Concerted and Stepwise Mechanisms in the Eliminations from 1,2-Dihalogenoacenaphthenes Promoted by Potassium *tert*-Butoxide and Potassium Ethoxide in the Corresponding Alcohols[1]

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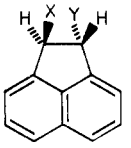
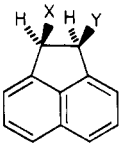
Anti and syn eliminations from *cis*- and *trans*-dihalogenoacenaphthenes, respectively, have been investigated in *t*-BuOK–*t*-BuOH and EtOK–EtOH. The leaving group ability order for the syn eliminations in *t*-BuOK–*t*-BuOH is F > Cl ≃ Br, which suggests an $(E1cB)_I$ mechanism. Also consistent with this mechanism is the observation that from *trans*-1-chloro-2-fluoroacenaphthene only HF is eliminated. In EtOK–EtOH the order of leaving group ability for the syn eliminations is Br > Cl > F, which might suggest an E2 mechanism; however, the leaving group effects are very small, and a stepwise mechanism cannot be excluded. The anti eliminations from the *cis*-dihalogenoacenaphthenes exhibit a substantial leaving group effect; on this basis and also on considering the β-halogen effect on the rate of elimination, a concerted mechanism is suggested.

In the last decade a renewed interest for mechanistic studies in the field of base-induced elimination reactions has arisen as a consequence of the recognition that stepwise mechanisms involving a carbanion intermediate (E1cB reactions) can play a much more important role than hitherto believed, certainly comparable to that of the concerted mechanism (E2 reaction).[2-6] In this context, studies aimed at distinguishing between E1cB and E2 eliminations and at defining the respective scope of the two mechanisms appear warranted.

In this paper we describe a kinetic study of the base-promoted syn and anti eliminations from the *trans*- and *cis*-1,2-dihalogenoacenaphthenes **1** and **2**. Since these



1a, X = Y = Br
b, X = Br; Y = Cl
c, X = Y = Cl
d, X = Cl; Y = F
e, X = Y = F



2a, X = Y = Cl
b, X = Cl; Y = F
c, X = Y = F

substrates allow a wide range of structural situations to be explored with respect to the nature of the leaving group, the β-substituent, and the reaction stereochemistry, it was hoped that this study would afford some evidence for the operation of either mechanism of elimination, possibly also allowing us to detect points of mechanistic change.

Results

The eliminations from **1** and **2** have been investigated in *t*-BuOK–*t*-BuOH and EtOK–EtOH. From **1a,c,e** and **2a,c**, where X = Y, the expected 1-halogenoacenaphthylene has been obtained as the sole reaction product. The product distribution from the dihalogenoacenaphthenes **1b,d** and **2b**, where X ≠ Y, is reported in Table I.

An interesting observation is that in both the base–solvent systems investigated, HF is eliminated in preference to HCl from **1d** and **2b**; in particular, 1-chloroacenaphthylene is the exclusive elimination product from **1d**. The elimination from **1b** in *t*-BuOK–*t*-BuOH affords more HCl than HBr; the reverse, however, holds in EtOK–EtOH. When the reactions of **1d** and **1e** have been carried out in *t*-BuOD and EtOD, no incorporation of deuterium in the unreacted substrates has been observed.

Table I. Product Distribution in the Elimination Reactions from *trans*-1-Bromo-2-chloroacenaphthene (1b) and *trans*- and *cis*-1-Chloro-2-fluoroacenaphthene (1d and 2b)

substrate	base–solvent system	reaction products (distribution, %)
1b	*t*-BuOK–*t*-BuOH	1-bromoacenaphthylene (52), 1-chloroacenaphthylene (48)
	EtOK–EtOH	1-bromoacenaphthylene (30), 1-chloroacenaphthylene (70)
1d	*t*-BuOK–*t*-BuOH	1-chloroacenaphthylene (100)
	EtOK–EtOH	1-chloroacenaphthylene (100)
2b	*t*-BuOK–*t*-BuOH	1-chloroacenaphthylene (95), 1-fluoroacenaphthylene (5)
	EtOK–EtOH	1-chloroacenaphthylene (98), 1-fluoroacenaphthylene (2)

The kinetics have been followed by monitoring the appearance of the formed 1-halogenoacenaphthylene spectrophotometrically at 320–335 nm. An excess of base, whose concentration ranged from 1×10^{-3} to 0.5 M for the reactions in *t*-BuOH and from 2×10^{-2} to 0.6 M for the reactions in EtOH, was used in all cases. Good first-order plots were always obtained, and the second-order rate constants, k_2, were calculated as usual.

