Radical-anion Intermediates. Part IV.[1] Radical Anions of Some 9-Substituted Fluorenes

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A large number of 9-substituted fluorenes react with alkali metals at −70 °C to give radical anions. At higher temperatures these radical anions are unstable and decay to give the corresponding anions. When either lithium or potassium was the counterion the radical anion decay was found to be first order in all but one system. When sodium was the counterion the decay was complicated by an equilibrium between metallic sodium and the hydrocarbon on one hand and the radical anion on the other. However it was possible in two such systems to determine ΔH° and ΔS° for this equilibrium. A small number of the 9-substituted fluorenes studied reacted at −70 °C to give both e.s.r. and u.v./visible absorption spectra identical to that of the fluorene radical-anion.

FLUORENE and many fluorene derivatives react with alkali metals at −70 °C to form the corresponding radical anions.[1-3] The radical anions decay when the temperature is raised, however, to form the corresponding anions. The radical anions have characteristic e.s.r. and u.v./visible absorption spectra either of which may be used to follow the kinetics of the decay. In most cases the absorption spectra of the anions are well known and may be used to characterise the reaction products.

This study extends the range of radical anions further with a number of 9-substituted fluorenes. It was hoped that this might lead to a further clarification of the reaction scheme.

EXPERIMENTAL

All operations were performed with standard high vacuum techniques.

Materials.—Tetrahydrofuran (B.D.H.) was purified as described.[4] 9-Methylfluorene (Aldrich) was recrystallised several times from AnalaR methanol, m.p. 46 °C (lit.,[5] m.p. 46—47 °C). 9,9′-Bifluorene (Aldrich), 9-chlorofluorene (Emanuel), and 9-bromofluorene (Fluka) were all used as supplied. The 9-ethyl, 9-n-propyl, and 9-n-butyl derivatives were prepared by heating a mixture of the corresponding sodium alkoxide and fluorene in a steel bomb for 16 h at 220 °C.[6] Purification was by t.l.c., a combination of large silica plates and 80% hexane–chloroform was found to be suitable for separation of the pure materials. The 9-isopropyl and 9-benzyl derivatives were prepared by reaction of the Grignard reagent (bromide) with fluorenone, followed by acetic acid–zinc reduction and then hydrogenolysis. Purification by repeated recrystallisation from AnalaR methanol gave 9-isopropylfluorene, m.p. 54—55 °C (lit.,[5] m.p. 55 °C) and 9-benzylfluorene, m.p. 134·5 °C (lit.,[7] m.p. 134—135 °C). 9-t-Butylfluorene was prepared by the method of Anet *et al.*[8] and recrystallised as before, m.p. 101·5 °C (lit.,[8] m.p. 101·5 °C). The authenticity of all samples was checked by n.m.r. and purity by t.l.c. or differential scanning calorimetry or both.

Lithium, sodium, and potassium (all B.D.H.) were washed in light petroleum before use.

Procedure.—Solutions of the 9-substituted fluorenes in tetrahydrofuran, and the corresponding radical anions, were prepared at −70 °C as described.[3] For the lithium reductions a lithium film was prepared by distilling liquid ammonia onto lithium chips. After dissolution of the lithium the ammonia was removed by vacuum distillation followed by pumping under high vacuum. The concentrations of the resulting solutions were in the range 1×10^{-3}—5×10^{-3}M.

Spectroscopic Measurements.—All u.v./visible absorption spectra were recorded on a Unicam SP 800 spectrophotometer over the range ±50 °C by means of the constant-temperature cell housing described.[4] The change in optical density at the required wavelength, with time was recorded as described.[2,4] E.s.r. spectra were recorded on a Varian

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Part III, D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1970, **1565**.

[2] D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1969, **887**.

[3] D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1970, **1560**.

[4] D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1969, **572**.

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

[6] K. L. Schoen and E. I. Becker, *Org. Synth.*, 1963, Coll. Vol. IV, p. 624.

[7] Y. Sprinzak, *J. Amer. Chem. Soc.*, 1956, **78**, 466.

[8] F. A. L. Anet and P. M. Bavin, *J. Canad. Chem. Soc.*, 1956, **34**, 991.

E3 spectrometer, the temperature of the sample being controlled by a Varian E-4557 variable-temperature unit. The change in intensity of the e.s.r. absorption, with time was recorded by following the amplitude of the first derivative e.s.r. spectrum at fixed magnetic field.

