically by cyclic voltammetry. At the conclusion of exhaustive electrolysis, the solutions were either oxidized at a potential which would oxidize all anions that had been produced or protonated in a dry helium atmosphere with diethylmalonate. Yields of tributylamine were variable and dependent upon the rate and extent of electrolysis, the time elapsed before addition of the proton donor, and the rate of the Hofmann elimination reaction.

## RESULTS

### (A) Fluorene

In an aprotic medium. The cyclic voltammetric reduction of fluorene ( $E_{p,c} = -2.04 \text{ V vs. Cd(Hg)}$ ) at a platinum cathode occurs near the cathodic limit of the DMF-(n-Bu)<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub> solvent-supporting electrolyte system (Fig. 1a). As evidenced by the ratio of anodic to cathodic peak heights, the one-electron reduction product, fluorene radical anion (FlH<sub>2</sub>), decomposes slowly on the time scale of this experiment ( $v = 0.2 \text{ V s}^{-1}$ ) to give a kinetically linked product which is oxidized irreversibly at a much more positive potential ( $E_{p,a} = 0.08 \text{ V}$ ). No additional electrochemical processes are seen on the second and subsequent cycles.

The exhaustive, controlled-potential electrolysis of fluorene at the potential of -1.95 V affords the conjugate base of fluorene (FlH<sup>-</sup>) as the only electroactive



Fig. 1. (a) Cyclic voltammogram of  $4.81 \times 10^{-3} M$  fluorene in 0.1 M TBAPF<sub>6</sub>-DMF at a planar platinum electrode with an area of 0.25 cm<sup>2</sup>. (b) Cyclic voltammogram of an exhaustively electrolyzed solution of  $10.47 \times 10^{-3} M$  fluorene in 0.1 M TBAPF<sub>6</sub>-DMF at a spherical platinum working electrode. The scan rate is 0.2 V s<sup>-1</sup>.

Represer	itative data for the co	ntrolled-potential electroly	rsis of several weak	carbon- and n	utrogen-centered a	cids
Entry no.	Compound	Concentration mM	$E_{applied}/V$	<i>n</i> value	Supporting electrolyte	Products, yields
1	Fluorene	4.91	-1.95	3.30	TBAPF <sub>6</sub>	Fluorene, $91\% a$ , tributylamine, $161\%$
2	Fluctene $b$	8 84	-1.95	1.84	TBAP	
1			0.40	0.69		Fluorene, 65% <sup>a</sup> , bifluorenyl, 34%; tributylamine, 74%
co co	Fluorene <sup>c</sup>	4.89	-1.95	2.00	TBAP	Fluorene, 98%
4	Fluorene <sup>d</sup>	5.71	-1.95	0.24	TBAP	Fluorenone, 98%
5	Bifluorenyl	8.52	-1.80	1.73	TBAP	Fluorene, 45% <sup>a</sup> ; bifluorenyl, 52%, tributylamine, 123%
9	<i>p</i> -Cyanoaniline	11.77	1.80	2.00	TBAP	<i>p</i> -Cyanoaniline, 96% <sup><i>a</i></sup> ; 4,4'- dıcyanobiphenyl, 4%, tributyl- amine, 107%
a The ele	otrad colution ma	se treated with diathvlmalo	mate prior to das o	hromatograph	ic analycic	

**TABLE 1** 

". The electrolyzed solution was treated with diethylmalonate prior to gas chromatographic analysis. <sup>b</sup> Upon completion of the reduction of fluorene to 9-fluorenyl anion, the electrolysis mixture was reoxidized at 0.40 V.

