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References and Notes

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- (41) **Note:** Recently, Kebabari and Hiraoka (*J. Am. Chem. Soc.*, **97**, 4179 (1975)) noted the occurrence of $\text{CH}_5(\text{CH}_4)_n^+$ clusters in a methane plasma containing CH_5^+ ions. Solvation of CH_5^+ by one CH_4 molecule was found to be energetically favorable ($\Delta G^\circ = 1.2 \text{ kcal mol}^{-1}$), while the addition of a second CH_4 molecule is less favorable ($\Delta G^\circ = -1.4 \text{ kcal mol}^{-1}$). Still weaker interactions are found for clusters with $n = 3, 4, \dots$. From their data one would conclude that asymmetric solvation (i.e., $\text{CH}_5^+(\text{CH}_4)$ is more likely to be found than a symmetric configuration ($\text{CH}_5^+(\text{CH}_4)_2$).
- (42) **Note:** The calculated proton affinities of CH_4 and C_2H_6 are 120 and 149 kcal mol^{-1} , respectively.⁵ Though no data are available for propane or isobutane, the latter compounds are certainly more basic in view of the fact that protolytic reactions (e.g., in $\text{HSO}_3\text{F}/\text{SbF}_5$) proceed much more rapidly with these alkanes than with methane or ethane.
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Carbanions. Electron Transfer vs. Proton Capture. 4. Products of Base-Catalyzed Reactions of Various 9-Substituted Fluorenes with Aromatic Nitro Compounds

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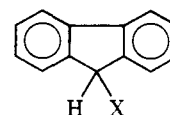
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Abstract: Fluorenes substituted in the 9 position with CH_3O -, CH_3 -, $(\text{CH}_3)_2\text{CH}$ -, H_2N -, and HO - react with potassium methoxide and aromatic nitro compounds in oxygen-free methanol. The reaction products are dimers, diphenylene-*N*-arylnitrones, trisubstituted hydroxylamines, mono- and disubstituted azoxy compounds, and dehydrogenation products. These are shown to arise from 9-substituted fluorenyl radicals produced by one-electron oxidation of the corresponding carbanions. The radicals undergo coupling, reaction with reduction products from the nitro compounds, or transfer a second electron.

It is well established that carbanions undergo one-electron transfer reactions to aromatic nitro compounds to give the radical anion of the nitro compound.¹ The fate of the carbanion derived radicals has not been thoroughly explored. In our efforts² to use electron-transfer oxidation as a probe of carbanion environment, we felt that it would be valuable in each case to provide a complete identification of reaction products. The present paper serves this function for the reaction of several 9-substituted fluorenyl ions with aromatic nitro compounds.

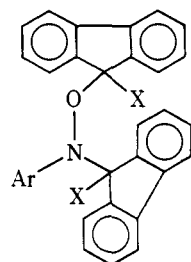
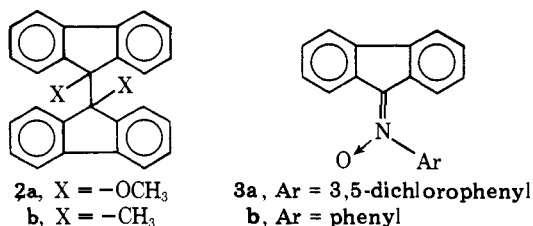
Results and Discussion

When **1a–e** were treated with potassium methoxide in

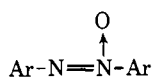


- 1a**, X = $-\text{OCH}_3$
b, X = $-\text{CH}_3$
c, X = $-\text{CH}(\text{CH}_3)_2$
d, X = $-\text{NH}_2$
e, X = $-\text{OH}$

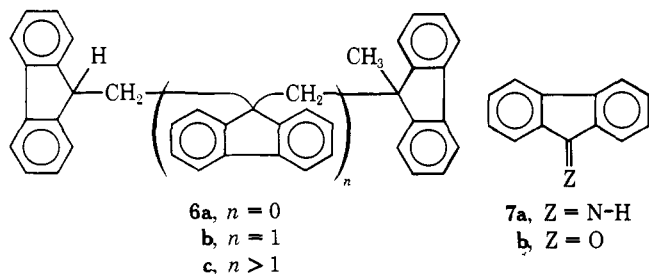
methanol in the presence of nitrobenzene or 3,5-dichloronitrobenzene (DCNB) under anaerobic conditions, compounds **2–7** were formed in the amounts listed in Table I. We suggest



4a, X = -CH₃, Ar = 3,5-dichlorophenyl
b, X = -CH₃, Ar = 4-(9-methyl-9-fluorenyl)phenyl
c, X = -CH(CH₃)₂, Ar = 3,5-dichlorophenyl



5a, Ar = Ar' = 3,5-dichlorophenyl
b, Ar = Ar' = 4-(9-methyl-9-fluorenyl)phenyl
c, Ar = phenyl, Ar' = 4-(9-methyl-9-fluorenyl)phenyl or vice versa
d, Ar = Ar' = 4-(9-isopropyl-9-fluorenyl)phenyl



that these products can be explained by various combinations of steps 1-11.

Steps 1 and 2 are common to all of the systems studied. Step 1 becomes irreversible and rate limiting when DCNB is used as electron acceptor. This has been most thoroughly demonstrated for **1a** as described in the following paper³ but was also confirmed for **1b** and **1d** by comparison of hydrogen-deuterium exchange rates with the rate of loss by electron transfer to DCNB (Table II).

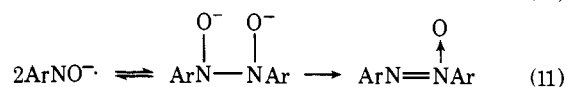
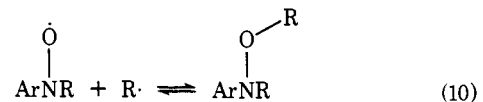
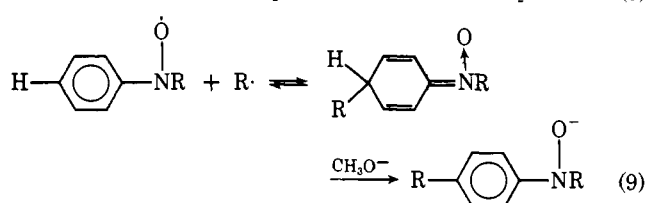
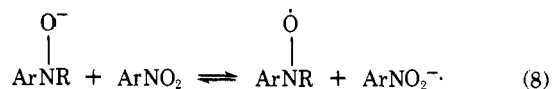
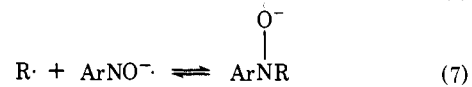
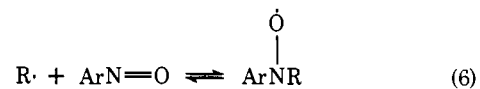
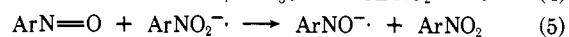
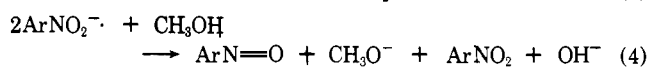
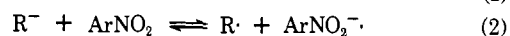
ESR monitoring of the reaction mixtures containing nitrobenzene as acceptor showed a substrate-dependent formation of nitrobenzenide ion, providing evidence for step 2. In the cases of **1a** and **1b**, step 2 is inefficient relative to the reverse of step 1, and the concentration of radical anion produced was only four-nine times greater than that resulting from direct reaction⁴ between potassium methoxide and nitrobenzene in a blank run. For the more efficiently trapped carbanions from **1d** and **1e**, conditions could be arranged such that nitrobenzenide was only observed in the presence of carbon acid. Nitrobenzenide ion reacts rapidly with methanol, and therefore the intensity of its spectrum remained greater than that of the blank only as long as a significant fraction of carbon acid remained unreacted. It was also possible to demonstrate the presence of nitrobenzenide by observing its exchange broadening effect on the ¹H NMR lines of nitrobenzene. This is illustrated for **1d** in Figure 1.

