(d) Addition of **3a** to (2,4-dinitrophenyl)hydrazine in ethanol at room temperature led to 1-naphthoyl (2,4-dinitrophenyl)hydrazide (**5m**): mp 275-278 °C dec; amide carbonyl absorption at 1640 cm^{-1}; mass spectrum, *m/e* 352 (M^+).[31] In a separate experiment reaction of **3a** (77 mg, 0.5 mm) occurred violently with (2,4-dinitrophenyl)hydrazine (99 mg, 0.5 mmol) in concentrated sulfuric acid to give, after the mixture was poured on ice, 1-naphthoic acid (50 mg, 58%), mp 159-161 °C, identical with an authentic sample.

Reaction of 3a with Methylenetriphenylphosphorane. *tert*-Butyllithium (1.5 equiv) in hexane was added to methyltriphenylphosphonium bromide (179 mg, 0.5 mmol) in tetrahydrofuran (10 mL) at 0 °C, and the mixture was warmed to ~25 °C and stirred until homogeneous. When the solutions were cooled to -78 °C, **3a** (77 mg, 0.5 mmol) in tetrahydrofuran (10 mL) was added by syringe and the mixture was stirred at -78 °C for 1 h and then slowly warmed to room temperature. TLC indicated that **2b** was not present. Aqueous sodium hydroxide was added, and the mixture was refluxed 24 h, cooled, and poured into water/ethyl ether. The ethereal layer, on drying ($MgSO_4$) and chromatography on silica gel (benzene as eluent), yielded 1-acetonaphthalene (**5o**; 15 mg, 18%), identical with an authentic sample. All attempts to prepare **2b** by reactions of **3a** with methylenetriphenylphosphorane were unsuccessful.

Acknowledgment. Discovery of and initial development of 1*H*-cyclobuta[*de*]naphthalene and its derivatives were made on National Institutes of Health Grant CA 11185 (1974-1978) and elaborated on National Science Foundation Grants CHE-77-0367 and CHE-80-19750. We should like to thank the National Institutes of Health and the National Science Foundation for support of this work.

Registry No. **1a**, 54125-11-0; **1b**, 24973-91-9; **1b**·picrate, 85924-72-7; **1c**, 85864-98-8; **1d**, 85924-73-8; **1e**, 85864-99-9; **1f**, 85924-74-9; **1g**, 85924-75-0; **1h**, 85924-76-1; **1h** methyl ester, 85924-77-2; **1i**, 85924-78-3; **1j**, 85924-79-4; **1k**, 85924-80-7; **1l**, 85924-81-8; **1m**, 85924-82-9; **1o**, 85924-83-0; **1p**, 85924-84-1; **1p**·picrate, 85924-85-2; **1r**, 85924-86-3; **1s**, 85924-87-4; **1t**, 85924-88-5; **1u**, 85924-89-6; **1w**, 85924-90-9; **2a**, 85924-91-0; **2b**, 85924-92-1; **2c**, 85924-93-2; **2d**, 85924-94-3; **2e**, 85924-95-4; **2g**, 85924-96-5; **3a**, 85924-97-6; **3c**, 85924-98-7; **5a**, 90-12-0; **5b**, 18410-58-7; **5c**, 66-77-3; **5d**, 33250-32-7; **5e**, 64002-53-5; **5f**, 13098-88-9; **5g**, 4780-79-4; **5i**, 16727-91-6; **5j**, 2459-24-7; **5l**, 6833-19-8; **5m**, 39164-30-2; **5n**, 826-74-4; **5o**, 941-98-0; **11**, 86-53-3; **15a**, 85924-99-8; **15b**, 85925-00-4; **15c**, 85925-01-5; **15d**, 85939-43-1; **17a**, 85939-44-2; **21**, 13638-84-1; **22**, 85925-02-6; **27**, 18093-83-9; **28**, 85925-03-7; **29**, 85925-04-8; **31**, 85925-05-9; **32**, 85925-06-0; **36**, 85925-07-1; **38**, 85925-08-2; **40a**, 15727-65-8; **40b**, 32137-38-5; **40c**, 4044-57-9; **41**, 85925-09-3; chlorotrimethylsilane, 75-77-4; ethylene oxide, 75-21-8; diphenylacetonitrile, 86-29-3; 9-cyanofluorene, 1529-40-4; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; benzophenone, 119-61-9; tetraphenylcyclopentadienone, 479-33-4; *p*-tosylhydrazine, 1576-35-8; 1-bromo-1-[bromo(1-naphthyl)methyl]-1*H*-cyclobuta[*de*]naphthalene, 85925-10-6; thiophenol, 108-98-5; 1-naphthoic acid, 86-55-5; (2,4-dinitrophenyl)hydrazine, 119-26-6; 3'-phenylspiro[1*H*-cyclobuta[*de*]-naphthalene-1,2'-oxirane], 85925-11-7; 2,2-diphenylacenaphthenone, 85925-12-8.

