β-Elimination of 9-Halogeno-9,9'-bifluorenyls. An *E*1cB Dehydrohalogenation

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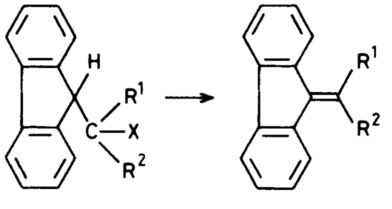
Unusually small leaving-group effects (*e.g.* k_{Cl}/k_F 0.7, k_{Br}/k_{Cl} 1.9) have been measured for the methoxide-promoted β-elimination of 9-acetoxy- and 9-halogeno-bifluorenyls to form bifluorenylidene in methanol. It is suggested that reaction occurs *via* an irreversibly formed carbanion intermediate and that formation of the carbanion is unassisted by halogen hyperconjugation. For β-eliminations showing larger halogen leaving-group effects a concerted mechanism is implied. Elimination of 9-bromo- and 9-chloro-bifluorenyls is accompanied by solvolysis leading to substitution product. For the bromide a non-linear kinetic dependence on base concentration was observed, formally consistent with formation of a carbonium ion intermediate common to substitution and elimination paths. Separation of substitution and elimination rate constants and measurements of solvent isotope effects, however, indicated competition between bimolecular elimination and a unimolecular solvolysis with the carbonium ion confined to the latter. The non-linear base dependence arose from a solvent isotope independent salt effect on the solvolysis reaction.

As discussed in the preceding paper, distinguishing between an *E*2 mechanism of elimination and an *E*1cB mechanism in which formation of a carbanion is rate determining can be difficult. The distinction is an important one in studying the borderline between concerted and stepwise mechanisms.[1,2] Normally, an *E*2 mechanism is inferred if the observed rate of elimination exceeds the expected rate of ionisation and shows a characteristic dependence on the nature of the leaving group.[1,2] For fluoren-9-ylalkyl halides (1) rates of elimination exceed extrapolated rates of ionisation by factors of up to 500 and the order of halogen reactivity, I > Br > Cl, is opposite to that expected of inductive stabilisation of a carbanion: for various bases and substituents α to the leaving group, rate ratios k_{Br}/k_{Cl} fall in the range 5—30. It is natural to infer that the mechanism of elimination is *E*2.[3]

Recently however Ahlberg and Thibblin have suggested the β-halogenocarbanion formation may be assisted by hyperconjugation, and that this offers an alternative to an *E*2 mechanism for explaining high reactivity in dehydrohalogentions activated by electron-withdrawing β-substituents.[4–6] In support of this, significant barriers to internal rotation of β-halogenocarbanions have been calculated,[7–9] and it has been proposed that these barriers offer an explanation of the retention of stereochemistry commonly observed in nucleophilic vinylic substitutions.[7,10]

Among the halogens, hyperconjugation has been most discussed for fluorine.[9] Ostensibly this is inconsistent with the reactivity order of I > Br > Cl > F observed in β-eliminations, but despite early popularity and some continuing controversy [11] hyperconjugation by fluorine is now generally acknowledged to be of limited experimental significance.[9] In principle the possibility remains that larger effects may be associated with the other halogens.[12] Thus Appeloig and Rappoport calculate a larger rotational barrier for a chloro- than fluoro-ethyl carbanion,[7] and Ahlberg notes the possibility, perhaps greater for the larger halogens, of through-space interaction with the carbanion centre.[4]

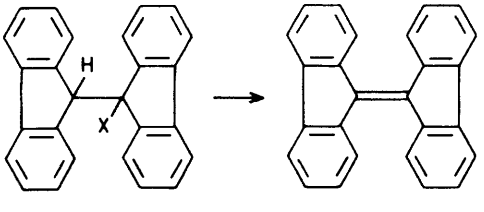
In the present paper we consider the likelihood that if hyperconjugation is *not* important we should find reactions proceeding with rate-determining carbanion formation in which β-halogen groups give no rate enhancement other than from their inductive effects, and in which the halogen reactivity order is F > Cl > Br > I, *i.e.* the opposite of the order of leaving or hyperconjugative reactivity.