The radical derived from the carbanion was present at concentrations too low for ESR detection. Nevertheless, its intermediacy could be inferred from the fact that when **1a** or

Table I. Products from the Anaerobic Reaction of 9-Substituted Fluorenes (**1a-e**) with Aromatic Nitro Compounds in Methoxide-Methanol^a

X	[KOMe], N	ArNO ₂	Product (% yield)
-OCH ₃	0.47	3,5-Cl ₂ Ph-NO ₂	2a (60), 3a (40)
-OCH ₃	1.4	3,5-Cl ₂ Ph-NO ₂	2a (58)
-OCH ₃	0.49	PhNO ₂	2a (50), 3b (25)
-CH ₃	0.33	3,5-Cl ₂ Ph-NO ₂	4a (95)
-CH ₃	0.50	PhNO ₂	6a (22), 5b (21) 2b (15), 5c (8) 6b (3), 6c (3)
-CH ₃	2.0	PhNO ₂	4b (73), 5b (3), 5c (5)
-CH(CH ₃) ₂	2.0	3,5-Cl ₂ Ph-NO ₂	4c (85)
-CH(CH ₃) ₂	1.4	PhNO ₂	5d (62)
-NH ₂	0.15	3,5-Cl ₂ Ph-NO ₂	7a (97)
-OH	2.0	3,5-Cl ₂ Ph-NO ₂	7b (99)

^a Reaction times, temperatures, and isolation techniques are given in the Experimental Section.



1b reacted with potassium methoxide and aromatic nitro compounds in an oxygen atmosphere, oxygenated products were obtained; **7b** from **1a** (quantitative) and 9-methyl-9-hydroxyfluorene (65-85%) from **1b**. Control reactions in which the nitro compounds were omitted from the reaction mixture showed that direct reaction of the carbanion with oxygen was too slow to compete under the reaction conditions. We conclude that oxygen reacts with the radical, giving rise to the observed products.

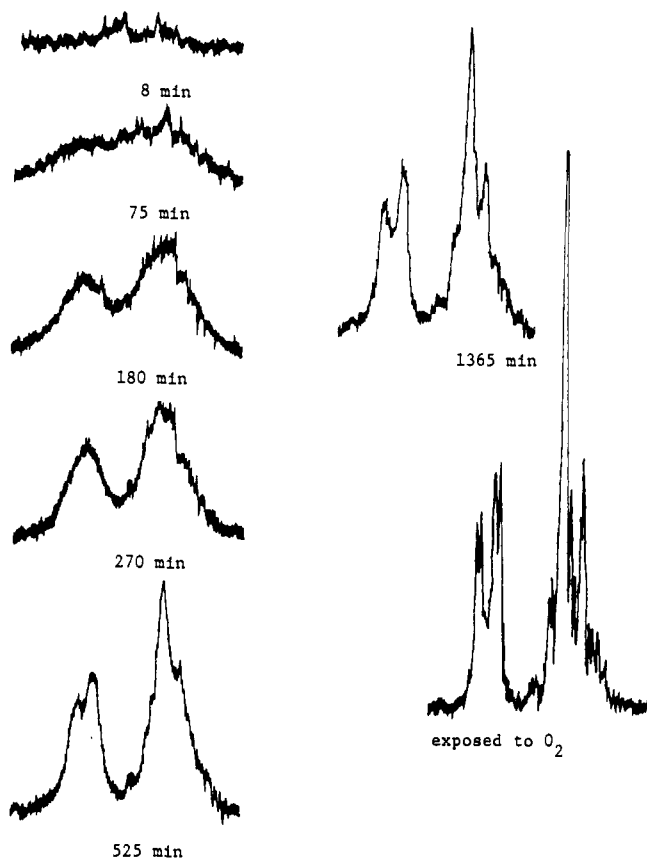


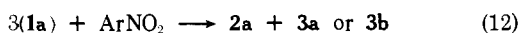
Figure 1. Spectra showing decrease in ^1H NMR broadening of nitrobenzene treated with 9-aminofluorene and potassium methoxide in methanol as the reaction proceeded at 37°C .

Table II. Comparison of the Rate of Hydrogen-Deuterium Exchange with the Rate of Reaction with 3,5-Dichloronitrobenzene for Various 9-Substituted Fluorenes in Methanol-*O-d*

Substrate ^a	$k_{\text{exchange}} \times 10^4, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{loss}}^b \times 10^4, \text{M}^{-1} \text{s}^{-1}$	[KOMe], M
1a	6.0	6.1 ^c	0.47
1b	5.6	5.6 ^c	0.50
1d	9.4	10.1 ^d	0.10

^a [Substrate] = 0.05 M. ^b [DCNB] = 0.20 M. ^c Followed loss of substrate by GC vs. internal hexadecane (for **1a**) or pentadecane (for **1b**). ^d Followed appearance of fluorenone after hydrolysis by GC vs. internal eicosane.

9-Methoxyfluorene (1a). The major product of the reaction of this substrate with either of the two aromatic nitro compounds was **2a**. Dimeric products have been observed previously from reactions of this type⁵ and have usually been assumed to arise via the sequence of steps 1, 2, and 3. In a preliminary communication, we erroneously reported that **2a** was the exclusive product of the reaction of **1a** with the two nitro compounds.⁶ Careful examination of the reaction mixtures, however, revealed the nitrones **3a** and **3b**, and NMR analysis indicated the stoichiometry was approximately that of the following equation:



Because 1 mol of **1a** would give $\frac{1}{3}$ mol of nitrosobenzene radical anion via steps 1, 3, and 4, then for every three 9-methoxyfluorenyl radicals formed, one could react to give nitron via

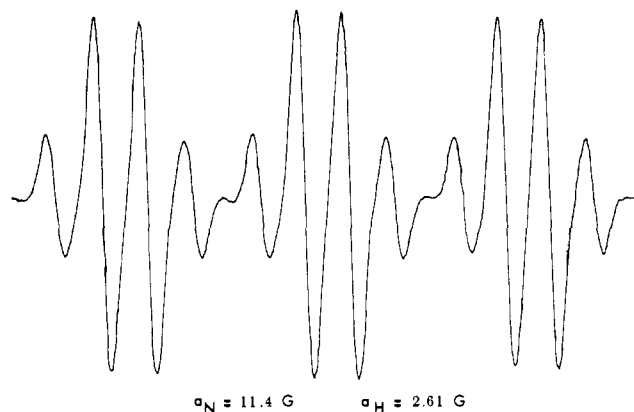
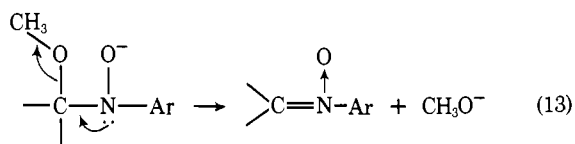
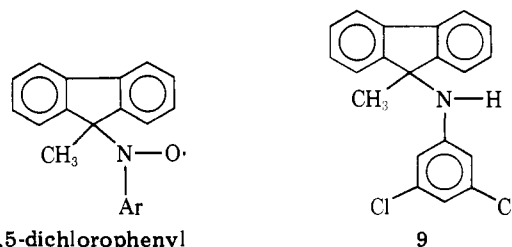


Figure 2. ESR spectrum of benzene solution of product (**4a**) from the reaction of 9-methylfluorene with 3,5-dichloronitrobenzene and 2 N potassium methoxide in methanol.



step 7, followed by loss of methoxide (step 13), rendering step 7 irreversible. This type of mechanism has been observed previously in the reaction of substituted carbanions with nitroso compounds.⁷ Alternatively, the sequence of step 6 followed by the reverse of step 8 could provide the precursor for step 13. Aromatic nitro compounds are known to react with methoxide-methanol to give azoxy compounds in a reaction which presumably proceeds through nitrosobenzene, its radical anion, or both.^{4,8} This could account for the observation of a slight excess of nitron over that predicted by (12). When reduction by substrate provides the only route to nitroso compound, the sequence terminating in step 13 leaves an excess of 2 equiv of fluorenyl radical with no alternative to dimerization.