In EtOK–EtOH the k_2 values were practically independent of base concentration when this was 0.02 M or lower. At higher EtOK concentration a significant increase in k_2 with increasing base concentration was observed. In *t*-BuOK–*t*-BuOH the k_2 values slightly increased as the *t*-BuOK concentration is increased, and an apparent kinetic order in *t*-BuOK of 1.1–1.2 was calculated. The phenomenon was of a very similar magnitude with all substrates investigated, at least up to [*t*-BuOK] = 0.02 M.

An increase in k_2 as the *t*-BuOK concentration rises had already been observed in the eliminations from *trans*-2,3-dibromo-2,3-dihydrobenzofurans promoted by this base.[7] The phenomenon seemed at that time limited to reactions with syn stereochemistry only, but the present

(1) For a preliminary report of part of this work see: Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V. *J. Chem. Soc. Chem. Commun.* **1980**, 807–808.
(2) Bordwell, F. G. *Acc. Chem. Res.* **1972**, *5*, 374–381.
(3) Koch, H. F.; Tumas, W.; Knoll, R. *J. Am. Chem. Soc.* **1981**, *103*, 5423–5429.
(4) Koch, H. F.; Dahlberg, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 6102–6107.
(5) Thibblin, A. *Chem. Scr.* **1980**, *15*, 121–127.
(6) Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1977**, *99*, 7926–7930; **1979**, *101*, 7311–7318.
(7) Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* **1979**, *44*, 28–31.

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Table II. Kinetic Data for the Syn Elimination from *trans*-1-X-2-Y-acenaphthenes Promoted by *t*-BuOK in *t*-BuOH at 30 °C[a]

substrate X	substrate Y	substrate no.	leaving group	k_2, L mol^{-1} s^{-1}
Br	Br	1a	Br	1.46[b]
Br	Cl	1b	Br	1.15
Br	Cl	1b	Cl	1.22
Cl	Cl	1c	Cl	0.92[b]
Cl	Cl	1c	Cl	14.5[b,c]
Cl	F	1d	F	3.88
Cl	F	1d	F	33.6[c]
F	F	1e	F	2.2×10^{-4} [b]

[a] The concentration of the base was ca. 0.02 M. [b] Data corrected for the statistical factor. [c] In the presence of 18-crown-6 ether.

Table III. Kinetic Data for the Syn Elimination from *trans*-1-X-2-Y-acenaphthenes Promoted by EtOK in EtOH at 30 °C[a]

substrate X	substrate Y	substrate no.	leaving group	k_2, L mol^{-1} s^{-1}
Br	Br	1a	Br	5.0×10^{-3} [b]
Br	Cl	1b	Br	2.6×10^{-3}
Br	Cl	1b	Cl	1.2×10^{-3}
Cl	Cl	1c	Cl	6.25×10^{-4} [b]
Cl	F	1d	F	1.7×10^{-4}
F	F	1e		*c*

[a] The concentration of the base was ca. 0.02 M. [b] Data corrected for the statistical factor. [c] The reaction rate was too slow to be determined.

results show no difference between syn and anti eliminations in this respect.

At *t*-BuOK concentrations higher than 0.02 M the reaction of *cis*-1,2-difluoroacenaphthene (**2c**) exhibited changes in the k_2 values with base concentration which were much larger than those observed with the trans isomer (**1e**). Under these conditions an apparent kinetic order in *t*-BuOK of ca. 2 was calculated. Probably, as the *t*-BuOK concentration increases, higher ionic aggregates in equilibrium with ion-paired *t*-BuOK, the dominant species in *t*-BuOH, can become the effective base promoting the anti elimination from **2c**. The hypothesis that anti eliminations can involve higher ionic aggregates than syn eliminations has already been put forward by Sicher and Schlosser.[8,9]

In the light of the above observations we feel that a meaningful discussion of the rate data for our systems is possible only if k_2 values obtained at the same base concentration (ca. 0.02 M) are considered. These values are collected in Tables II–IV.