(1)

(1)

R^1, R^2 = H, Me, Ph



(2)

(2)

In looking for a suitable reaction, the rather small rate ratio of $k_{Br}/k_{Cl} \simeq 3$ reported by Bethell and Cockerill in the elimination of 9-halogeno-9,9'-bifluorenyls [(2), equation (2)] with piperidine in t-butyl alcohol seemed interesting,[13] and we decided to investigate this reaction for a wider range of leaving groups, with methanolic sodium methoxide as solvent and base. One complication introduced by the methanol solvent was that the chloro- and bromo-substrates become subject to competing solvolysis reactions. In the case of the bromide the reaction was sufficiently important that the methoxide-promoted elimination had to be separated with care.

Results

The kinetics of elimination of 9-bromo-, 9-chloro-, 9-fluoro-, and 9-acetoxy-bifluorenyls were measured in methanolic sodium methoxide at 25° by observing the increase in optical density of the product bifluorenylidene [13] at its absorption maximum of 462 nm ($\varepsilon_{max.}$ 23 400 [14]). First-order rate constants at various concentrations of sodium methoxide are shown in Tables 1 and 2 for both protio- and deuterio-solvents. In the case of 9-bromo-9,9'-bifluorenyl the elimination reaction is accompanied by extensive substitution, and in Table 1 the observed rate constants are factored into

Table 1. First-order rate constants (s^{-1}) for elimination and substitution of 9-bromo-9,9′-bifluorenyl in NaOMe–MeOH and MeOD at 25° [a]

MeOH			MeOD		
[MeO⁻] M	10^4k_E	10^4k_s	[MeO⁻] M	10^4k_E	10^4k_s
0.015	0.4	18.6	0.055	4.5	15.6
0.073	2.2	20.9	0.056	4.5	15.6
0.108	3.3	20.5	0.058	4.6	15.5
0.108	3.4	21.1	0.095	8.1	17.2
0.215	6.3	19.7	0.100	7.4	15.0
0.323	9.5	18.6	0.199	15.5	16.1
0.363	10.5	17.7	0.207	16.5	16.3
0.433	11.8	16.6 [b]	0.302	22.0 [b]	14.3
0.538	14.2	15.6 [b]	0.395	27.8 [b]	13.3

[a] Measured rate constants correspond to $k_E + k_s$. Values of k_E and k_s are calculated using the product ratios [olefin]/[methyl ether]. [b] Mean of three values.

Table 2. Measured first-order rate constants for elimination of 9-halogeno- and 9-acetoxy-9,9′-bifluorenyls in NaOMe–MeOH and MeOD at 25°

Cl(MeOH)		Cl(MeOD)		F(MeOH)		OAc(MeOH)	
[MeO⁻] M	10^4k s^{-1}	[MeO⁻] M	10^4k s^{-1}	[MeO⁻] M	10^4k s^{-1}	[MeO⁻] M	10^4k [a] s^{-1}
0.117	3.14	0.060	2.76	0.115	2.22	0.104	3.2
0.238	3.84	0.114	4.68	0.216	4.66	0.210	6.9
0.261	5.32	0.210	7.37	0.381	7.94	0.320	11.7
0.390	6.66	0.303	11.75	0.465	11.2	0.425	17.1
0.470	8.51	0.385	13.91	0.540	13.0	0.527	20.7
0.601	9.84						

[a] Sum of elimination (k_E) and transesterification (k_T) rate constants (k_T/k_E = 9.7, independently of base concentration).

Table 3. Product ratios of olefin to methyl ether for reaction of 9-bromo-9,9′-bifluorenyl with NaOMe in MeOH and MeOD solvents at 25°

MeOH		MeOD	
[MeO⁻] M	[olefin]/[ether]	[MeO⁻] M	[olefin]/[ether]
0.045	0.06	0.055	0.29
0.045	0.05	0.112	0.55
0.091	0.12	0.210	1.00
0.125	0.26	0.210	1.05
0.180	0.26	0.311	1.30
0.362	0.61	0.407	1.48
0.453	0.84		
0.452	0.74		
0.678	1.18		
0.904	1.79		

contributions, k_E and k_S for elimination and substitution, respectively, making use of product ratios of olefin to methyl ether interpolated from spectrophotometric measurements of the proportion of olefin product as a function of base concentration shown in Table 3. The identity of the substitution product (2; X = OMe) was confirmed by isolation.