9-Methylfluorene (1b). When **1b** was allowed to undergo methoxide-catalyzed reaction with 3,5-dichloronitrobenzene, a crystalline product separated nearly quantitatively from the reaction mixture. This was found to be a new type of product, the trisubstituted hydroxylamine, **4a**, on the basis of elemental analysis, spectral data, and degradative experiments. It had the interesting property that, while the solid showed no ESR signal, its benzene solution gave the ESR spectrum of Figure 2. This spectrum was identical with that of *N*-(9-methyl-9-fluorenyl) 3,5-dichlorophenyl nitroxide (**8a**), which was prepared from **9** using *p*-nitroperbenzoic acid.



8a, Ar = 3,5-dichlorophenyl

b, Ar = 4-(9-methyl-9-fluorenyl)phenyl

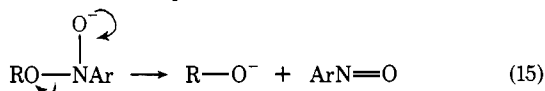
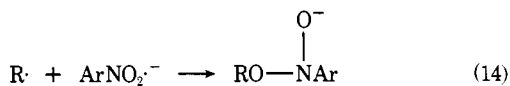
There was no evidence of 9-methyl-9-fluorenyl radical in the ESR spectrum of the benzene solution of **4a**. In an effort to trap this species, **4a** was heated in benzene in the presence of thiophenol. A complex mixture was obtained which contained some of the expected **1b** (27% based on 1 mol of **1b** from 1 mol of **4a**) along with **9** (24%) which possibly results from reduction of **8a** and an unexpected 24% of **2b** possibly from a cage recombination reaction. Roughly 10% of **5a** was also

obtained, suggesting that steps 6 and 10 are reversible. Literature examples of step 10 can be found.⁹ The reverse of step 10 is indicated by the observation¹⁰ that triphenylmethyl radical can coexist with nitroxides so that with sufficiently stable radicals the equilibrium of eq 10 lies to the left. Isolation of **4a** is probably a fortunate consequence of its extreme insolubility in the reaction medium.

When nitrobenzene was substituted for 3,5-dichloronitrobenzene in the reaction of **1b**, a product with properties similar to those of **4a** was obtained in reasonable yield, provided that the methoxide concentration was very high (2 M gave 73%). Elemental analysis and spectral data showed, however, that the compound contained three 9-methylfluorenyl residues. The ESR spectrum of a benzene solution of this compound is shown in Figure 3a and is very similar to that of *N*-(9-methyl-9-fluorenyl) phenyl nitroxide with the exception of a one-hydrogen additional splitting in the pattern for the latter compound. By using nitrobenzene deuterated in the ortho positions, a compound which gave the ESR spectrum of Figure 3b was obtained. Although the deuteration produces a broadening of the spectral lines, preventing resolution of splitting by the meta hydrogens, it is clear that the phenyl nitroxide moiety contains no para hydrogen, and structure **4b** was assigned.

Curiously when the reaction of **1b** with nitrobenzene was carried out at lower methoxide concentration (0.5 M), a set of products was obtained which did not include an appreciable amount of **4b**. The observed products were those which would have resulted from dimerization and disproportionation of 9-methyl-9-fluorenyl radical (**2b**, **6a**, **6b**, **6c**) along with para-substituted azoxy compounds, **5b** and **5c**, which are preceded in reactions of this type.^{2a,5b} Although this dramatic change in reaction course would seem an unlikely consequence of a mere fourfold change in base concentration, data obtained from kinetic studies on **1a**³ suggest that the rate of radical production could be reduced by a factor of 60 at the lower concentration. This would cause a correspondingly lower steady state concentration of 9-methyl-9-fluorenyl radicals, reducing the rate of step 10 relative to the reverse of step 6.

It will be noted that our mechanism does not include a reaction between the intermediate fluorenyl radicals and the nitroaromatic radical anion. We have discounted this possibility for two reasons. One is simply the difficulty of writing reasonable mechanisms incorporating this step. If coupling occurs at either nitrogen or oxygen, it is then necessary to lose one oxygen atom to produce the observed products, and there is no obvious way to do this. The second objection to this alternative is an experimental one. When 9-methylfluorenyl ion prepared from 9-methylfluorene and potassium *tert*-butoxide in Me₂SO was treated with nitrobenzene, the products proved to be the dimer, **2b** (62%) and 9-methyl-9-hydroxyfluorene (31%). Alcohol formation thus appears to be favored by the absence of a proton source which is sufficiently acidic to protonate nitrobenzene ion. This also explains our previous observation^{2a,11} of triphenylcarbinol as the major product from the reaction of triphenylmethide ion with nitrobenzene in *tert*-butyl alcohol. A reasonable mechanism for alcohol production is shown in steps 14 and 15. This route apparently does



not make a significant contribution in methanol as indicated by the absence of alcohol formation from **1b** and **1c**. A trace of fluorenone was observed from **1a** and could have arisen via this route, but reaction with adventitious oxygen seems more likely.

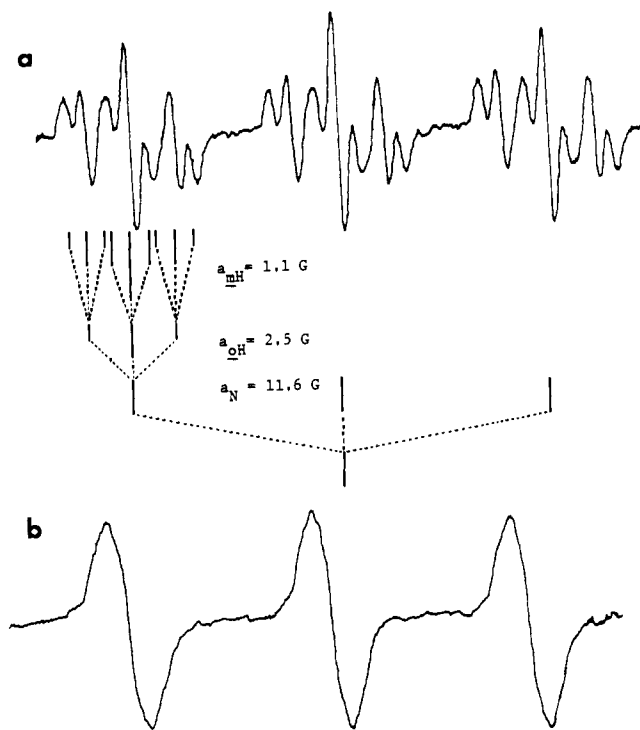


Figure 3. ESR spectra of benzene solution of product from the reaction between 9-methylfluorene and nitrobenzene at high base concentration; (a) from nitrobenzene, (b) from nitrobenzene-2,6-*d*₂.