Calculations.—Calculations were performed with the aid of an I.C.L. 1909 computer.

RESULTS

Spectra.—The 9-methyl, 9-ethyl, 9-n-propyl, 9-isopropyl, 9-n-butyl, 9-t-butyl, and 9-benzyl derivatives all reacted at −70 °C with alkali metals in tetrahydrofuran to give the corresponding radical anions. The resulting radical-anion solutions were blue and had characteristic e.s.r. and u.v./visible absorption spectra (see Table 1). A typical absorption spectrum, of the 9-ethylfluorene radical-anion, is shown in Figure 1B.

TABLE 1

The absorption spectra of the radical anions and anions of the 9-substituted fluorenes studied, with lithium as the counterion, in tetrahydrofuran. (In some systems the relative intensities of the absorption maxima varied with temperature)

Subst.	$\lambda_{max.}$/nm Radical anion [a]	$\lambda_{max.}$/nm Anion
9-Me	*ca.* 635, 682	384, 446, 478, 514, 553
9-Et	*ca.* 635, 678	385, 444, 474, 512, 549
9-Pr^n	*ca.* 635, 680	384, 446, 475, 511, 550
9-Pr^i	*ca.* 635, 682	385, 476, 510, 550
9-Bu^n	*ca.* 635, 676	384, 446, 474, 510, 549
9-Bu^t	*ca.* 635, 670	372, 384, 442, 502, 540

[a] Other radical-anion absorptions are present in the region 380—400 nm (see Figure 1) but are not recorded here.

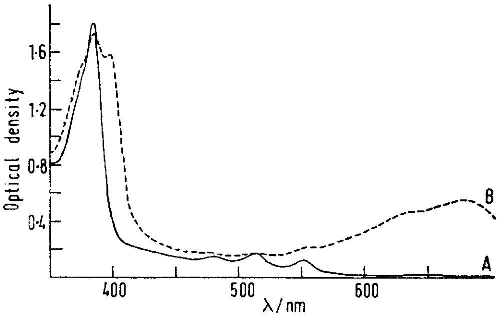


FIGURE 1 A, The absorption spectrum of the 9-ethylfluorene anion in tetrahydrofuran at −9·6 °C, with lithium as the counterion. B, The absorption spectrum of the 9-ethylfluorene radical-anion in tetrahydrofuran at −9·6 °C, with lithium as the counterion (absorptions due to the anion are also present)

At higher temperatures the radical anions were relatively unstable and decayed to give a pale yellow-pink solution in which the e.s.r. absorption had completely disappeared. The latter solutions were stable indefinitely at room temperature and the u.v./visible absorption spectra were identical to those for the corresponding anions where these had been previously published.[5] Details of the absorption spectra of the anions are given in Table 1, and a typical absorption spectrum, of the 9-ethylfluorenyl anion, is shown in Figure 1A. The relative intensities of some of the radical-anion absorptions in the region 380—400 nm were found to be sensitive to the nature of the alkali-metal counterion.

Each of the radical anions had a characteristic e.s.r. spectrum and these will be the subject of Part V of this series.

Kinetics.—*Lithium and potassium.* The kinetics of the radical-anion decay were studied by recording either the decrease in intensity of the absorption due to the radical anion in the visible region of the spectrum or the decrease in the intensity of the e.s.r. absorption. The former technique was used for following slow reactions above −30 °C, and the latter technique for following fast reactions and for all reactions below −30 °C. Measurements using both techniques on the same system at the same temperature gave identical values for the velocity constant within experimental error.

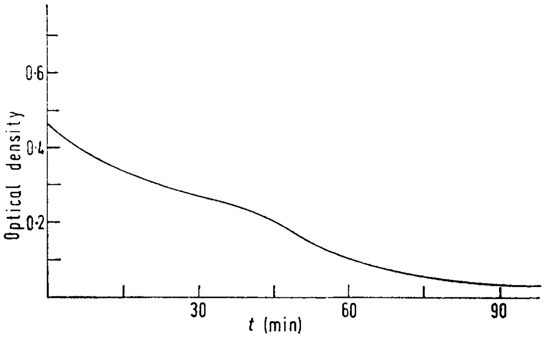


FIGURE 2 The reaction curve for the decay of the 9-methylfluorene radical-anion in tetrahydrofuran at −26·5 °C, with sodium as the counterion