<sup>c</sup> Reduction was effected in the presence of 14.86 mM diethylmalonate. <sup>d</sup> The electrolysis was terminated at n = 0.24, oxygen was then bubbled through the electrolysis mixture for approximately 60 s.

product ( $E_{p,a} = 0.08$  V) and variable, non-integral *n* values (1.5 < n < 3.5) (Fig. 1b). If the electrolyzed solution is then permitted to stand for a period of several hours, the anodic wave which we attribute to the oxidation of 9-fluorenyl anion disappears and is replaced by the cathodic wave for the reduction of fluorene to its radical anion ( $E_{p,c} = -2.04$  V). Gas chromatographic analysis of the electrolyzed solution which has been treated with diethylmalonate (but not water!) shows that fluorene can be recovered in nearly quantitative yield (Table 1, entry 1). In addition, the presence of a substantial but variable amount of tributylamine is noted (150–330%). Since the latter product probably arises by a Hofmann elimination reaction involving the cation of the supporting electrolyte and the 9 fluorenyl anion, the variable n value generally reflects the amount of fluorene which has been regenerated by this reaction pathway. A more exact relationship between *n* value and tributylamine yield is precluded, however, because of electron transfer from fluorene radical anion (vide infra) to adventitious proton donors and varying times between the termination of the electrolysis and the protonation of the reduction product.

Effect of diethylmalonate. Although the cyclic voltammetric reduction of fluorene in DMF- $(n-Bu)_4$ NClO<sub>4</sub> is nearly reversible at a scan rate of 0.2 V s<sup>-1</sup>, the addition of diethylmalonate as an electroinactive proton donor ([DEM]/[FlH<sub>2</sub>] = 1.84) causes the cathodic wave for the reduction of fluorene to increase by a factor of 2.41, and, concomitantly, the anodic wave for the oxidation of the fluorene radical anion to disappear. Since  $\iota_p/v^{1/2}$  for the cyclic voltammetric reduction of fluorene increases with decreasing scan rate, a follow-up chemical reaction involving the fluorene radical anion and diethylmalonate is indicated. The reaction cannot involve protonation of the fluorene radical anion and further reduction of the resulting radical, since the passage of 2 electrons per molecule of fluorene in the presence of diethylmalonate results in no appreciable decrease in the concentration of fluorene (Table 1, entry 3).

Effect of oxygen. Although adventitious oxygen is sufficiently small so as to pose no problem in our electrochemical reductions of fluorene, the deliberate introduction of oxygen to a partially electrolyzed solution of fluorene (n = 0.24 electron per molecule of fluorene) results in the rapid loss of 9-fluorenyl anion and all remaining unreduced fluorene and the formation of fluorenone in nearly quantitative yield (Table 1, entry 4).

# (B) Bifluorenyl

The cyclic voltammetric reduction of bifluorenyl,  $(FlH)_2$ , gives rise to the major, irreversible process near -1.84 V and a small, kinetically controlled peak near -2.04 V (Fig. 2a). Although there is no peak corresponding to the reoxidation of the bifluorenyl radical anion at all scan rates up to 100 V s<sup>-1</sup> on the reverse, positive-going sweep, oxidation of a product or products arising from the decomposition of  $(FlH)_2^-$  occurs near 0.08 V. A cathodic peak corresponding to the reverse cathodic sweep unless the scan rate is in excess of 20 V s<sup>-1</sup>.

Single-potential-step chronoamperometry at a potential sufficiently negative



Fig. 2. (a) Cyclic voltammogram of  $6.95 \times 10^{-3} M 9.9'$ -bifluorenyl in 0.1 M TBAP-DMF at a spherical platinum electrode. (b) Cyclic voltammogram of exhaustively electrolyzed (a). The scan rate is 0.2 V s<sup>-1</sup>.

to reduce bifluorenyl ( $E_{p,c} = -1.84$  V), but not so negative as to reduce the decomposition product, fluorene ( $E_{p,c} = -2.04$  V), indicates that this reduction is a two-electron, diffusion-controlled process for  $t \leq 0.1$  s. However, for t > 0.1 s, *n* becomes kinetically controlled, decreasing to values significantly smaller than 2; e.g., at t = 7 s, *n* equals 1.65. Coulometric reduction of bifluorenyl (Fig. 2b) at its cathodic peak potential gives fluorene and starting material in approximately equal yield after the exhaustively electrolyzed mixture is protonated with diethylmalonate (Table 1, entry 5).