Discussion

Syn Eliminations in *t*-BuOK–*t*-BuOH. The data in Table II allow us to evaluate the leaving group effects in the syn eliminations from *trans*-dihalogeno derivatives. A bromine/chlorine leaving group effect (k_{Br}/k_{Cl}) as low as 1.2 is calculated by comparing either the reactivities of **1a** and **1b** (loss of HCl) or those of **1b** (loss of HBr) and **1c**. Likewise, the chlorine/fluorine leaving group effect (k_{Cl}/k_F) is provided by the comparison of the rate data for **1c** and **1d** (loss of HF). A value of 0.2 is obtained which is very remarkable as it indicates that fluorine departs faster than

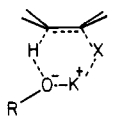
Table IV. Kinetic Data for the Anti Eliminations from *cis*-1-X-2-Y-acenaphthenes Promoted by *t*-BuOK *t*-BuOH and by EtOK in EtOH at 30 °C[a]

substrate X	substrate Y	substrate no.	base-solvent system	leaving group	k_2, L mol^{-1} s^{-1}
Cl	Cl	2a	*t*-BuOK–*t*-BuOH	Cl	~35[b,c]
Cl	F	2b		F	1.06
Cl	F	2b		Cl	0.056
F	F	2c		F	1×10^{-3} [b]
Cl	Cl	2a	EtOK–EtOH	Cl	0.28[b]
Cl	F	2b		F	2.3×10^{-3}
Cl	F	2b		Cl	3.8×10^{-5}
F	F	2c			*d*

[a] The concentration of the base was ca. 0.02 M. [b] Data corrected for the statistical factor. [c] The concentration of the base was 0.001 M. [d] The reaction rate was too slow to be determined.

chlorine (and bromine) in these reactions, in spite of the fact that the carbon–fluorine bond is by far the strongest one among the carbon–halogen bonds.

Since we are dealing with a syn elimination promoted by a strongly associated base, it could be suggested that fluorine (the most electronegative halogen) is made a better leaving group than either bromine or chlorine by a more favorable interaction with the base counterion in the cyclic transition state **3** suggested for the E2 syn eliminations



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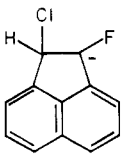
promoted by ion pairs and (or) ionic aggregates.[10] This possibility appears, though, to be excluded by the observation (Table II, lines 5 and 7) that fluorine remains a better leaving group than chlorine even when the reaction is carried out in the presence of a crown ether which is expected to convert ion pairs and ionic aggregates into dissociated ions.

Thus, for the syn eliminations from the *trans*-1,2-dihalogenoacenaphthenes **1a–d** in *t*-BuOK–*t*-BuOH the actual order of leaving group ability is Br ≃ Cl < F, which suggests that the carbon–halogen bond breaking has practically made no progress in the transition state of these reactions. A concerted mechanism therefore seems unlikely, whereas the data are consistent with an E1cB mechanism of the irreversible type, $(E1cB)_I$ mechanism, for which no significant leaving group effect is expected, as the slow formation of the carbanion is followed by the fast departure of the leaving group.

The small differences in rates between the different leaving groups may probably be related to the effect that these groups exert on the rate of carbanion formation. If only inductive effects were operating, a leaving group ability order of F ≥ Cl ≥ Br is predicted by the σ^* values of the CH_2X groups (for X = halogen),[12] which is substantially in agreement with the observed order.

The $(E1cB)_I$ mechanism can also nicely explain the exclusive loss of fluorine from **1d**. Accordingly, out of the two possible carbanions **4** and **5**, which are formed from