The reaction curves for each system were analysed by plotting the functions $1/(a - x)$ and $\log_{10}(a - x)$ against time and were found to be of the first order with respect to the radical-anion concentration with the exception only of the 9-methylfluorene–lithium system. In this latter system first-order kinetics were observed in the temperature range +20·2 to −1·2 °C, and second-order kinetics in the range −12 to −20 °C. For all systems studied, when potassium or lithium was the counterion, good linear plots were obtained for at least 90% reaction. The temperature dependence of the velocity constant for the two counterions, lithium and potassium, was determined for each of the fluorene derivatives (Table 2). The values of $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ at 25 °C (determined by computer extrapolation if necessary) are summarised in Table 3.

Sodium. When sodium was the counterion the kinetics for the radical-anion decay were far more complex than for lithium or potassium and did not respond well to kinetic analysis. Figure 2 shows a typical reaction curve for these systems and clearly shows a 'hump' between *ca.* 20 and 60 min of reaction. The magnitude of this 'hump' decreased in significance as the temperature of reaction was decreased. However, the latter part of the reaction curves did give reasonably good straight lines for first-order analysis. The 9-methylfluorene radical-anion is an example of such a system where it was possible to obtain values for the first-order velocity constants in this way. The resulting plot of $\log_{10} k$ *vs.* $1/T$ (Figure 3) gives a value for $\Delta H^‡ = 8·9 \pm 0·8$ kcal mol^{-1} and $\Delta S^‡ = -36·9$ cal deg^{-1} mol^{-1} at 25 °C.

This type of reaction curve had been obtained previously

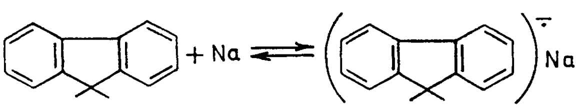
TABLE 2

Temperature-dependence of the velocity constant for the 9-substituted fluorenes studied in tetrahydrofuran

	Counterion—lithium		Counterion—potassium	
Subst.	k/s^{-1}	Temp. (°C)	k/s^{-1}	Temp. (°C)
9-Me	2.12×10^{-3}	20·2	5.31×10^{-3}	−50·0
	9.45×10^{-4}	15·1	4.15×10^{-3}	−55·4
	1.01×10^{-3}	15·0	1.69×10^{-3}	−60·8
	4.72×10^{-4}	10·6	1.23×10^{-3}	−60·8
	3.34×10^{-4}	4·8	1.63×10^{-3}	−65·9
	1.62×10^{-4}	−1·2	1.13×10^{-3}	−71·0
			1.14×10^{-3}	−71·0
			2.66×10^{-4}	−76·3
9-Et	5.43×10^{-3}	15·6	2.47×10^{-2}	−39·0
	2.67×10^{-3}	10·5	9.87×10^{-3}	−44·5
	2.37×10^{-3}	5·1	6.30×10^{-3}	−50·0
	1.64×10^{-3}	0·3	2.91×10^{-3}	−55·4
	5.25×10^{-4}	−6·0	1.26×10^{-3}	−60·8
	4.13×10^{-4}	−10·5		
9-Pr^{n}	3.07×10^{-3}	10·4	1.29×10^{-2}	−39·0
	1.88×10^{-3}	5·4	6.99×10^{-3}	−44·5
	8.25×10^{-4}	0·0	5.06×10^{-3}	−50·0
	3.45×10^{-4}	−5·5	2.88×10^{-3}	−55·4
	2.02×10^{-4}	−10·5	1.22×10^{-3}	−60·8
	1.39×10^{-4}	−16·3	6.60×10^{-4}	−66·0
9-Pr	2.40×10^{-3}	38·1	1.47×10^{-2}	−28·0
	3.25×10^{-3}	37·6	4.45×10^{-3}	−33·5
	1.62×10^{-3}	34·1	3.03×10^{-3}	−39·0
	1.11×10^{-3}	34·1	1.99×10^{-3}	−44·5
	1.19×10^{-3}	30·3	6.77×10^{-4}	−50·0
	9.01×10^{-4}	26·3		
	5.65×10^{-4}	23·6		
	5.71×10^{-4}	23·0		
	2.07×10^{-4}	19·6		
	1.29×10^{-4}	15·5		
9-Bu^{n}	4.37×10^{-3}	10·4	7.03×10^{-3}	−22·0
	2.43×10^{-3}	5·6	5.37×10^{-3}	−28·0
	1.32×10^{-3}	0·0	2.93×10^{-3}	−33·5
	9.08×10^{-4}	−6·5	1.07×10^{-3}	−44·5
	4.20×10^{-4}	−11·5	6.12×10^{-4}	−50·0
9-Bu^{t}	8.95×10^{-3}	14·9	8.19×10^{-3}	−16·5
	5.15×10^{-3}	10·0	8.30×10^{-3}	−22·5
	2.50×10^{-3}	4·6	2.67×10^{-3}	−28·0
	1.49×10^{-3}	0·7	1.43×10^{-3}	−33·5
	8.55×10^{-4}	−2·4	8.10×10^{-4}	−39·0
	4.16×10^{-4}	−6·4	4.80×10^{-4}	−44·5
	1.96×10^{-4}	−11·0		
9-PhCH$_2$	4.24×10^{-2}	−66·3		
	1.30×10^{-2}	−71·5		
	5.17×10^{-3}	−75·8		
	2.68×10^{-3}	−81·5		
	8.27×10^{-4}	−86·5		
9-Me	1.92×10^{-1} *	−12·0		
	1.57×10^{-1}	−14·3		
	3.79×10^{-2}	−17·3		
	2.37×10^{-2}	−19·3		