Another mechanistic alternative omitted from our scheme is one in which nitrosobenzene or its radical anion couples at its para position with a fluorenyl radical. This route would predict a para-substituted nitron from **1a** and nitrobenzene, whereas only **3b** was observed. Once one bulky fluorenyl group is added at nitrogen, the second apparently prefers the para position, and thus step 9 occurs faster than step 10. This preference is evidently reversed when step 9 is slowed by the two ortho chlorines in **8a**.

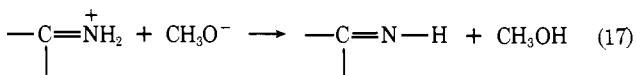
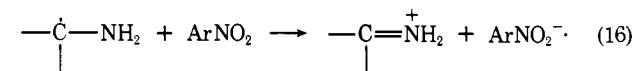
9-Isopropylfluorene (1c). In contrast to **1b**, the reaction of **1c** with methoxide and nitrobenzene and methanol gave azoxy compound **5d** even at high methoxide concentrations. We suggest that this is due to the slower ionization rate of **1c**, which keeps the steady state concentration of isopropylfluorenyl radicals low. The same argument used to explain the effect of base concentration on the products from **1b** applies. Step 6 or its equivalent can occur, followed by 9, but, if the para-substituted nitroxide undergoes the reverse of step 6 faster than it couples in step 10, an opportunity for the formation of azoxy compounds (steps 5 and 11) is presented. A contributing factor may also be that the elevated temperature required to carry out the reaction between **1c** and nitrobenzene decreases the equilibrium constant in step 10. If this explanation were correct, we reasoned that it should be possible to convert the tri-substituted hydroxylamines, **4**, into the corresponding azoxy compounds, **5**, by subjecting them to reaction conditions favoring formation of **5**. Although **4b** was very insoluble in methanol, we found that heating it at 50 °C with 0.5 N methanolic potassium methoxide gave **5b** in low yield. The experiment clearly indicates the reversibility of steps 10 and 6.

Reaction between **1c** and DCNB gave **4c** as expected from the preceding arguments. With the more efficient acceptor, the reaction could be carried out at 30 °C and was rapid enough to maintain the requisite concentration of isopropylfluorenyl radicals.

9-Amino fluorene (1d). Compound **1d** reacted with methoxide and aromatic nitro compounds to give the imine, **7a**, in essen-

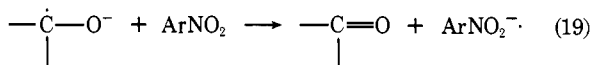
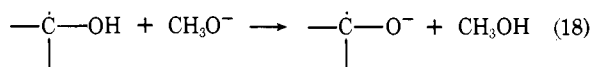
tially quantitative yield. The reaction was shown to be ionization limited, and the presence of the radical anion of the aromatic nitro compound was demonstrated by ESR. Under anaerobic conditions, $\frac{1}{3}$ mol of azoxy derivative was produced for every mole of **1d** converted to **7a**. In the presence of molecular oxygen the radical anions are apparently oxidized back to the neutral nitro compound¹² faster than they react with methanol, because the formation of the azoxy compound is not observed. Oxygen does not affect the formation of **7a**.

These results suggest that the 9-aminofluorenyl radical is too short-lived to undergo steps such as 6 or 7. Steps 16 and 17



seem logical alternatives. In the aerobic reaction, oxygen could possibly serve as the electron acceptor in step 16. There are previous reports of base-catalyzed dehydrogenation of 9-aminofluorene using diphenyleneethylene and azobenzene as acceptors, but a nonradical mechanism was proposed.¹³ More recently Russell and co-workers have suggested an electron-transfer alternative.¹⁴ Such dehydrogenations hold particular interest because of their biological analogies. Particularly relevant is the interesting suggestion that a carbanion or carbanion-like intermediate is involved in the action of amino acid oxidases.¹⁵ There is almost certainly a continuum of mechanistic alternatives for dehydrogenation of H-C-X-H' systems. We are suggesting that the reaction of **1d** with base and aromatic nitro compounds is of the class $\text{A}_{\text{BH}}\text{D}_{\text{CH}} + \text{A}_{\text{CA}}\text{D}_{\text{CA}} + \text{A}_{\text{CA}}\text{D}_{\text{AC}} + \text{A}_{\text{BH}'}\text{D}_{\text{XH}'}$,¹⁶ where the subscripts B and A represent base and acceptor respectively. The electron-transfer steps are represented as concerted for simplicity and for lack of evidence to the contrary.

9-Hydroxyfluorene (1e). This reaction was very similar to that of **1d** and under the usual conditions gave a quantitative yield of fluorenone, **7b**, recovered as its 2,4-dinitrophenylhydrazone. With DCNB, **5a** was a byproduct in the same stoichiometry as from the reaction of **1d**. The ESR spectrum of nitrobenzenide was observed under anaerobic conditions. A mechanism identical with that for **1d** could be written. However, the low $\text{p}K_{\text{a}}$ (6.3^{17}) of the 9-hydroxyfluorenyl radical suggests that proton removal (step 18) would be diffusion controlled. This would be rapidly followed by step 19. In digital



notation this mechanism is $\text{A}_{\text{BH}}\text{D}_{\text{CH}} + \text{A}_{\text{CA}}\text{D}_{\text{CA}} + \text{A}_{\text{BH}'}\text{D}_{\text{XH}'}$ + $\text{A}_{\text{CA}}\text{D}_{\text{AC}}$ with the order of the third and fourth terms reversed from the case of **1d**.¹⁸ This order seems unlikely in the case of **1d** because of the ca. 20 pK unit difference between comparable N-H and O-H acidities.

Summary

A complex and delicately balanced network of reactions is indicated as product forming sequences in the reactions of carbanions with aromatic nitro compounds. If the initially formed radical can be easily oxidized or deprotonated, dehydrogenation is a likely outcome. If these alternatives are not possible, the second choice seems to be reaction with nitroso compounds or their radical anions, provided that the reaction medium is sufficiently acidic to allow production of these at a rate comparable with radical formation. Mechanisms for these pathways have been suggested. The last choice seems to

be dimerization, disproportionation, or reactions with the nitroaromatic radical anion. These seem to occur when the radical anion is stable to the reaction conditions or when its degradation products are removed by reactions which leave an excess of free radicals. This will occur if a suitable leaving group is attached to the reaction site such as in **1a**.

Experimental Section

Solvents, Solutions, and Reagents. Most of these are described in the following paper.³ Nitrobenzene-2,6-*d*₂ was prepared as previously described.¹⁹

Substrates. 9-Methoxyfluorene was prepared as described in the following paper.³ 9-Methylfluorene was synthesized²⁰ and purified by recrystallization from methanol and sublimation, mp 44–45 °C (lit.²⁰ mp 44–45 °C). 9-Isopropylfluorene, **1c**, was prepared by a procedure analogous to that for **1b**. Fluorenone was removed by the procedure described for **1a**³ and the sublimed product had mp 51–52 °C (lit.²¹ mp 54–55 °C). 9-Aminofluorene, **1d**, was prepared by a published procedure²² and was stored and used as its hydrochloride salt. 9-Hydroxyfluorene (Aldrich) was used without purification.