In the absence of methoxide both 9-bromo- and 9-chloro-bifluorenyls were subject to solvolysis reactions, as shown by the significant intercepts of plots of observed elimination rate constants ($k_E + k_S$) *versus* methoxide concentration (Figure 1). The solvolysis reactions gave no detectable elimination product and their rates were independently determined by carrying out the reaction in the presence of a small amount of the strong amine base 1,8-bis(dimethylamino)naphthalene (proton sponge)[15] and following the decrease in absorbance accompanying protonation by HBr or HCl produced in the reaction, as described by Luton and Whiting.[16] Agreement between the directly measured and extrapolated solvolysis rate constants was good. Extrapolation of the product ratios of substitution to elimination to high methoxide concentrations suggested that the reaction with solvent accounts for all the methyl ether formed, though up to 10% substitution by methoxide ion is not excluded.

The effect of added sodium bromide on the solvolysis of 9-bromo-9,9′-bifluorenyl was measured. No mass law rate depression was seen and following a sharper increase of 20% a small linear increase in rate with increasing salt concentration occurred, described by a Winstein-salt effect parameter[17,18] of b 0.4; the effect of added sodium chloride was similar. Sodium methoxide itself exhibited a salt effect on the dissected solvolysis (substitution) rate constants but not on elimination. Freedom from salt effects has been observed in other eliminations of fluorenylalkyl halides.[19]

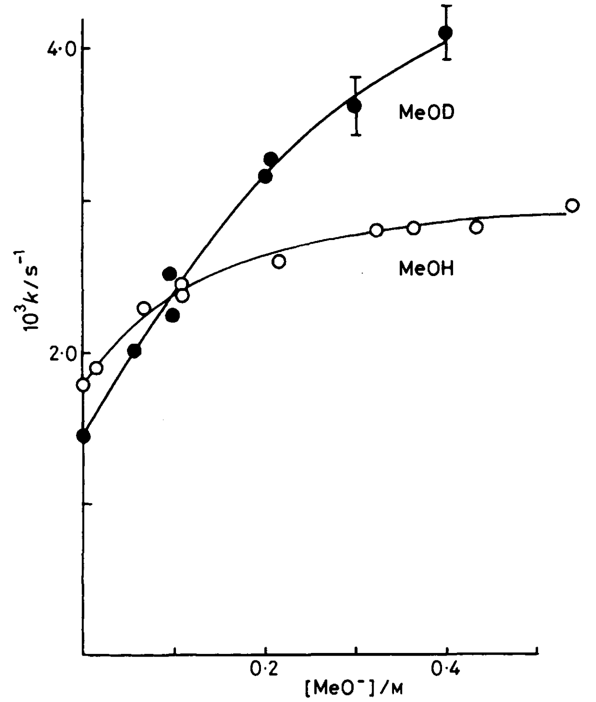
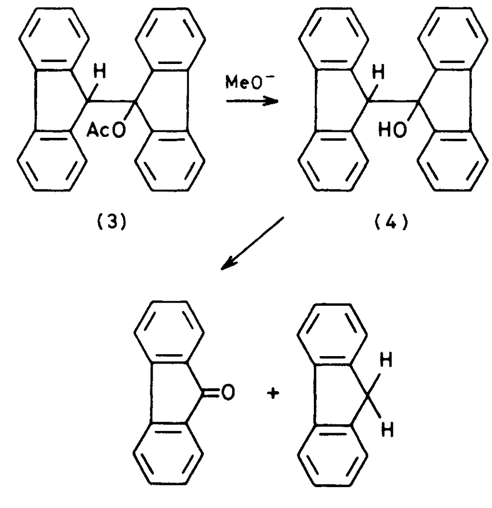


Figure 1. First-order rate constants for reaction of 9-bromo-9,9′-bifluorenyl in MeOH plotted against [MeO⁻]



Scheme

Measurements of solvolysis rates of both chloro- and bromo-bifluorenyls in MeOD gave small solvent isotope effects, $k_{MeOH}/k_{MeOD} = 1.22$ and 1.24, respectively, consistent with those for solvolysis reactions in H_2O and D_2O.[20] By contrast, methoxide-promoted elimination rates were appreciably faster in MeOD than MeOH with k_{MeOD}/k_{MeOH} 2.3 and 2.6 for the chloride and bromide, respectively. The result for the chloride is the more precise as correction for competing solvolysis was unimportant.