* Second-order temperature region, units of k are l mol^{-1} s^{-1}.

in the sodium–fluorene–tetrahydrofuran system.[2] A reasonable explanation seemed to be the presence of equilibrium (1). Evidence for this equilibrium in the present study



(1)

was found, as in the fluorene–sodium system, by observing the disappearance of the blue radical-anion colour upon warming and its reappearance upon rapid recooling. Two systems were chosen for further study in which the radical-anion decay was relatively slow at 0 °C. These systems presented an opportunity of obtaining further evidence for equilibrium (1) from e.s.r. measurements of the radical-anion concentration as a function of temperature. The results of these experiments are shown in Figure 4. Radical-anion concentrations were measured starting from −70 °C

TABLE 3

A summary of the values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ at 25·0 °C for each of the radical anions studied in tetrahydrofuran

	$\Delta G^{\ddagger}$ /kcal mol^{-1}		$\Delta H^{\ddagger}$ /kcal mol^{-1}		$\Delta S^{\ddagger}$ /cal deg^{-1} mol^{-1}	
Subst.	Li$^+$	K$^+$	Li$^+$	K$^+$	Li$^+$	K$^+$
9-Me	20·9	17·8	17·7 ± 1·5	7·8 ± 1·5	−10·9	−33·2
9-Et	20·1	16·1	14·3 ± 1·5	12·6 ± 0·7	−19·2	−11·9
9-Pr^{n}	20·0	17·1	17·3 ± 1·3	10·1 ± 0·6	−9·0	−23·4
9-Pr^{i}	21·9	17·1	22·1 ± 0·2	13·3 ± 1·7	+0·5	−12·8
9-Bu^{n}	20·0	18·5	14·3 ± 1·1	9·6 ± 0·5	−19·0	−29·8
9-Bu^{t}	19·4	18·4	21·8 ± 0·6	11·3 ± 0·3	+8·2	−24·0
9-PhCH$_2$	13·0		14·0 ± 1·0		+3·3	
9-Me	12·5 *		41·0 ± 6·6 *		+95·7 *	

* Second-order temperature region.

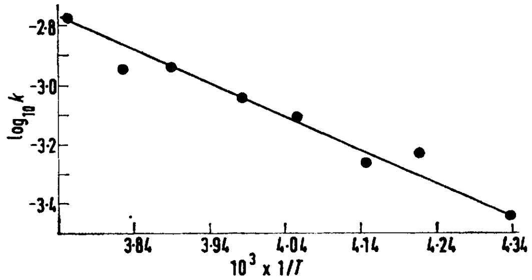


FIGURE 3 Plot of $\log_{10} k$ vs. $1/T$ for the decay of the 9-methylfluorene radical-anion, in tetrahydrofuran with sodium as the counterion, values of k taken from the latter part of the reaction curves