(8) Schlosser, M.; Jan, G.; Byrne, E.; Sicher, J. *Helv. Chim. Acta* **1973**, *56*, 1630–1637.
(9) Schlosser, M.; Dinh An, T. *Angew. Chem.* **1981**, *20*, 1039–1041.
(10) This possibility has been recently suggested to account for the preferential loss of HF with respect to HCl in the syn eliminations from *trans*-1-chloro-2-fluorocyclopentane and -cyclohexane promoted by a complex base (*t*-BuONa–$NaNH_2$) in THF.[11]
(11) Lee, J. G.; Bartsch, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 228–229.
(12) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley-Interscience: New York, 1975; p 89.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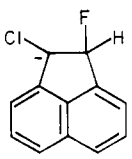
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this substrate, the much more stable one should be that (**5**) with the chlorine atom in the α-position (with respect to the negative charge)[13] since it is well-known that an α-chlorine is by far more effective than an α-fluorine in stabilizing a planar carbanion such as that deriving from the acenaphthene system.[14-16] The effect of the β-halogen on the carbanion stability also operates in the same direction, as a β-fluorine atom should be slightly more effective than a β-chlorine atom in this respect (see above). Thus, if **5** is practically the sole carbanion which is formed from **1d**, the exclusive loss of HF from this substrate is easily accounted for.

Likewise, the preferential loss of HCl with respect to HBr from **1b** can be explained on the same basis since an α-bromine stabilizes a carbanion slightly better than an α-chlorine.[16,17] The differences are, however, much smaller than those between fluorine and chlorine; thus, the loss of chlorine is favored over that of bromine to a small extent.

It should, however, be noted that these results could also be consistent with a concerted mechanism of β-elimination provided that the transition state is highly carbanionic. In this case too the different capacity of the halogen to stabilize the developing negative charge (Br > Cl $\gg$ F) could become the major factor determining the direction of the elimination reaction, thereby resulting in the preferential loss of the poorer leaving group.

An $(E1cB)_I$ mechanism probably holds also for the syn eliminations from *trans*-1,2-difluoroacenaphthene. This suggestion is based on the observation that **1e** is more than 10^4-fold less reactive than **1d** (loss of HF), a difference in reactivity fully consistent with the already mentioned greater capacity of an α-chlorine atom to stabilize a carbanion relative to an α-fluorine atom. Accordingly, in the hydrogen isotope exchange reactions of 9-halogenofluorenes promoted by CH_3O^- in CH_3OH, a reaction certainly involving a carbanion intermediate, the reactivity of the chloro derivative is ca. 3×10^3-fold greater than that of the fluoro derivative.[16]

It is finally interesting to note that an E1cB mechanism was also considered likely by Cristol and co-workers for the syn eliminations from **1c** promoted by OH^- in EtOH,[19] even though no experimental support was given.

Syn Elimination in EtOK–EtOH. From the data of Table III, leaving group effect values of 4.2 (k_{Br}/k_{Cl}) and 3.7 (k_{Cl}/k_F) can be calculated. Certainly, an $(E1cB)_I$ mechanism of elimination is still compatible with these very small leaving group effects, and indeed a k_{Br}/k_{Cl} value of 4 has been observed in the E1cB eliminations from 2-(phenylsulfonyl)cyclohexyl halides.[20]

Table V. Reactivity Ratios between *cis*- and *trans*-1-X-2-Y-acenaphthenes (Anti/Syn Ratios) in Some Elimination Reactions Promoted by *t*-BuOK in *t*-BuOH and EtOK in EtOH at 30 °C

X	Y	base–solvent system	leaving group	anti/syn ratio[a]
Cl	Cl	*t*-BuOH–*t*-BuOH	Cl	38
		EtOK–EtOH	Cl	500
Cl	F	*t*-BuOK–*t*-BuOH	F	0.27
		t-BuOK–*t*-BuOH–18C6[b]	F	20
		EtOK–EtOH	F	13
F	F	*t*-BuOK–*t*-BuOH	F	4
		t-BuOK–*t*-BuOH–18C6[b]	F	60

[a] Reactivity ratios between *cis*- and *trans*-1-X-2-Y-acenaphthenes. [b] 18C6 = 18-crown-6 ether.

However, the observed leaving group ability order, Br > Cl > F, is "normal", and an E2 mechanism of elimination, involving a highly carbanionic transition state, could be compatible as well with the results in Table III. A change in mechanism, from $(E1cB)_I$ to E2, as the base–solvent system is changed from *t*-BuOK–*t*-BuOH to EtOK–EtOH is not unreasonable, owing to the greater basicity of the former medium which should favor the formation of an intermediate carbanion.