For 9-acetoxy-9,9′-bifluorenyl the elimination rate constants shown in Table 2 had to be corrected for competing transesterification to 9-hydroxy-9,9′-bifluorenyl [(4) first step of Scheme], again making use of spectrophotometric measurements to estimate the fraction of olefin formed (*ca.* 10%). The product of transesterification was characterised as 9-hydroxy-9,9′-bifluorenyl from the rate of its independently measured subsequent retro-Knoevenagel elimination to fluorenone (Scheme, second step, k 2.7 × 10^{-4} l mol^{-1} s^{-1}).

The fluorenone-forming elimination of 9-hydroxy-9,9′-bifluorenyl was noteworthy in that the reaction was not previously observed under similar conditions for other 9-hydroxymethylfluorene derivatives with methyl or phenyl substituents α to the hydroxy-group,[19] although it is seen for the related α-hydroxyisopropylindene.[21] Its observation for (4) is probably the result of steric interactions between the fluorene rings.

Discussion

Competing Elimination and Substitution.—Eliminations of 9-bromo- and 9-chloro-bifluorenyls in methanolic sodium methoxide are subject to competing solvolysis reactions yielding bifluoren-9-yl methyl ether, in contrast to reactions of the corresponding fluoride and acetate which show only elimination. For 9-bromo-bifluorenyl a non-linear dependence of measured first-order rate constants upon base concentration was observed, with an apparent change from first to zero order in base with increasing concentration in both MeOH and MeOD, as seen in Figure 1. The behaviour is reminiscent of that reported by Sneen and Robbins for substitution and elimination of α-phenethyl bromide in ethanolic sodium ethoxide and interpreted by them as signifying reaction *via* a carbonium ion pair intermediate, with base attack upon the carbonium ion rate determining at low base concentrations and formation of the carbonium ion rate determining at high concentrations.[22]

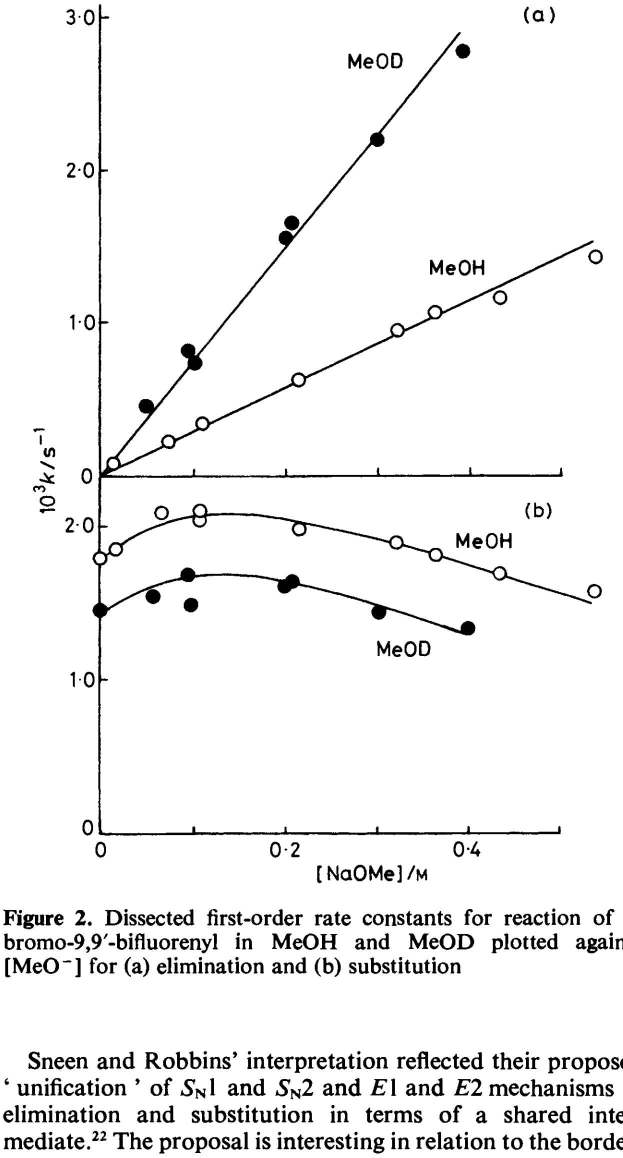


Figure 2. Dissected first-order rate constants for reaction of 9-bromo-9,9′-bifluorenyl in MeOH and MeOD plotted against $[MeO^-]$ for (a) elimination and (b) substitution