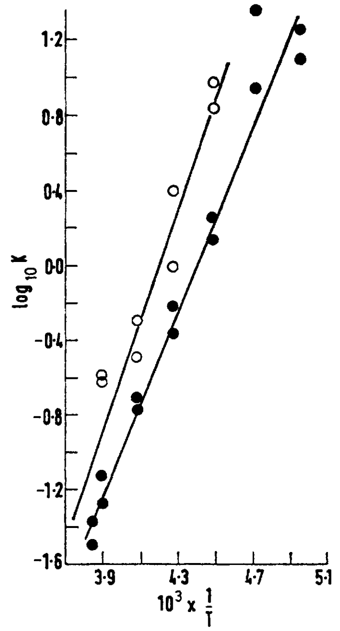


FIGURE 4 Plot of $\log_{10} K$ vs. $1/T$ for equilibrium (1) in tetrahydrofuran for the 9-isopropylfluorene–Na (●) and 9-t-butylfluorene–Na (○) systems

in 10° intervals. Some decay of the radical-anion occurred during these measurements but a correction was made for this in calculating the radical-anion concentration at each temperature. Figure 4 shows clear evidence for equilibrium (1) in the two systems, and allows approximate values for ΔH° to be calculated (Table 4). Further, the Figure also shows the equilibrium to favour the radical anion at low temperatures, which is consistent with the decrease in the significance of the ' hump ' at these temperatures, and indeed with the observation of the loss of the blue colour upon warming.

TABLE 4

A summary of the values of ΔG°, ΔH°, and ΔS° at 25 °C for equilibrium (1) with sodium as the counterion in tetrahydrofuran

Subst.	ΔG° /kcal mol^{-1}	ΔH° /kcal mol^{-1}	ΔS° /cal deg^{-1} mol^{-1}
9-Pr^i	+3·3	−10·4	−45·9
9-Bu^t	+3·0	−12·6	−52·3

9,9′-Bifluorene and the 9-Bromo- and 9-Chloro-derivatives.—Each of these derivatives reacted with lithium in tetrahydrofuran at −70 °C to give both u.v./visible and e.s.r. spectra identical to that of the fluorene radical-anion. The radical-anion concentration in all cases was considerably greater than could have been obtained from any trace impurities of fluorene in the samples used.

DISCUSSION

Lithium and Potassium as Counterions.—It was hoped that a kinetic study of the radical anions of the 9-substituted fluorenes would indicate the presence of steric effects. However, perhaps the most striking feature of the results for the 9-alkyl derivatives given in Table 3 is found in a comparison of the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for each of the radical anions in changing the counterion from lithium to potassium. The values of $\Delta H^\ddagger$ are always smaller for potassium (by varying amounts) and, with only one exception (9-ethylfluorene), the values of $\Delta S^\ddagger$ are more negative.

By analogy with the solvent separated nature of the fluorenyl anion/Li ion pair in tetrahydrofuran in this temperature region,[9] the 9-substituted fluorenyl anions would also be expected to have a solvent-separated arrangement with lithium as the counterion. Evidence for this may be found in the u.v./visible absorption spectra of the anions given in Table 1 and ref. 5. These spectra show a single absorption maxima at approximately 384 nm in tetrahydrofuran; there is little evidence in most of the anions for a shoulder at lower wavelengths corresponding, by analogy, to the contact ion-pair. In contrast, however, this is not the case for each of the alkali-metal counterions. For example, the absorption spectrum of the 9-methylfluorene anion with lithium, sodium, or potassium as the counterion. When lithium is the counterion only a single absorption at 384 nm is present. However, when sodium is the counterion maxima are present at 369 and 384 nm. The former is favoured by an increase in temperature and presumably corresponds to the contact ion-pair. When potassium is the counterion only the former maxima, shifted slightly to 374 nm, is present. This behaviour complements that of the fluorenyl anion and leads to the conclusion that in the case of the 9-substituted fluorenyl anions, the ions exist as solvent-separated ion-pairs when lithium is the counterion and as contact ion-pairs when potassium is the counterion. In the 9-substituted fluorene radical-anions the coulombic interaction between the ions should be smaller than with the corresponding anions reflecting the delocalisation of the negative charge compared to the anion. This would be expected to favour the formation of solvent-separated ion-pairs but even so it is doubtful if, over the temperature range of the kinetic study, an appreciable fraction of the radical-anion ion-pairs are solvent separated when potassium is the counterion.