A third possibility is that in EtOK–EtOH an E1cB mechanism of the reversible type, $(E1cB)_R$ mechanism, is operating, where the halogen is lost, in a slow step, from a reversibly formed carbanion. This mechanism is consistent with the observation of a leaving group effect and should have more chance to occur in EtOK–EtOH than in *t*-BuOK–*t*-BuOH since the tendency of the carbanion to revert back to reactants should be stronger in the former system.[3] However, as no isotopic exchange with the solvent has been observed in the eliminations promoted by EtOK in EtOD, the additional suggestion should be made that a hydrogen-bonded carbanion is actually formed, $(E1cB)_{ip}$ mechanism,[2] undergoing internal return faster than or in competition with elimination and undergoing elimination faster than exchange.

With the data at hand no choice between these three mechanistic possibilities can be made. On the basis of the previous discussion, the observation that only fluorine is lost from **1d** in EtOK–EtOH is also compatible with both an E1cB and an E2 mechanism.

Anti Elimination in *t*-BuOK–*t*-BuOH and EtOK–EtOH. In *t*-BuOK–*t*-BuOH substantial k_{Cl}/k_F values, between 33 and 56, can be calculated by the kinetic results reported in Table IV [comparison of **2a** and **2b** (loss of HCl) with **2b** (loss of HF) and **2c**, respectively]. These values suggest a substantial degree of carbon–halogen bond breaking in the transition state of the anti HCl elimination from **2a** and **2b** promoted by *t*-BuOK in *t*-BuOH and consequently point to an E2 mechanism for these reactions. A similar conclusion holds for the corresponding eliminations in EtOK–EtOH as a k_{Cl}/k_F value of 120 can be obtained by comparing the reactivity of **2a** and **2b** (loss of HF) in this base–solvent system.

Also consistent with an E2 mechanism for the anti eliminations of HCl is the observation that the reactivity in the anti process is significantly greater than in the syn one in both *t*-BuOK–*t*-BuOH and EtOK–EtOH, as shown by the reactivity ratios reported in Table V for the dichloroacenaphthene system.

(13) When we specifically refer to a carbanion, α and β indicate the position bearing the negative charge and that adjacent to it, respectively.
(14) Reference 12, p 181.
(15) Hine, J.; Wiesboeck, R.; Ghirardelli, R. G. *J. Am. Chem. Soc.* **1961**, *83*, 1219–1222.
(16) Streitwieser, A.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444–2445.
(17) However, in the dehydrofluorination of $C_6H_5CHXCF_3$ (X = Br, Cl), bromine and chlorine behave almost identically.[18]
(18) Koch, H. F.; Dahlberg, D. B.; McEntee, M. F.; Klecha, C. J. *J. Am. Chem. Soc.* **1976**, *98*, 1060–1061.
(19) Cristol, S. J.; Stermitz, F. R.; Ramey, P. S. *J. Am. Chem. Soc.* **1956**, *78*, 4939–4941.
(20) Bordwell, F. G.; Weinstock, J.; Sullivan, T. F. *J. Am. Chem. Soc.* **1971**, *93*, 4728–4735.

An $(E1cB)_{ip}$ mechanism in which internal return is competing with eliminations could also be invoked to account for the observed leaving group effects. However, on consideration of the results obtained with the syn eliminations in *t*-BuOK–*t*-BuOH, this suggestion would necessarily imply that internal return has more chance to compete with the expulsion of the leaving group with the carbanion formed from the *cis*-dihalide than with that formed from the *trans*-dihalide. This is highly unlikely since in the former carbanion the electron pair is ideally situated for the expulsion of the leaving group, and a higher rate of formation of the alkene is expected.

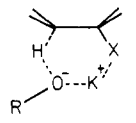
Less certain are the mechanistic conclusions concerning the anti elimination of HF from **2b** and **2c**. Tentatively, an approach to the problem can be made by considering the effect of the β-halogen substituent on the rate of the elimination reactions.