Sneen and Robbins' interpretation reflected their proposed ' unification ' of S_N1 and S_N2 and $E1$ and $E2$ mechanisms of elimination and substitution in terms of a shared intermediate.[22] The proposal is interesting in relation to the borderline between concerted and stepwise mechanisms of elimination [3] in that it represents one view of this borderline. For 9-bromo-9,9′-bifluorenyl, however, separation of rate constants for elimination and substitution shows clearly that the data for this substrate are consistent with a simple competition between bimolecular elimination and unimolecular solvolysis, with the solvolysis reaction subject to a small non-linear salt effect (Figure 2), for which there is precedent.[18,22-26] This interpretation is confirmed by measurements of normal, base-independent solvent isotope effects [19,27] of k_{MeOD}/k_{MeOH} 2.6 for elimination and 0.8 for the solvolysis, and a leaving group rate ratio of $k_{Br}/k_{Cl} = 35$ for solvolysis. There seems no way in which the solvent isotope data (Figure 1) can be reconciled with a common intermediate for substitution and elimination. In so far as the results resemble those for α-phenethyl bromide therefore, they lend support to the suggestion of McLennan that there too bimolecular elimination may not involve a carbonium ion.[23,24]

Mechanism of Halide Eliminations and the Question of Halogen Hyderconjugation.—The choice of mechanisms for elimination of 9,9′-bifluorenyl halides and acetate sensibly lies between $E2$ and $E1cB$. In principle an $E1cB$ mechanism could involve reversible or irreversible formation of a carbanion intermediate; in practice, for fluorene derivatives,

Table 4. First- (k_0) and second-order (k_2) rate constants for solvolysis and elimination of 9-X-9,9′-bifluorenyls in NaOMe–MeOH and NaOMe–MeOD at 25°

	X =	Br	Cl	F	OAc
$\frac{10^4k_2}{\text{l mol}^{-1}\text{ s}^{-1}}$	MeOH	26.6	15.7	25.3	2.67
	MeOD	69.9	35.1		
$\frac{10^4k_0\,^a}{\text{s}^{-1}}$	MeOH	17.9	0.65		
	MeOD	14.4 [b]	0.535 [c]		

[a] Measured with proton sponge. [b] Solvent isotope effect k_{MeOH}/k_{MeOD} 1.24. [c] Solvent isotope effect k_{MeOH}/k_{MeOD} 1.22.

reversible carbanion formation is expected only for much poorer leaving groups than the halogens.[1,2] Thus Bethell and Cockerill's measurement of primary isotope effects of $k_H/k_D = 6.0$—8.1 for reaction of pyridine or t-butoxide bases with the bromide [13] is as expected inconsistent with reaction *via* a reversibly formed carbanion.

Rate constants for elimination of the 9-halogeno- and 9-acetoxy-9,9′-bifluorenyls are shown in the first row of Table 4. It is clear from these that the dependence of the rate constants on leaving group is not that expected of an *E*2 mechanism. The 9-fluoro-9,9′-bifluorenyl reacts faster than the corresponding 9-chloro-substrate, and to our knowledge this is the only example of this reactivity order in β-eliminations. The bromide and chloride show their normal order but the k_{Br}/k_{Cl} rate ratio of 1.9 is unusually small: only Naso and his co-workers' measurements of $k_{Br}/k_{Cl} = 1.7$ and 2.2 for *erythro*- and *threo*-1-halogeno-1,2-diphenyl-2-*p*-tolylsulphonylethanes in NaOMe–MeOH [28] and those of Marshall *et al.* of 1.8 for 1-halogeno-1-phenyl-2-phenylsulphonylethanes in NaOEt–EtOH [29] and Baciocchi [30] of 1.2 for dihalogenoacenaphthenes in KOBu^t–Bu^{t}OH give values as small.

Figure 3 shows a crude plot of elimination rate constants against σ_I with a line of slope 5.9 corresponding to ρ_I for the carbanion-forming ionisation of 9-XCH$_2$-substituted fluorenes [1] drawn through the points for fluoride, chloride, acetate, and benzoate (from the preceding paper). The rate constant for bromide is seen to be high and this may represent a fluctuation in the normal bromo-inductive effect or a small contribution of *E*2 elimination.[13] Only for the bromide is there a hint of departure from a carbanion mechanism.