Reaction Procedures. These are essentially as described in other articles in this series.^{2a,3}

Products of the Anaerobic Reaction of 9-Methoxyfluorene (1a) with 3,5-Dichloronitrobenzene. 9-Methoxyfluorene, **1a**, (198 mg, 1.01 mmol) and 3,5-dichloronitrobenzene (386 mg, 2.01 mmol) were dissolved in 10 ml of 0.47 N methanolic potassium methoxide under oxygen-free nitrogen. The reaction was allowed to proceed for 2 weeks at 30 °C. The precipitate which had formed was separated by filtration and washed with benzene to give 87 mg of white crystalline material, mp 272–274 °C, which was recrystallized from benzene: mp 274–276 °C; NMR (CDCl₃) δ 7.0–7.6 (8 H, m), 3.0 (6 H, s); ir (KBr) 3020–3030 (m), 2900–2910 (m), 2820 (m), 1570 (m), 1580 (m), 1440 (s), 1200 (m), 1110 (s), 1080 (s), and 740 (s) cm⁻¹. Anal. Calcd for C₂₈H₂₂O₂: C, 86.16; H, 5.82. Found: C, 86.26; H, 5.82. Based on these data this compound was deduced to be 9,9'-dimethoxy-9,9'-bifluorene, **2a**. No molecular ion could be detected in this mass spectrum, the highest peak appearing at $m/e = 195$ amu.

The filtrate and washings were combined and treated with 100 ml of H₂O in 50 ml of saturated aqueous NaCl solution. This was extracted with 200 ml of ether in three portions and the combined extracts dried over Na₂SO₄ (anhydrous). Evaporation of the ether left a residue which was partially soluble in pentane-dichloromethane. The insoluble part, 19.8 mg, was identical with **2a**, above. The soluble part was recrystallized from hexane to give 40.1 mg of yellow crystals: mp 183–184 °C; mass spectrum (70 eV) m/e (rel intensity) 343 (4.2), 341 (23.9), 339 (35.5), 327 (5.3), 325 (31.5), 323 (45.8), 181 (15.0), and 180 (100); ¹H NMR (60 MHz, CDCl₃) δ 8.8–9.0 (m, 1), 6.7–7.7 (m, 9), 5.9–6.0 (m, 1); ir (CHCl₃) 3040, 1580 s (C=N),²³ 1230, 1215, 1140, 965, 1140, 965, 865, 812, and 645 cm⁻¹. Anal. Calcd for C₁₉H₁₁NOCl₂: C, 67.1; H, 3.26; N, 4.12. Found: C, 66.75; H, 3.36; N, 4.29. This material was identical (mixture melting point) with α,α -(2,2-diphenylene)-*N*-(3,5-dichlorophenyl)nitrene, **3a**, which was prepared by the following synthetic sequence.

***N*-(9-Fluorenylidene)-3,5-dichloroaniline.** This compound was prepared by adapting the method of Billman and Tai.²⁴ Fluorenone (2.20 g, 12 mmol) and 3,5-dichloroaniline (2.99 g, 18 mmol) were dissolved in benzene, and 0.1 ml of 48% HBr was added. The reaction mixture was refluxed for ca. 10 h with magnetic stirring using a Dean-Stark trap to remove water. The solvent was removed by distillation and the melt extracted with hot CHCl₃. Filtration and evaporation of the chloroform gave a residue which was recrystallized twice from methanol to give 84% of the desired imine: mp 133–134 °C; ¹H NMR (CCl₄) δ 6.6–7.9 (m); ir (CCl₄) 3029, 1658, 1600, 1579, 1559, 1453, 1425, 1310, 1102, 950, 791, 665, and 655 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 327 (11), 325 (65), 323 (100), 290 (26), 288 (78), 253 (49), 165 (74).

***N*-Fluorenylidene-3,5-dichlorophenylaniline *N*-Oxide.** A procedure similar to that of Johnson²⁵ was followed. *N*-(9-Fluorenylidene)-3,5-dichloroaniline (1.08 g, 3.3 mmol) was dissolved in 5 ml of CH₂Cl₂ and treated with a mixture of 5 ml of 40% peracetic acid and 5 ml of CH₂Cl₂ at 5 °C with stirring. The solution was washed consecutively with water, dilute aqueous ammonia, and saturated aqueous sodium chloride. Drying over Na₂CO₃ (anhydrous) and evaporation of solvent gave a residue which was recrystallized from hexane to give a first crop

of 96 mg (8.5%) of yellow crystals, mp 183–184 °C. The spectral properties of this material were identical with those of the product obtained from the reaction of **1a** with 3,5-dichloronitrobenzene.

Stoichiometry of the Anaerobic Reaction of 9-Methoxyfluorene (1a) with 3,5-Dichloronitrobenzene. 9-Methoxyfluorene, **1a**, (108.4 mg, 0.55 mmol) and 3,5-dichloronitrobenzene (98.4 mg, 0.51 mmol) were dissolved in 10 ml of 0.47 N potassium methoxide in methanol, and the mixture was allowed to react in a sealed ampule for 26 h at 30 °C. The dimer, **2a** (41.7 mg, 0.11 mmol), was recovered after thorough washing of the precipitated solids with hot methanol and benzene. The basic methanol solution and the washings were combined and added to a mixture of 25 ml of H₂O and 75 ml of saturated aqueous NaCl. This was extracted with 100 ml of pentane in three portions. After drying and removal of solvent, the residue was found to contain 0.22 mmol of the nitron, **3a**, and 0.06 mmol of dimer, **2a**, by ¹H NMR integration vs. added 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT), which had a peak δ 4.7 (s, 1) conveniently located between δ 6.0 (m, 1) for **3a** and δ 2.8 (s, 6) for **2a**. GC analysis vs. added hexadecane showed 0.25 mmol of unreacted 3,5-dichloronitrobenzene.

Products of the Anaerobic Reaction of 9-Methoxyfluorene (1a) with Nitrobenzene. 9-Methoxyfluorene, **1a**, (93.0 mg, 0.47 mmol) and nitrobenzene (258 mg, 2.10 mmol) were sealed in an ampule with 10 ml of 0.49 N potassium methoxide in methanol. The reaction was allowed to proceed for 144 h at 30 °C. The dimer, **2a**, (45.2 mg, 0.12 mmol) was separated by filtration. The filtrate was placed in a mixture of pentane, H₂O, and saturated aqueous NaCl. The pentane extract was evaporated and a weighed amount of DDT added as an NMR standard. Analysis by NMR showed 0.12 mmol of α,α -(2,2'-diphenylene)-*N*-phenylnitron, **3b**. In a separate experiment, this product was isolated, mp 192–193.5 °C (lit.²⁶ mp 192–193 °C). This material was identical in physical and spectral properties with an authentic sample. A mixture melting point was undepressed.

Product of the Reaction of 9-Methoxyfluorene (1a) with Nitrobenzene or 3,5-Dichloronitrobenzene in an Oxygen Atmosphere. When **1a** was treated with either of the two aromatic nitro compounds in methanolic potassium methoxide and the mixture stirred at 30 °C in an oxygen atmosphere under the conditions described in the following paper,³ fluorenone was isolated and shown to be identical with an authentic sample by mixture melting point and spectral analysis. It was shown by GC vs. internal hexadecane to account quantitatively for the loss of **1a**.

Product of the Anaerobic Reaction of 9-Methylfluorene (1b) with 3,5-Dichloronitrobenzene. 9-Methylfluorene, **1b**, (6.09 g, 33.8 mmol), 3,5-dichloronitrobenzene (6.60 g, 34.4 mmol), and pentadecane (270 μ l) were placed in a 200-ml ampule, and a 1-ml aliquot was removed for GC analysis. A 1.33 N solution of potassium methoxide in methanol (20 ml) was then added and the resultant solution degassed. The ampule was sealed under reduced pressure and kept at 30 °C for 9 days. The ampule was then opened and the precipitate separated by filtration to give, after washing with methanol, 8.55 g of crystalline product (95% as **4a**), mp 128–130 °C dec. After recrystallization from benzene–pentane, the compound had mp 130–131.5 °C dec; ir (CCl₄) 3020–3080 (m), 3000 (m), 2960 (m), 1565 (s), 1450 (s), 1430 (s), 1375 (m), 1210 (m), 1250 (m), 1180–1200 (s), 940 (m), 690 (w), and 670 (w) cm⁻¹; ¹H NMR (CDCl₃) δ 7.1–7.8 (m, 16), 6.7 (t, 1), 6.3 (d, 2), 1.7 (s, 3), 1.4 (s, 3); ¹³C NMR (internal Me₄Si in CDCl₃) δ 22.7 (CH₃), 24.0 (CH₃), 74.8 (fluorenyl C-9), 87.9 (fluorenyl C-9), and at least 12 peaks 119–152 (aromatic C). A mass spectrum could not be obtained due to decomposition at required inlet temperature. Anal. Calcd for C₃₅H₂₅NOCl₂: C, 76.40; H, 4.71; N, 2.62; Cl, 13.26. Found: C, 76.65; H, 4.95; N, 2.92; Cl, 13.73. GC analysis showed that 19.3 mmol of 3,5-dichloronitrobenzene was consumed in the reaction.