# (C) Oxidation of 9-fluorenyl anion

The 9-fluorenyl anion was prepared in situ by the exhaustive, controlled-potential electrolysis of fluorene. The cyclic voltammogram (Fig. 1b) of this carbanion exhibits a single, irreversible peak near 0.08 V on the positive-going sweep and two cathodic peaks at -1.85 V and -2.04 V on the reverse, cathodic sweep. The two cathodic waves arise from the reduction of products resulting from subsequent chemical reactions of the 9-fluorenyl radical and are readily identified as being due to bifluorenyl ( $E_{p,c} = -1.85$  V) and fluorene ( $E_{p,c} =$  -2.04 V). Controlled-potential electrolysis of 9-fluorenyl anion at a potential of 0.40 V results in an *n* value of 0.69 and the formation of bifluorenyl and fluorene in yields of 34% and 65%, respectively (Table 1, entry 2).

# (D) p-Cyanoaniline

Cyclic voltammetry. The cyclic voltammetric reduction of p-cyanoaniline (Fig. 3) at a platinum cathode in DMF-(n-Bu)<sub>4</sub>NClO<sub>4</sub> occurs near the cathodic limit of this solvent-electrolyte system ( $E_{p,c} = -1.90$  V). Although no anodic wave is seen for the reoxidation of the corresponding radical anion on the reverse, anodic sweep for  $v \leq 100$  V s<sup>-1</sup>, two small, reversible couples are observed in the regions of -0.90 and -1.30 V. By comparison to an authentic sample, these couples are readily identified as arising from the stepwise reversible reduction of 4,4'-dicyanobiphenyl to its dianion.

Coulometry. The exhaustive, controlled-potential reduction of p-cyanoaniline typically requires 1.5-2.0 electrons per molecule and afford the corresponding anilide, p-NCC<sub>6</sub>H<sub>4</sub>NH<sup>-</sup>, as the principal product. This species is unstable in this solvent-electrolyte system and slowly decomposes by the abstraction of a proton from the cation of the supporting electrolyte to regenerate the starting material. Gas chromatographic analysis of numerous electrolyzed solutions showed that p-cyanoaniline is regenerated in greater than 95% yield while 4,4'-dicyanobiphenyl is formed in yields of 1-5%. In addition, the expected product of the Hofmann degradation reaction, tributylamine, is found in substantial amount (Table 1, entry 6).



Fig. 3. Cyclic voltammogram of  $1.89 \times 10^{-3} M p$ -aminobenzonitrile in 0.1 M TEAP-DMF at a planar platnum electrode. The number 2 indicates the current-voltage curve for the second cathodic sweep. The scan rate is 0.2 V s<sup>-1</sup>.

# DISCUSSION

# Fluorene and bifluorenyl

*Reduction of fluorene in an aprotic medium.* The pathway proposed for the reduction of fluorene in an aprotic medium is described by eqns. (1) and (2).

$$FlH_2 + e^- \rightleftharpoons FlH_{\overline{2}} \rightarrow FlH^- + 1/2 H_2$$
(1)

 $\operatorname{FlH}^- + (n-\operatorname{Bu})_4 \operatorname{N}^+ \xrightarrow{\operatorname{slow}} \operatorname{FlH}_2 + \operatorname{butene} + (n-\operatorname{Bu})_3 \operatorname{N}$  (2)

The fluorene radical anion, although reasonably stable on the cyclic voltammetric time scale, decomposes during the course of the exhaustive electrolysis experiment to give the conjugate base of fluorene [13]. Since this carbanion subsequently slowly regenerates fluorene in quantitative yield by abstraction of a proton from the cation of the supporting electrolyte, the exhaustive reduction of fluorene results in a non-integral n value which is determined by the relative rates of reduction and proton abstraction.

Effect of diethylmalonate on the reduction of fluorene. The addition of 0.1 M hydroquinone as a weak proton donor (HA) to solutions of three monosubstituted 9-fluorenes in DMF was reported by Lagu et al. [3] to increase the polarographic limiting current of the substituted fluorene by a factor of 7 to 13. We note a similar effect when diethylmalonate is added to fluorene: the cathodic peak height for the fluorene reduction is markedly increased while the lifetime of the fluorene radical anion is reduced correspondingly. Although this result has been interpreted previously to be due to the regeneration of fluorene by protonation of the 9-fluorenyl anion (eqn. 3), that proposal is incompatible with the relatively slow decomposition of the fluorene radical anion which is observed when no added proton donor is present.

$$FIR^- + HA \rightarrow FIHR + A^-$$

Accordingly, we believe that a more plausible explanation for the rapid regeneration of fluorene involves electron transfer from the fluorene radical anion to the proton donor (eqns. 4-5).

$$\mathrm{FlH}_2 + e^- \rightleftharpoons \mathrm{FlH}_2^- \tag{4}$$

(3)

(5)

 $FlH_{\overline{2}} + HA \rightarrow FlH_2 + 1/2 H_2 + A^-$ 

No evidence was obtained for protonation of the fluorene radical anion by either fluorene (self-protonation) or added proton donor.