What is interesting is that the absence of an appreciable halogen leaving-group effect, and apparent lack of enhanced ionisation rates for the halides, not only excludes a significant contribution from concerted elimination but rules out acceleration of carbanion formation by hyperconjugation. It would appear that in polar solvents and for carbanions as strongly delocalised as fluorenyl hyperconjugation is of little importance. As has been emphasised by Streitwieser there is no conflict between such a conclusion and the calculation of rotational barriers for unstabilised ethyl carbanions in the gas phase.[9] Ethyl carbanions in the gas phase lack charge stabilisation by either π-delocalisation or solvation and an exceptional demand is made upon σ-substituents. However, it does follow that for fluorenyl-activated dehydrohalogenations where appreciable leaving-group effects are observed an *E*2 mechanism, rather than halogen hyperconjugation, is implied.

Experimental evidence for hyperconjugation in β-eliminations has been cited by Ahlberg and Thibblin. Thibblin has argued for a role for hyperconjugation from the free-energy correlation of leaving-group reactivities shown in equation (3).[5]

$$\log(k_X/k_0) = \rho^*\sigma^* + lL \qquad (3)$$

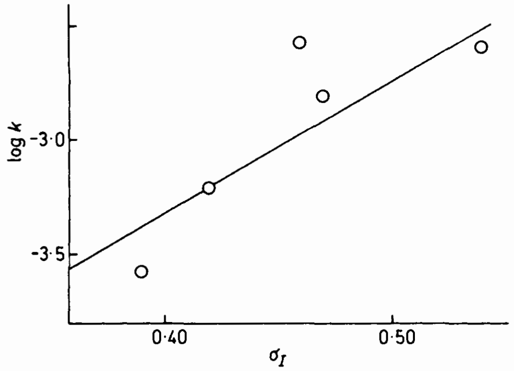


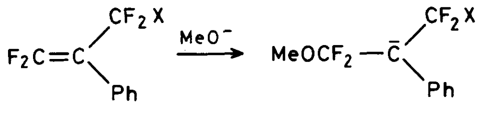
Figure 3. A plot of log *k versus* σ_I for elimination of 9-substituted 9,9′-bifluorenyls

In this equation σ* and ρ* are Taft substituent and reaction constants expressing the inductive effect of a leaving group, and *L* and *l* are substituent and reaction constants reflecting its hyperconjugative or leaving ability. Values of *L* are defined from rate constants for elimination of 9-fluorenylmethyl derivatives, for which ρ* is known. For other reactions, ρ* is chosen to optimise linearity of a plot of log $(k_X/k_0) - \rho^*\sigma^*$ *versus* *L*, which then has a slope *l*.

For reaction series with strong carbanion-stabilising β substituents, such as indenyl or phenylsulphonyl, equation (3) gives good correlations. But for phenethyl derivatives and other series lacking strong activation no choice of ρ* leads to a linear dependence of log $(k_X/k_0) - \rho^*\sigma^*$ upon *L*. Thibblin reasonably concludes that the departures from linearity reflect a dependence of carbanion character in *E*2 transition states upon the nature of the leaving group, and that this leads to the variable ρ* values. Noting the corollary that where linear correlations are obtained ρ* must be constant, Thibblin suggests that with strongly β-activating substituents, for which this is true, an *E*2 mechanism no longer prevails, and that deviations from conventional Taft correlations represent hyperconjugative acceleration of carbanion formation within an irreversible *E*1cB mechanism.

An alternative interpretation of the apparently constant values of ρ* can be considered, however. The linearity of log (k_x/k_o)-ρ*σ* plots with respect to *L* for β-activated eliminations may arise simply because the parameters *L* are defined for a similar reaction. Such activated eliminations should also be subject to a small leaving-group with only a mild influence of the leaving group upon ρ* of an *E*2 mechanism. Departures from simple Taft correlations accommodated by equation (3) then become consistent with *E*2 mechanisms of eliminations.