Hydrogenation of Thermal Decomposition Products of *N,O*-Bis(9-methyl-9-fluorenyl)-*N*-(3,5-dichlorophenyl)hydroxylamine (4a). In order to provide additional evidence that two 9-methyl-9-fluorenyl residues were present in **4a**, **4a** (269 mg, 0.50 mmol) was heated in 10 ml of benzene at 65 °C for 24 h under anaerobic conditions. The resultant solution was hydrogenated over Pd/C catalyst and took up 3.5 mmol of H₂. GC analysis showed 0.75 mmol of 9-methylfluorene, **1b**, to be present.

Thermal Decomposition of *N,O*-Bis(9-methyl-9-fluorenyl)-*N*-(3,5-dichlorophenyl)hydroxylamine, 4a, in the Presence of Thiophenol. Compound **4a** (997 mg, 1.87 mmol) was treated with thiophenol (2 ml) and benzene (8 ml), and the resultant solution was degassed, sealed in an ampule, and heated at 65 °C for 24 h. The contents of the

ampule were added to 30 ml of 2 N NaOH, and the mixture was extracted with ether. The ether was evaporated and the residue chromatographed on silica gel using mixtures of pentane and CH₂Cl₂. The following compounds were recovered and identified from their melting point and spectral properties: 3,3',5,5'-tetrachloroazoxybenzene, **5a**, (34 mg, 0.10 mmol), 9-methylfluorene, **1b**, (90 mg, 0.50 mmol), 3,5-dichloronitrobenzene (23 mg, 0.12 mmol) and 9,9'-dimethyl-9,9'-bifluorene, **2b** (160 mg, 0.45 mmol). Also isolated was *N*-(9-methyl-9-fluorenyl)-3,5-dichloroaniline, **9** (200 mg, 0.45 mmol, identical with the product of independent synthesis described below). Two unidentified sulfur-containing compounds were also recovered (84 mg and 50 mg).

***N*-(9-Methyl-9-fluorenyl)-3,5-dichloroaniline (9).** A solution of *N*-(9-fluorenylidene)-3,5-dichloroaniline (1.0 g, 3.08 mmol) in 10 ml of ether was added dropwise to 5 ml of 1 M methylolithium in ether with cooling. Water was added dropwise until effervescence ceased and an additional 25 ml added. The ether layer was separated, dried, and evaporated. Four recrystallizations from methanol gave a small yield of the desired product (100 mg, 0.29 mmol) as white prisms: mp 193–194 °C; ir (CHCl₃) 3400, 3030, 1592, 1578, 1451, 1374, 1319, 1269, 1103, 1085, 990, and 176 cm⁻¹; ¹H NMR (60 MHz, CDCl₃) δ 1.6 (s, 3), 5.7–5.9 (m, 2), 6.3–6.5 (m, 1), 7.1–7.8 (m, 8); mass spectrum (70 eV) *m/e* (rel intensity) 343 (0.7), 341 (3.8), 339 (5.9), and 179 (100). Anal. Calcd for C₂₀H₁₅NCl₂: C, 70.60; H, 4.44; N, 4.12. Found: C, 70.77; H, 4.45; N, 4.16.

***N*-(9-Methyl-9-fluorenyl) *N*-(3,5-Dichlorophenyl) Nitroxide (8a).** A procedure similar to that of Rassat²⁷ was used. Approximately 10 mg of 9-methyl-9-fluorenyl-3,5-dichloroaniline, **9**, and 10 mg of *p*-nitroperbenzoic acid were dissolved in 0.1 ml of degassed benzene in a 2-mm pyrex tube under purified N₂. The tube was sealed in vacuo. The ESR spectrum observed was identical with that of a benzene solution of **4a**.

Products of the Anaerobic Reaction between 9-Methylfluorene (1b) and Nitrobenzene in 2.0 N Potassium Methoxide in Methanol at 30 °C. 9-Methylfluorene, **1b** (541 mg, 2.96 mmol) and nitrobenzene (738 mg, 6.0 mmol) were dissolved in 30 ml of 1.98 N potassium methoxide in methanol under purified N₂. After 19 h at 30 °C, the precipitated solid was separated by filtration (fritted glass funnel) to give 454 mg, 71.5% as **4b**, mp 110–120 °C. Two recrystallizations from methanol–ether gave white crystals: mp 134–135 °C; ir (CHCl₃) 3020, 2960, 2920, 3880, 1500, 1450, 1370, 1300, 1090, 910, and 629 cm⁻¹; ¹H NMR (60 MHz, CDCl₃) δ 6.8–7.8 (m, 24), 6.3 (s, 4), 1.6 (s, 6), and 1.3 (s, 3). Anal. Calcd for C₄₈H₃₇NO: C, 89.55; H, 5.79; N, 2.18. Found: C, 89.90; H, 5.66; N, 2.07.

The methanol solution was poured into aqueous NaCl and extracted with ether. The ether solution was washed with saturated aqueous NaCl, dried (anhydrous Na₂SO₄), and the ether evaporated. Column chromatography on alumina (Woelm grade III) allowed recovery of nitrobenzene (450 mg, 3.65 mmol), additional **4b** (21 mg, 0.033 mmol, 3.3%), **5c** (56.7 mg, 0.151 mmol, 5.1%), and **5b** (24.6 mg, 0.0443 mmol, 3.0%). Compounds **5b** and **5c** were identified by comparison with larger quantities of these compounds from the subsequently described run at lower base concentration.

ESR Spectrum of *N*-(9-Methylfluorenyl) *N*-(4-(9-Methylfluorenyl)phenyl) Nitroxide (8b). When **4b** was dissolved in benzene, the ESR spectrum of Figure 3a was observed. A product analogous to **4b** formed from 9-methylfluorene and nitrobenzene-2,6-*d*₂ gave the spectrum of Figure 3b.

Products of the Anaerobic Reaction between 9-Methylfluorene (1b) and Nitrobenzene in 0.5 N Potassium Methoxide in Methanol at 30 °C. 9-Methylfluorene, **1b**, (1.039 g, 5.77 mmol), nitrobenzene (2.4 g, 19.5 mmol), and 100 ml of 0.5 N potassium methoxide in methanol were sealed in an ampule and kept at 30 °C for 4 weeks. The reaction mixture was then added to 250 ml of water and extracted several times with ether. The ethereal extract was washed with saturated aqueous NaCl, dried (anhydrous Na₂SO₄), and the ether evaporated. The residue was chromatographed on Woelm grade III alumina using a mixture of pentane and CH₂Cl₂ and separated into several fractions from which the products indicated in Table I were isolated by fractional crystallization. The listed yields were estimated from the recovered weights and from NMR spectral measurements on the mixtures.