The anti HCl eliminations from **2a** and **2b**, which have been suggested to occur by an E2 mechanism, differ in rate by ca. 600-fold. This factor, that should represent the effect of replacing a β-chlorine with a β-fluorine in a reaction taking place by a concerted mechanism, is much smaller than that (ca. 18 000) observed in the syn eliminations from the trans substrates, for which an $(E1cB)_I$ mechanism has been suggested. This is expected since in a concerted process, where substantial breaking of the carbon–leaving group bond takes place in the transition state, less buildup of negative charge at the β-carbon is expected relative to an E1cB process, with a consequent smaller sensitivity to the electronic effects of β-substituents.

If we now consider the anti eliminations of HF from **2b** and **2c**, a β-chlorine/β-fluorine reactivity ratio of ca. 1000 can be calculated, which is very close to that observed in the E2 eliminations of HCl from **2a** and **2b**. Thus, it would appear that the eliminations of HF from **2b** and **2c** also occur by a concerted mechanism. The observation that similar values of k_{Cl}/k_F are calculated either from the reactions of **2a** and **2b** (loss of HF) or from those of **2b** (loss of HCl) and **2c** seems to support this suggestion, as it should indicate that all four reactions probably occur by the same mechanism.

If the mechanism is E2 in *t*-BuOK–*t*-BuOH, nearly certainly it will also be E2 for the corresponding reactions in EtOK–EtOH.

The observation that the reactivities of these substrates in *t*-BuOK–*t*-BuOH are very similar to those of the corresponding *trans*-dihalides (Table V; in fact, with the chlorofluoro compound the syn elimination is faster than the anti one) cannot be taken as evidence against the E2 mechanism, since significantly higher anti/syn ratios are observed in the presence of a crown ether (Table V). This clearly suggests that the small ratios found in the absence of the crown ether are probably due only to base association disfavoring the syn elimination less than the anti one. Indeed, an E1cB syn elimination can take advantage of the base association as well as an E2 reaction can, as clearly shown by a study of E1cB elimination reactions from 1-methoxyacenaphthene promoted by *t*-BuOK in *t*-BuOH.[21] Evidently the transition state of the deprotonation step can be stabilized by the electrostatic interaction between the base counterion and the leaving group, as shown in structure **6** which is not much different from the transition state **3** of a concerted reaction. On the other hand, this is plausible since concerted syn eliminations are generally characterized by highly carbanionic transition states with



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very little C–X bond breaking. Interestingly, it seems that the strength of the interaction between the base counterion and X in **6** is not much affected by the nature of X; accordingly, the addition of a crown ether and/or the solvent change from *t*-BuOH to EtOH exert a rate effect that is only 2–3-fold larger when X = F than when X = Cl.

Concluding Remarks. The mechanistic attributions made on the basis of the foregoing discussion suggest that the stereochemical pathway is the main factor determining the elimination mechanism in the reactions of *trans*- and *cis*-dihalogenoacenaphthenes in *t*-BuOK–*t*-BuOH, the syn processes occurring via an $(E1cB)_I$ mechanism and the anti ones via an E2 mechanism. Leaving group ability and β-activation seem less important in this respect.

The mechanistic crossover from stepwise and concerted mechanisms in an alkene-forming elimination has been related by Gandler and Jencks to a decrease of the carbanion stability up to the point at which the carbanion ceases to exist.[22] On the basis of this hypothesis, the mechanistic crossover observed in the present work on going from a syn to an anti elimination can be rationalized by assuming the disappearance of a lifetime for the carbanion derived from the *cis*-dihalide. This is quite reasonable since in this carbanion the lone pair is anti to the leaving group and therefore, as already noted, is in an ideal situation for the expulsion of the latter.

Anti elimination from *cis*-dihalogenoacenaphthenes in EtOK–EtOH also takes place by an E2 mechanism. However, no firm mechanistic attribution has been possible concerning the syn eliminations from the trans derivatives in this base–solvent system. As a consequence no conclusion can be drawn, at present, with regard to the role possibly played by the nature of the base–solvent system with respect to the reaction mechanism.

Experimental Section

All melting points were measured with a Koffler electrothermal apparatus. ^1H NMR spectra at 90 and at 60 MHz were registered with Varian EM 390 and JEOL C-60HL spectrometers, respectively. GLC analyses of the reaction products were performed on a Model G1 Carlo Erba gas chromatograph. Mass spectra were recorded on an MAT 311 A spectrometer. Kinetic experiments were carried out on a Beckman DB-GT spectrophotomer.