Effect of oxygen. The introduction of oxygen to a partially electrolyzed solution of fluorene was shown here to result in the rapid and quantitative conversion of 9-fluorenyl anion and unreduced fluorene into fluorenone [4,14]. We suggest that this transformation occurs by a chain process in which the 9-fluorenyl anion is the chain-carrying species and termination involves the abstraction of a proton from a component of the solvent-electrolyte system (e.g.,  $(n-Bu)_4N^*$ ) by

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Initiation: 
$$\operatorname{FlH}_2 + e^- \rightleftharpoons \operatorname{FlH}_2^- \xrightarrow{\mathrm{slow}} 1/2 \operatorname{H}_2 + \operatorname{FlH}^-$$
 (6)

Propagation: 
$$FlH^- + O_2 \rightarrow Fl = O + OH^-$$
 (7)

$$OH^- + FlH_2 \rightarrow FlH^- + H_2O \tag{8}$$

Termination:  $OH^- + HA \rightarrow H_2O + A^-$ 

The unusually small autoprotolysis constants which have been reported for water in dipolar aprotic solvents ( $pK_w = 28$  in DMSO containing 0.5 mol % water and 37 in acetonitrile containing 0.3 mol % water) [15] are consistent with our observation that water does not protonate 9-fluorenyl anion in DMF ( $pK_a$  of fluorene in DMSO is 22.6) [16].

Reduction pathway for bifluorenyl. The scheme which we propose for the reduction of bifluorenyl is described by eqns. (10)-(12).

$$(\text{FlH})_2 + e^- \approx (\text{FlH})_2^- \xrightarrow{\text{rast}} \text{FlH}^+ + \text{FlH}^-$$
(10)

$$FlH^{*} + e^{-} \rightarrow FlH^{-}$$
(11)

 $\operatorname{FlH}^- + (\operatorname{FlH})_2 \xrightarrow{\operatorname{slow}} \operatorname{FlH}_2 + \operatorname{FlH} - \operatorname{Fl}^-$  (12)

Although bifluorenyl and fluorene are both weak carbon acids, the radical anion of the former compound is much shorter lived than that of the latter. In addition, whereas decomposition of fluorene radical anion was shown above to occur by carbon-hydrogen bond cleavage, the formation of fluorene and bifluorenyl anion in equimolar amounts in the exhaustive reduction of bifluorenyl requires that bifluorenyl radical anion decompose by carbon-carbon bond cleavage. The initial chronoamperometric n value of 2 then requires the fluorenyl radical, one of the two fragments of bifluorenyl radical anion decomposition, to be reduced to its anion, either at the electrode or in the bulk of the solution by bifluorenyl radical anion. Kinetic control of the n value results when 9-fluorenyl anion abstracts a proton from the more acidic starting material to give fluorene and the conjugate base of bifluorenyl (eqn. 12). The latter species is then oxidized slightly less readily ( $E_{p,a} = 0.10$  V) than 9-fluorenyl anion on the positive-going sweep (Fig. 2a).

Although the above reaction scheme successfully predicts the products and the product distribution, the *n* values which are obtained from exhaustive electrolyses exceed the predicted value of 0.67 electron per molecule of starting material (Table 1, entry 5). This is probably the result of inadequate potential control which results in the concomitant reduction of fluorene and bifluorenyl. This suggestion is supported by the observations that the magnitude of the fluorene reduction wave ( $E_{p,c} = -2.04 \text{ V}$ ) in the exhaustively electrolyzed solution (Fig. 2b) is smaller than the corresponding oxidation wave for bifluorenyl anion ( $E_{p,a} = 0.10 \text{ V}$ ) and that tributylamine, the product of 9-fluorenyl anion attack on the cation of the supporting electrolyte (eqn. 2), is found in relatively large amounts in the exhaustively electrolyzed solutions.