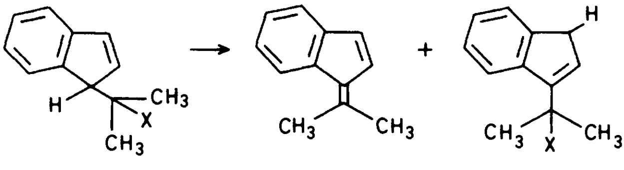
Confining equation (3) to *E*2 eliminations has a corollary. For a reaction series within which a change from *E*2 to irreversible *E*1cB mechanisms accompanies a decrease in leaving-group reactivity, those groups reacting by the carbanion mechanism should show abnormally high reactivity as judged by the leaving-group parameter *L*. A hint of this behaviour is obtained from measurements of elimination reactions of fluorides,[31] of which an extreme example may be cited. As noted by Thibblin the halogens have similar σ* s so values of *L* (if ρ* is constant) should be directly reflected in halogen rate ratios. For β-phenethyl halides eliminating in NaOEt–EtOH[32] $k_{Br}/k_{Cl} = 60$ and $k_{Cl}/k_F = 80$, relative magnitudes qualititatively consistent with their respective *L* values. For αα-dimethyl-9-fluorenylmethyl halides, however, $k_{Br}/k_{Cl} = 29$ while k_{Cl}/k_F is only 4.2. Although no firm conclusion can be drawn from an isolated measurement the low value of k_{Cl}/k_F is consistent with a change to a carbanion mechanism for the fluoro-substrate.



(5)

A recent illustration of the similar stabilising effect of Cl and F on a β-carbanion has been given by Koch *et al.*[33] For the carbanion-forming nucleophilic attack of methoxide ion in methanol upon (5) with X = Cl or F the ratio k_{Cl}/k_F was 1.3.

Ahlberg and Thibblin invoked hyperconjugation to explain results of a study of competing elimination and allylic rearrangement of the indenyl derivatives shown in equation (4). By a combination of isotopic kinetic and product analyses they showed unambiguously that elimination of the leaving groups [X in (6)] OMe, OAc, Cl, and Br occurred by a carbanion pathway. For the halogen leaving groups, despite the fact that the carbanion is formed irreversibly, the reaction was subject to a significant leaving-group effect, with k_{Br}/k_{Cl} = 10, and rates of elimination exceeded rates of carbanion formation extrapolated from a Taft correlation of ionisation of other indenyl substrates. It was natural to conclude that formation of the halogenocarbanions is assisted by hyperconjugation.



(4)

(6)

These results again admit of an interpretation in terms of a contribution of *E*2 elimination. While the results require reaction *via* a carbanion mechanism they do not exclude the presence of competing *E*2 eliminations with rate constants of a magnitude to account for differences of observed elimination rates from the expected rates of carbanion formation. For the chloride this difference is small but for the bromide it is substantial. In the light of the present study and of the certainty that the change in leaving group from acetate to chloride to bromide strongly favours an *E*2 mechanism, we prefer this interpretation of the behaviour both for indenyl substrates and for the related fluorenyl systems.

Two questions remain. First, is it possible that for 9,9′-bifluorenyl reactants hyperconjugation is precluded by some special structural constraint? The answer is that it may be, but observations of other low k_{Br}/k_{Cl} and k_{Cl}/k_F ratios tend to suggest not. Secondly, why is it that the 9-halogeno-9,9′-bifluorenyls react by an *E*1cB mechanism when k_{Br}/k_{CL} ratios > suggest an *E*2 mechanism for a variety of apparently related fluorenyl substrates [*e.g.* (1; R^1,R^2 = H, H; Me, H; Bu^t, H; Ph, H; Me, Me)]. A satisfying answer to this question must await further investigation of the borderline between concerted and stepwise mechanisms of elimination, but one may guess that the difference reflects destabilisation of the *E*2 transition state leading to a relatively strained bifluorenylidene olefin.

Experimental

9-Hydroxy-9,9′-bifluorenyl (4) was prepared from fluoren-9-yl-lithium and fluorenone in the manner described by Suzuki.[34] Recrystallisation from cyclohexane–benzene (1 : 1) gave crystals, m.p. 195—196° (lit.,[35] 193—195°).