A white solid decomposing at 290 °C and insoluble in all organic solvents was tentatively concluded to be the polymer of dibenzofluorene.²⁸

Nitrobenzene (1.88 g, 15.3 mmol) was evaporated from a fraction

which also contained two dimers: 9,9'-dimethyl-9,9'-bifluorene, **2b**, mp 217–218 °C (lit.²⁹ mp 209 °C); ¹H NMR (60 MHz, CDCl₃) δ 6.7–7.5 (m, 16 ± 2), 2.9 (m, 6); mass spectrum (70 eV) *m/e* (rel intensity) 358 (0.56), 179 (100), 165 (0.25). This fraction also contained fluoren-9-yl-9-methylfluoren-9-ylmethane, **6a**, as evidenced by the NMR spectrum of the mixture.

Compound **6a** was separated from a subsequent fraction by fractional crystallization: mp 175–176 °C (lit.³⁰ 172–173 °C); ¹H NMR (60 MHz, CDCl₃) δ 1.6 (s, 3), 2.6 (d, 2), 3.1 (t, 1), 6.5–7.8 (m, 16); mass spectrum (70 eV) *m/e* (rel intensity) 358 (17), 193 (14), 179 (100), and 165 (26).

A subsequent fraction gave a small amount of white crystalline material: mp 211–212 °C; ¹H NMR (60 MHz, CDCl₃) δ 1.3 (s, 3), 2.5 (d, 2), 2.8 (t, 1), 3.2 (s, 2), 6.3–7.4 (m, 24); mass spectrum (70 eV) *m/e* (rel intensity) 537 (5.5), 536 (12.1), 358 (1.7), 193 (10.5), 179 (100), and 165 (53.2). From these data the structure was deduced to be that of 1,3,5-tris(2,2'-diphenylene)hexane, **6b**.

Further elution produced a viscous yellow oil: ¹H NMR (60 MHz, CDCl₃) δ 1.8 (s, 3), 7.0–8.2 (m, 17); mass spectrum (70 eV) *m/e* 376, 361, 255, 179, and 165. Although this compound was not purified, spectral data suggested a 9-methylfluoren-9-ylazoxybenzene, **5c**. It seems likely that the compound was present in at least two isomeric forms.

The final compound obtained was recrystallized from CHCl₃-ethanol to give light yellow crystals: mp 193–195 °C; ¹H NMR (60 MHz, CDCl₃) δ 1.8 (s, 6), 6.9–7.4 (m, 16), 7.5–8.1 (m, 8); ir (CHCl₃) 3030, 2980, 2940, 2900, 1600, 1500, 1480, 1460, 1415, 1380, 1335, 1305, 1295, 1210, 1070, 1030, and 1015 cm⁻¹; mass spectrum (70 eV) *m/e* 554, 255, and 179. It was concluded that this compound was bis(9-methyl-9-fluoren-9-yl)azoxybenzene, **5b**, although elemental analysis gave consistently low % C by 1–2%. Contamination with **5c** was suspected.

Products from the Anaerobic Reaction between 9-Methylfluorene (1b) and Nitrobenzene in *tert*-Butoxide–Dimethyl Sulfoxide. 9-Methylfluorene, **1b**, (99.8 mg, 0.55 mmol) was treated with 10 ml of a degassed solution of 0.5 N potassium *tert*-butoxide in Me₂SO under argon. The solution immediately became cherry red in color. Nitrobenzene (240 mg, 1.95 mmol) was then added producing an instantaneous change to a deep-red color. After 30 min, oxygen was bubbled through the solution until the red color disappeared. The reaction mixture was added to 60 ml of water and extracted with 125 ml of ether in four portions. The combined ether extracts were washed with saturated aqueous NaCl and dried (anhydrous Na₂SO₄). The ether and nitrobenzene were evaporated, and 1,2-dibromoethane (105.7 mg, 0.563 mmol) was added to the residue as a ¹H NMR standard. ¹H NMR analysis then showed 9,9'-dimethyl-9,9'-bifluorene, **2b**, (0.17 mmol, 62%) and 9-methyl-9-hydroxyfluorene (0.17 mmol, 31%). Similar experiments on a larger scale allowed isolation and identification of both of these compounds.

Product of the Reaction of 9-Methylfluorene (1b) with Aromatic Nitro Compounds in Methoxide–Methanol in an Oxygen Atmosphere. 9-Methylfluorene, **1b**, (296 mg, 1.64 mmol) and nitrobenzene (855 mg, 6.95 mmol) were treated with 15.0 ml of 1.8 N potassium methoxide in methanol. The reaction was allowed to proceed under an atmosphere of oxygen at room temperature for 11 days. The reaction mixture was poured into pentane and water and the pentane layer separated and dried (anhydrous Na₂SO₄). Concentration of the pentane solution gave white crystals (274 mg, 85% as 9-methyl-9-hydroxyfluorene), mp 178–179 °C. After recrystallization from benzene, this product had mp 177–177.5 °C (lit.³¹ mp 175 °C). Its ¹H NMR and elemental analysis agreed with this assignment.

Product of the Anaerobic Reaction of 9-Isopropylfluorene (1c) with Nitrobenzene in Methoxide–Methanol at 50 °C. 9-Isopropylfluorene, **1c**, (830 mg, 4.0 mmol) and nitrobenzene (1.326 g, 10.8 mmol) were treated with 42.2 ml of 1.4 N potassium methoxide in methanol. This solution was kept at 50 °C under purified N₂ for 2 weeks. A yellow material (308 mg, 25.1% as **5b**) precipitated from the reaction mixtures. The supernatant was poured into a mixture of pentane and water, and the pentane layer was separated. The water layer was neutralized with dilute HCl and further extracted with ether. The ether and pentane layers were combined, dried (anhydrous MgSO₄) and the solvents removed under reduced pressure. The residue was column chromatographed on silica gel using pentane containing increasing amounts of CH₂Cl₂. In this way, unreacted **1c** (279 mg, 33.4%), nitrobenzene (1.086 g, 81.5%), and more **5b** (452 mg, 36.8%) were recovered along with 84 mg of an unidentified product. A total

of 760 mg of **5b** was obtained: mp 276–277 °C; ¹H NMR (60 MHz, CDCl₃) δ 7.8–8.2 (d, 4), 7.4–7.7 (m, 4), 7.0–7.4 (m, 16), 3.0 (m, 2), 0.7 (d, 12); ir (CCl₄) 3040 (s), 2940 (s), 2880 (m), 1960 (w), 1890 (w), 1590 (s), 1440 (s), 1450 (s), 1460 (s), 1400 (w), 1380 (w), 1360 (w), 1320 (m), 1290 (m), 1270 (m), 1160 (m), 1100 (m), 1010 (m), 900 (m), 680 (s), 640 (m), and 620 (w) cm⁻¹; mass spectrum (70 eV) *m/e* 610, 594, 567, 551, 508, 361, 345, 256, 254, 240, and 239. Anal. Calcd for C₄₄H₃₈N₂O: C, 86.53; H, 6.27; N, 4.58. Found: C, 86.58; H, 6.51; N, 4.56. Based on these data the major product was deduced to be 4,4'-bis(9-isopropylfluoren-9-yl)azoxybenzene, **5d**. The assignment of position of substitution must be regarded as tentative, although the ¹H NMR spectrum, steric arguments, and analogies^{2a} strongly suggest that it is correct.