(9)

Oxidation of 9-fluorenyl anion. Since bifluorenyl radical anion undergoes rapid carbon-carbon bond cleavage, it is unlikely in the oxidation of 9-fluorenyl anion that bifluorenyl formation occurs by coupling of 9-fluorenyl radical and anion. Instead, we suggest that bifluorenyl arises by dimerization of 9-fluorenyl radical (eqn. 13), while fluorene is formed by both hydrogen atom abstraction by 9-fluorenyl radical (eqn. 14) and proton abstraction by 9-fluorenyl anion (eqn. 2). Involvement of the latter pathway is supported by an experimental n value (0.69) which is significantly smaller than the value of one that is predicted by eqns. (13) and (14).

$$FlH^{-} - e^{-} \rightarrow FlH^{\bullet} \qquad (13)$$

$$\xrightarrow{\text{SH}} \operatorname{FlH}_2 \tag{14}$$

Reduction pathways for p-cyanoaniline

The reduction of *p*-cyanoaniline in DMF has been reported by Rieger et al. to afford 4,4'-dicyanobiphenyl radical anion as product [5]. Although the formation of this species and its subsequent stepwise reduction to its stable dianion are clearly discernible by cyclic voltammetry, product studies of exhaustively electrolyzed solutions show that this is but a minor reaction channel. Our results indicate that the reduction of *p*-cyanoaniline is initially a one-electron process (eqn. 15). The resulting radical anion then decomposes mainly by carbon-hydrogen bond cleavage to form the corresponding nitranion, *p*-NCC<sub>6</sub>H<sub>4</sub>NH<sup>-</sup>. Abstraction of a proton from the tetraalkylammonium cation of the supporting electrolyte by this nitranion regenerates the starting material, completing the reaction pathway (eqn. 16).

$$p\text{-NCC}_{6}\text{H}_{4}\text{NH}_{2} + e^{-} \rightarrow p\text{-NCC}_{6}\text{H}_{4}\text{NH}_{2}^{-} \xrightarrow{\text{fast}} 1/2 \text{ H}_{2} + p\text{-NCC}_{6}\text{H}_{4}\text{NH}^{-}$$
(15)

$$p\text{-NCC}_{6}\text{H}_{4}\text{NH}^{-} + (n\text{-Bu})_{4}\text{N}^{+} \rightarrow p\text{-NCC}_{6}\text{H}_{4}\text{NH}_{2} + \text{butene} + (n\text{-Bu})_{3}\text{N}$$
(16)

Because the original electroactive species is slowly regenerated in the bulk of solution (eqn. 16), the experimental n values are nonintegral and increase in magnitude as the ratio of the rate of proton abstraction to the rate of electrolytic reduction increases. In principal, the yield of trialkylamine should be a quantitative measure of the amount of p-cyanoaniline which is being reformed by proton abstraction. In practice, however, the yield of trialkylamine is also dependent upon the elapsed time between the completion of the electrolysis and the acidification of the solution with diethylmalonate and upon the concentrations of adventitious proton donors and/or electron acceptors.

#### CONCLUSIONS

In contrast to earlier reports [3-5], fluorene and *p*-cyanoaniline radical anions decompose principally by cleavage of carbon-hydrogen and nitrogen-hydrogen bonds, respectively, to form their corresponding, relatively long-lived anions. The redox behavior of these compounds is therefore similar to that of several other carbon- and nitrogen-centered acids [12,17-19] and may be rationalized

on the basis of the acidities of the starting materials: fluorene,  $pK_a = 22.6$  in DMSO [16], and *p*-cyanoaniline,  $pK_a = 25.3$  in DMSO [20]. Bifluorenyl, which is also a weak carbon acid, offers a contrasting mode of radical anion decomposition by undergoing carbon-carbon bond cleavage. While this mode of bond cleavage is similar to that reported by Lagu et al. [3] for the decomposition of 9,9-dibenzylfluorene radical anion, it should be noted that it differs from that of 9-benzylfluorene radical anion where decomposition occurs by fission of the carbon-hydrogen bond.

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