Materials. Acenaphthylene (Merck) was chromatographed on silica gel with petroleum ether as the eluent. Silver fluoride (Merck) was kept under vacuum (0.5–1 mmHg) at 40–50 °C in the dark for about 2 h immediately before use.

***trans*-1,2-Dibromo- (1a) and *trans*- (1c) and *cis*-1,2-Dichloroacenaphthene (2a)** were prepared as reported by Cristol et al.;[19] the melting points and NMR spectra were in agreement with the literature data.[2,3,19]

***trans*-1-Bromo-2-chloroacenaphthene (1b).** Monopyridinebromine(I) chloride (1.5 g, 7.7×10^{-3} mol), prepared as previously described,[24] was added in small portions over a period of 50 min to a solution of acenaphthylene (1 g, 6.6×10^{-3} mol) in carbon tetrachloride (150 mL) at room temperature, and the heterogeneous mixture was stirred for about 2 h. The reaction mixture was filtered and the filtrate washed successively with saturated aqueous sodium bisulfite, hydrochloric acid (2 N), and water. The organic layer was separated and dried (Na_2SO_4), and,

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after solvent evaporation under vacuum, the crude reaction product was crystallized twice from petroleum ether. The white solid was identified as **1b**: yield 54%; mp 94–95 °C; NMR ($CDCl_3$) δ 5.80 (1 H, s, 2-H), 5.90 (1 H, s, 1-H), 7.46–7.88 (6 H, m, Ar H); mass spectrum (32 eV), *m/e* (relative intensity) 266 (M^+, 100), 268 (131), 270 (33).

***trans*- (1d) and *cis*-1-Chloro-2-fluoroacenaphthene (2b).** Silver fluoride (4 g, 3.2×10^{-2} mol) was added to a solution of **1b** (5 g, 1.9×10^{-2} mol) in benzene/acetonitrile (4:1, 50 mL) at ca. −8 °C in the dark, and the mixture stirred for about 2.5 h (reaction time from the NMR analysis). After removal by filtration of the silver halides, the organic layer was washed with water and dried on sodium sulfate. The crude product was chromatographed on neutral silica gel (230 mesh) with petroleum ether as the eluent, and the fractions were monitored by TLC and NMR analyses. The elimination products (1-chloro- and 1-fluoroacenaphthylene) were first collected, and then a white solid [mp 28.5–29.5 °C (from petroleum ether)] was eluted. To this compound was attributed the structure of **1d** (yield 38%) on the basis of its NMR spectrum in C_6D_6 [δ 5.46 (1 H, d, $^3J_{HF}$ = 21 Hz, 1-H), 6.25 (1 H, d, $^2J_{HF}$ = 54 Hz, 2-H), 7.10–7.60 (6 H, m, Ar H)], identical with that reported in the literature,[25] and of its mass spectrum at 70 eV: *m/e* (relative intensity) 206 (M^+, 100), 208 (33). Further elution with 20% methylene chloride in petroleum ether afforded a highly colored material which was purified by twofold column chromatography on silica gel as above and finally by recrystallization from petroleum ether. The white solid (mp 85 °C) was identified as **2b** (yield 5%) on the basis of its NMR spectrum in C_6D_6 [δ 5.12 (1 H, dd, $^3J_{HF}$ = 10 Hz, $^3J_{HH}$ = 6 Hz, 1-H), 5.62 (1 H, dd, $^2J_{HF}$ = 54 Hz, $^3J_{HH}$ = 6 Hz, 2-H), 7.10–7.60 (6 H, m, ArH)], identical with that reported in the literature,[25] and of its mass spectrum at 70 eV: *m/e* (relative intensity) 206 (M^+, 100), 208 (32).