Undoubtedly the two most important factors involved in the variation of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ between the two counterions are the variation of the coulombic interaction and solvation effects. For both counterions the coulombic interaction should be greater in the transition state than in the radical-anion ion-pairs. This should facilitate formation of the transition state possibly more so in the contact ion-pair arrangement, *i.e.* when potassium is the counterion. Solvation will be more important in the solvent-separated ion-pair arrangement and the more positive $\Delta S^\ddagger$ with lithium as the counterion presumably reflects this. The increased coulombic interaction in the transition state could well be reponsible for a rearrangement of solvent molecules around the lithium counterion resulting in a larger $\Delta H^\ddagger$ and a more positive $\Delta S^\ddagger$ compared to potassium.

Perhaps some evidence for the presence of steric effects may be found in comparing the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the 9-n-propyl and 9-n-butyl derivatives with the values for the 9-isopropyl and 9-t-butyl derivatives respectively. For both counterions the values of $\Delta H^\ddagger$ are smaller and of $\Delta S^\ddagger$ are more negative for the n-derivatives. This could reflect steric hindrance to the counterion in forming the transition state. Presumably if the counterion is able to approach the anion more closely in the n-derivatives, the coulombic interaction will be somewhat greater. Both these effects should result in a lower $\Delta H^\ddagger$ for the n-derivatives and the latter effect should also contribute to a more negative $\Delta S^\ddagger$.

Sodium as Counterion.—The e.s.r. measurement of the variation in the radical-anion concentration with temperature together with the reversible disappearance of the blue radical-anion colour indicates the presence of equilibrium (1) in the 9-isopropylfluorene–Na and 9-t-butylfluorene–Na systems. The experimental values for ΔH° and ΔS° given in Table 4 agree well with values obtained for this equilibrium with other hydrocarbons such as *N*-ethylcarbazole [10] and biphenyl.[11] The nega-

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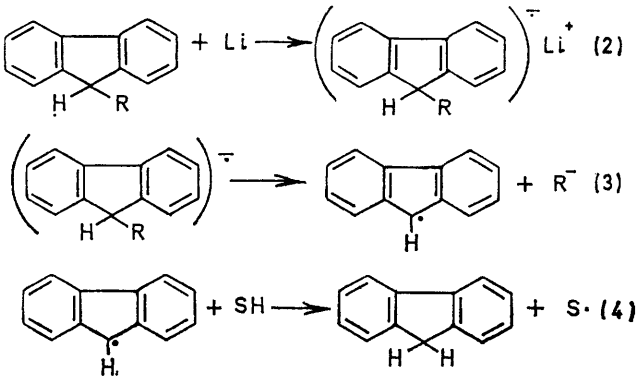
[9] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 307.

[10] A. Rembaum, A. Eisenberg, R. Haack, and R. F. Landel, *J. Amer. Chem. Soc.*, 1967, **89**, 1062.

[11] R. V. Slates and M. Szwarc, *J. Amer. Chem. Soc.*, 1967, **89**, 6043.

tive values of $\Delta S°$ would be expected in view of the much increased solvation of the radical anion and of the sodium counterion compared to the hydrocarbon and metallic sodium. Szwarc has offered evidence to suggest that four factors would be important in determining the magnitude of $\Delta H°$.[11] Of these the coulombic interaction between the ions and the electron affinity of the aromatic hydrocarbon would be expected to be the main variables in these systems. Indeed Rembaum *et al.* have found a good correlation between the value of $\Delta H°$ and the energy of the lowest unoccupied molecular orbital for similar hydrocarbons.[10] However, coulombic interaction could also play a part in the 9-substituted fluorene–Na systems due to the variation of steric effects at the 9-position with the nature of the substituent.

9,9′-Bifluorene and the 9-Chloro- and 9-Bromo-derivatives.—The experimental e.s.r. spectra show that the reaction of 9,9′-bifluorene and the 9-chloro- and 9-bromo-derivatives with lithium gave the fluorene radical-anion. N.m.r. spectra indicate that no fluorene was present in these samples at the start of the experiments and it appears that the formation of the derivative radical-anion [reaction (2)] is followed by rapid decomposition [reaction (3)] and subsequent abstraction of a hydrogen atom [reaction (4)]. The fluorene formed would then react with alkali metal in the usual way to form the fluorene radical-anion. These observations are consistent with those of Bauld *et al.*[12] who found that the fluorene dianion-radical was the ultimate product from the reaction of 9-bromofluorene with Na–K alloy in dimethoxyethane.



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[12] N. L. Bauld and J. H. Zoeller, *Tetrahedron Letters*, 1967, 885.