Product of the Anaerobic Reaction of 9-Isopropylfluorene (1c) and 3,5-Dichloronitrobenzene in Methoxide–Methanol at 30 °C. 9-Isopropylfluorene, **1c**, (289.8 mg, 1.39 mmol) and 3,5-dichloronitrobenzene (786.4 mg, 4.10 mmol) were sealed in an ampule with 10 ml of 1.98 N potassium methoxide in methanol. After 2 days at 30 °C, the ampule was opened and the precipitate was separated by filtration (351 mg, 0.595 mmol, 85% as **4a**), mp 151–152 °C. Three recrystallizations from ether–methanol gave white cubes, mp 154.5–156 °C; ¹H NMR (60 MHz, CDCl₃) δ 6.7–7.6 (m, 16), 6.5–6.6 (m, 1), 5.9 (s, 2), 2.3–3.0 (m, 2), 0.8 (d, 6), 0.3 (d, 6). Anal. Calcd for C₃₈H₃₃NOCl₂: C, 77.28; H, 5.63; N, 2.37; Cl, 12.00. Found: C, 77.10; H, 5.63; N, 2.37; Cl, 12.06. When this product was dissolved in benzene, an ESR spectrum similar to that of the 9-methyl analogue was observed. The spectrum, a triplet of quartets, had *a*_N = 12.1 G and *a*_H = 2.42 G. From these data, the product was deduced to be *N,O*-bis(9-isopropyl-9-fluorenyl)-*N*-(3,5-dichlorophenyl)hydroxylamine, **4a**.

Products and Stoichiometry of the Anaerobic Reaction between 9-Aminofluorene (1d) and Aromatic Nitro Compounds. 9-Aminofluorene hydrochloride (109 mg, 0.50 mmol) and 3,5-dichloronitrobenzene (395 mg, 2.06 mmol) were treated with 6.8 ml of methanol and 3.2 ml of 0.47 N potassium methoxide in methanol. The mixture was sealed in an ampule and allowed to react at 30 °C for 24 h (ca. 6 exchange half-lives). The ampule was then opened and the precipitate separated by filtration, washed with water, and dried over P₂O₅ to give 49.3 mg (0.15 mmol) of 3,3',5,5'-tetrachloroazoxybenzene, **5a**, mp 174 °C (lit.³² mp 172–173 °C). The filtrate was treated with a measured amount of hexadecane (GC standard) and placed in a separatory funnel with 80 ml of saturated aqueous NaCl solution. This was extracted with 100 ml of pentane in three portions. Three milliliters of the total pentane extract was used for GC analysis and showed 3,5-dichloronitrobenzene (1.70 mmol). The remaining pentane extract was treated with dry HCl gas and precipitated the orange hydrochloride of 9-aminofluorene, **7a** (103 mg, 0.48 mmol). Anal. Calcd for C₁₃H₁₀NCl: C, 72.3; H, 6.5; N, 4.7; Cl, 16.4. Found: C, 71.3; H, 6.5; N, 4.7; Cl, 17.0. Treatment of the orange solid either with aqueous NaOH or with liquid ammonia gave **7a**: mp 114–120 °C and mp 125–126 °C, respectively (lit.¹³ mp 124 °C); ¹H NMR (60 MHz, CDCl₃) δ 7.0–7.6 (m, 8), 9.2 (s, 1); ir (KBr) 3200 (s), 1630 (m) cm⁻¹; mass spectrum (70 eV) *m/e* 179 amu. Anal. Calcd for C₁₃H₉N: C, 87.15; H, 5.26; N, 7.57. Found: C, 87.12; H, 5.06; N, 7.82. If the reaction mixture was injected into 3 N HCl and extracted immediately with pentane, only 0.008 mmol of fluorenone was detected. If the precipitated orange solid was allowed to stand in contact with the HCl solution, hydrolysis occurred and fluorenone could be extracted quantitatively. The reaction with nitrobenzene was similar except that azoxybenzene did not precipitate.

Product of the Reaction of 9-Aminofluorene (1d) with 3,5-Dichloronitrobenzene in an Oxygen Atmosphere. The results were essentially identical except that, in contrast to the nearly quantitative precipitation of **5a** in the anaerobic reaction, no **5a** was observed.

Products and Stoichiometry of the Anaerobic Reaction between 9-Hydroxyfluorene (1e) and 3,5-Dichloronitrobenzene. 9-Hydroxyfluorene, **1e**, (193.2 mg, 1.06 mmol) and 3,5-dichloronitrobenzene (415.1 mg, 2.16 mmol) were sealed in an ampule with 10 ml of 1.98 N potassium methoxide in methanol. The ampule was placed in a constant temperature bath at 30 °C and precipitation commenced immediately. After 4 h the ampule was opened and the precipitate of **5a**, mp 168–170 °C (lit.³² mp 172–173 °C), collected on a fritted-glass funnel (119.9 mg, 0.36 mmol). The filtrate was acidified with concentrated HCl and treated with an excess of 2,4-dinitrophenylhydrazine in methanol. The solution was boiled for 30 min and filtered to give the 2,4-dinitrophenylhydrazone of fluorenone (379.4 mg, 1.05 mmol, 99.4%), identical with an authentic sample.

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Carbanions. Electron Transfer vs. Proton Capture. 5. Reaction of 9-Methoxyfluorene with Aromatic Nitro Compounds Catalyzed by Alkali Metal and Tetraalkylammonium Methoxides

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Abstract: 9-Methoxyfluorene ion exists in dynamic equilibrium with 9-methoxyfluorene and methoxide ion at 30 °C in methanol. Although the concentration of this carbanion remains small and its reprotonation by methanol is rapid, it can be trapped through one-electron oxidation when aromatic nitro compounds are added to the reaction mixture. Acceptors having sufficiently high reduction potentials, 1,3-dinitrobenzene, 4-cyanonitrobenzene, and 3,5-dichloronitrobenzene, trap most of the carbanions produced, resulting in an ionization-limited formation of oxidation products. Nitrobenzene is a relatively inefficient electron acceptor and reacts reversibly with the carbanion as evidenced by a synergistic improvement in trapping efficiency for the system: nitrobenzene–molecular oxygen. The ionization rate of the carbon acid, the trapping efficiency of nitrobenzene, and the degree to which the electron transfer is reversible are all influenced by the nature and the concentration of the base employed. The second-order rate constant for ionization increases with increasing methoxide concentration for all of the counterions studied. At any particular $[\text{M}^+\text{OMe}]$ the second-order rate constants are in the order: $\text{Me}_4\text{NOMe} > \text{KOMe} > \text{NaOMe} > \text{LiOMe}$. The same order is observed in the nitrobenzene trapping efficiency when the trapping is irreversible (oxygen present). With nitrobenzene alone, however, the electron transfer is highly reversible for the Me_4NOMe reaction and, in the absence of oxygen, the trapping efficiency with $\text{KOMe} > \text{Me}_4\text{NOMe} \approx \text{LiOMe}$.

The papers of this series describe our efforts to relate the environment of carbanions to the efficiency of their electron transfer reactions. The medium chosen for most of our previous work had been *tert*-butyl alcohol, a protic but nonpolar solvent in which carbanions are believed to exist as contact ion pairs. We had found¹ that the type of ion pairing dramatically affects the electron transfer efficiency.

By contrast with *tert*-butyl alcohol, the environment of carbanions in polar protic solvents is enigmatic. In methanol, for example, rates and equilibria of carbanion reactions are cation dependent² but the usual spectroscopic³ and stereochemical⁴ tests for ion pairing give somewhat ambiguous re-

sults. We therefore decided to study the electron transfer efficiency of a carbanion in this medium as a function of the nature and concentration of its counterion. Of the various systems described in the preceding paper,⁵ we selected 9-methoxyfluorene ion for detailed investigation because the products of its reaction with aromatic nitro compounds were most unequivocally the result of one-electron transfer.

Results and Discussion

The reaction of carbon acids with alkoxide bases and aromatic nitro compounds has been discussed previously^{1,2f} and is related to the present study in Scheme I, where $k_e = k_e'$