***trans*- (1e) and *cis*-1,2-Difluoroacenaphthene (2c).** Silver fluoride (2.5 g, 2×10^{-2} mol) was added to a solution of **1a** (1.5 g, 4.8×10^{-3} mol) in benzene/acetonitrile (4:1, 30 mL) in the dark, and the mixture stirred for about 2.5 h. The reaction mixture was worked up and chromatographed by following the procedure described for **1d** and **2b**. The products obtained had the following characteristics. For **1e**: yield 40%; mp 44–45 °C (lit.[25] mp 47 °C); NMR ($CDCl_3$) δ 6.15 (2 H, m, 1-H and 2-H), 7.35–7.90 (6 H, m, Ar H), in agreement with the literature;[25] mass spectrum (70 eV), *m/e* 190 (M^+). For **2c**: yield 16%; mp 109 °C (lit.[25] mp 113 °C); NMR ($CDCl_3$) δ 6.35 (2 H, m, 1-H and 2-H), 7.35–7.90 (6 H, m, Ar H), in agreement with the literature;[25] mass spectrum (70 eV), *m/e* 190 (M^+).

Another procedure to obtain a mixture of **1e** and **2c** was the direct fluorination of acenaphthylene described in a previous paper.[26] By this procedure a major amount of cis adduct (yield 30%) is obtained.

1-Bromo- (7), 1-chloro- (8), and 1-fluoroacenaphthylene (9) were prepared by treating **1a**, **1c**, and **2c**, respectively, with potassium *tert*-butoxide (0.2 M) in *tert*-butyl alcohol at room temperature. The reaction mixtures were worked up as described in the literature.[19,24,25] The spectral characteristics are as follows. For **7**: NMR ($CDCl_3$) δ 7.03 (1 H, s, 2-H), 7.40–7.85 (6 H, m, Ar H); mass spectrum (70 eV), *m/e* (relative intensity) 230 (M^+, 100), 232 (97). For **8**: NMR ($CDCl_3$) δ 6.80 (1 H, s, 2-H), 7.25–7.80 (6 H, m, Ar H); mass spectrum (70 eV), *m/e* (relative intensity) 186 (M^+, 100), 188 (32). For **9**: NMR ($CDCl_3$) δ 6.30 (1 H, s, 2-H), 7.35–7.85 (6 H, m, Ar H); mass spectrum (70 eV), *m/e* (relative intensity) 170 (M^+).

18-Crown-6 ether (18C6), a commercial material (Fluka), was purified by crystallization from *n*-hexane.

Base–Solvent Solutions. *tert*-Butyl and ethyl alcohols (Erba RPE) were purified and dried as previously described.[7] Solutions, of alkoxide were obtained by reaction, under nitrogen, of freshly cut potassium with the alcohol.

Kinetics Studies. Kinetic experiments were carried out by following spectrophotometrically the appearance of the reaction products at 320–335 nm. At this wavelength no appreciable absorbance is exhibited by the substrates. The base solution (2 mL) in a silica cell was placed in the thermostated compartment of the spectrophotometer. After about 20 min, the substrate solution (10–30 μL) in the same solvent was added. After being shaken rapidly, the cell was rapidly placed again in the spectrophotometer. The reference cell contained a solution of alkali alkoxide at the same concentration used in the kinetic run to compensate for the absorption exhibited by the alkoxide itself at 320–335 nm. The concentration of the substrate was in the range 9×10^{-5}–2×10^{-4} M, and the base concentration ranged from 1×10^{-3} to 0.5 M for *t*-BuOK in *t*-BuOH and from 2×10^{-2} to 0.6 M for EtOK in EtOH.

Product Analysis. A known amount of the dihalide was added, under strong stirring, to a 0.02 M solution of alkoxide in alcohol placed in a flask surrounded by a jacket for the circulation of the thermostating liquid. After a variable time (depending on the reactivity of the substrate), the reaction mixture was poured into water and the mixture extracted several times with petroleum ether. After the mixture was dried, most of petroleum ether was removed, and the resulting solution (ca. 2 mL) was analyzed by GLC with a 1.0×0.002 m column packed with 10% LAC 728 on 60–80-mesh Chromosorb W at 170 °C. The molar response of **8** with respect to **7** and **9** was 1.0. The retention times of **7–9** were 32, 19, and 7 min, respectively (N_2 carrier gas at ~20 mL/min).

H–D Exchange Experiments. ROK in ROD (0.50 mL) was added to a known amount of the dihalide **1d** or **1e** (the base/substrate molar ratio was 0.5), and the mixture was analyzed by NMR. When the reaction was completed, the ratio between aromatic and aliphatic protons was half the original one, thus showing no appreciable deuterium incorporation in the substrate.

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