9-Bromo- and 9-chloro-9,9′-bifluorenyls (2; X = Br, Cl) were prepared by passing HBr or HCl gas respectively through solutions of the alcohol (1 g) in ether (70 ml), cooling to 0° and collecting the precipitated halides. Careful recrystallisation from benzene–cyclohexane (1 : 1) gave the bromide, m.p. 165—166° (lit.,[13] 166—167°), and chloride, m.p. 155—157° (lit.,[13] 157—158°). *9-Fluoro-9,9′-bifluorenyl* (2; X = F) was prepared by treating the alcohol with 70% HF in pyridine following the procedure of Olah *et al.*[36] Recrystallisation from cyclohexane–benzene (1 : 1) gave crystals, m.p. 140—141°, δ ($CDCl_3$) 5.0—5.2 (1 H, d, CH) and 6.96—7.76 (16 H, m, ArH) (Found: C, 98.3; H, 4.7; F, 5.15. $C_{26}H_{17}F$ requires C, 89.7; H, 4.9; F, 5.45%). *9-Acetoxy-9,9′-bifluorenyl* (2; X = OAc) = (3) was prepared by dissolving 9-hydroxy-9,9′-bifluorenyl (1 g) in acetic anhydride (20 ml) and adding zinc chloride (20 mg) dried at 100°. The mixture was heated to 120° (1 h), poured into ice–water, and extracted with ether. Recrystallisation from light petroleum (b.p. 60—80°) gave the desired product, m.p. 203—204°, δ ($CDCl_3$) 2.12 (3 H, s, $OOCCH_3$), 4.9 (1 H, s, CH), and 6.8—7.5 (16 H, m, ArH) (Found: C, 86.55; H, 5.15. $C_{28}H_{20}O_2$ requires C, 86.6; H, 5.15%). *9-Methoxy-9,9′-bifluorenyl* was prepared by reaction of the corresponding bromide in methanol at room temperature, m.p. 142—143°, δ ($CDCl_3$) 2.92 (3 H, s, OCH_3), 4.8 (1 H, s, CH), and 7.0—7.65 (16 H, m, ArH) (Found: C, 90.25; H, 5.85. $C_{27}H_{20}O$ requires C, 90.0; H, 5.55%).

Methyl alcohol was dried by distillation from magnesium and stored under nitrogen. Deuteriomethanol was Aldrich Gold Label grade and was used without further purification. Solutions of sodium methoxide were prepared from Alfa inorganics sodium (99.95% purity) by dissolving in methanol under nitrogen.

Kinetic measurements were made by following the increase in absorption at 455 nm for formation of bifluorenylidene or at 256 nm for formation of fluorenone as appropriate. Reactions were conducted in the cell compartment of a Perkin-Elmer–Hitachi 124 spectrophotometer thermostatted at 25 ± 0.1°. Kinetic measurements were initiated by injection of a few μl of stock solutions of substrate into a thermostatted cell containing methanolic sodium methoxide. Stock solutions of 9-bromo- and 9-chloro-9,9′-bifluorenyls, which reacted with the methanol solvent, were prepared in dioxan. The percentage of dioxan in a reaction solution was normally <0.7%.

First-order rate constants were calculated using a weighted least-squares computer program that optimised an infinity point by iteration; normally, determinations were based on at least 20 points covering three half-lives of the reaction. Second-order rate constants were calculated as slopes of linear plots of first-order constants against base concentration except for the fluorenone-forming reaction for which second-order rate constants increase significantly with base concentration. This value was extrapolated to dilute solution.

Product ratios of bifluorenylidene to 9-methoxy-9,9′-bifluorenylidene were obtained by measuring the optical density of the product formed from a known amount of reactant. The reactant was introduced by microlitre syringe calibrated both directly and by analysis of the product from elimination of 9-fluoro-9,9′-bifluorenyl which was presumed to form bifluorenylidene quantitatively. The quantitative nature of this reaction was confirmed by measurement of an apparent extinction coefficient of 23 200 for bifluorenylidene formed from a known amount of fluoride reactant, which compares with the literature value of 23 400.[14] The effect of the presence of dioxan on the product ratio of olefin to methyl ether was determined and the proportion of olefin found to increase with dioxan concentration. However for the amount (<1%) normally used in the reactions the effect on the product ratio was too small to detect.

Measured first-order rate constants (k_{obs}) for 9-bromobifluorenyl were separated into contributions from elimination (k_E) and substitution (k_s) by the relationships $k_s = k_{obs}/(1 + R)$ and $k_E = k_{obs} - k_s$ where R is the product ratio of olefin to ether interpolated at the appropriate methoxide concentration from a plot of R against [MeO$^-$].

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Received 1st *March* 1982; *Paper* 2/355