Anti and Syn Eliminations from 2,3-Dihalo-2,3-dihydrobenzofurans. The Role of the Substrate Structure and the Base–Solvent System on the Reaction Mechanism

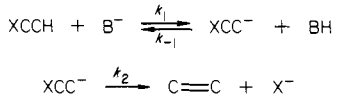
Enrico Baciocchi,* Renzo Ruzziconi, and Giovanni V. Sebastiani

Contribution from the Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy.
Received January 4, 1983

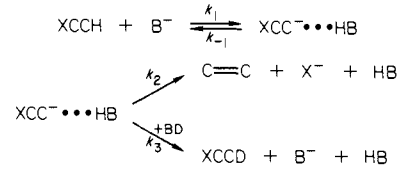
Abstract: The anti and syn β-eliminations from a series of 31 2,3-dihalo-2,3-dihydrobenzofurans (to give 3-halobenzofuran) have been kinetically investigated in *t*-BuOK–*t*-BuOH, in the presence and in the absence of 18-crown-6 ether (18C6), and in EtOK–EtOH. Reaction mechanisms have been assigned on the basis of leaving group, kinetic deuterium isotope, ring substituent (5-chlorine), and β-halogen effects. These data have provided information concerning structure and solvent effect on the mechanism of β-elimination reactions that lead to the following conclusions: (a) an $E1cB_I$ mechanism is likely to be operating, regardless of stereochemistry, with chlorine as a β-activating atom and fluorine as the leaving group and (b) an E2 reaction is likely to be operating for the opposite structural situation, i.e., with β-fluorine activation and chlorine as the leaving group. The mechanism is likely to change from E2 to $E1cB_I$ as the reaction stereochemistry changes from anti to syn and as we move from EtOK–EtOH to *t*-BuOK–*t*-BuOH and from here to *t*-BuOK–*t*-BuOH–18C6.

The determination of the factors that determine the crossover from a stepwise to a concerted mechanism (and vice versa) for a given reaction are receiving continuous attention.[1] The HX β-elimination is certainly one of the reactions that has been more intensively investigated in the last decade, from this point of view.[2-12]

Scheme I



Scheme II



A concerted mechanism (E2 reaction) has been long considered most probable for β-eliminations,[13] but more recently this view

(1) Jencks, W. P. *Chem. Soc. Rev.* **1982**, *11*, 345-375.
(2) Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937-1951. Keeffe, J.; Jencks, W. P. *Ibid.* **1981**, *103*, 2457-2459.
(3) Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* **1982**, *47*, 3237-3241.
(4) More O'Ferrall, R. A. *J. Chem. Soc., Perkin Trans. 2*, in press.
(5) Koch, H. F.; Tumas, W.; Knoll, R. *J. Am. Chem. Soc.* **1981**, *103*, 5423-5429.
(6) Koch, H. F.; Dahlberg, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 6102-6107.
(7) Thibblin, A. *Chem. Scr.* **1980**, *15*, 121-127.
(8) (a) Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1977**, *99*, 7926-7930. (b) *Ibid.* **1979**, *101*, 7311-7318.
(9) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1914-1919.
(10) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 19-25.
(11) Fiandanese, V.; Marchese, G.; Naso, F. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1538-1542.

0002-7863/83/1505-6114$01.50/0

has changed and it is now generally recognized that stepwise processes involving a carbanion intermediate (E1cB reaction) are much more frequent than hitherto believed.[12,14]

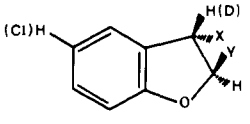
Research in the area has been strongly stimulated by the appreciation of the difficulty in obtaining a clear-cut distinction between E2 and E1cB reactions. This is especially true when the carbanion is formed irreversibly, mechanism $E1cB_I$ (Scheme I, $k_2 >> k_{-1}$), or when both internal return and loss of the leaving group X occur at a faster rate than isotopic exchange with a labeled solvent, mechanism $E1cB_{ip}$ (Scheme II, k_2 and $k_{-1} > k_3$). In the latter case if k_{-1} and k_2 are of comparable magnitude, the stepwise mechanism will exhibit the main features characteristic of an E2 reaction (no hydrogen isotope exchange with the solvent and substantial values of both kinetic hydrogen isotope effect and leaving group effect).

Furthermore, doubts have also been raised concerning the significance of mechanistic criteria widely used in the past, thus further contributing to the uncertainty of many mechanistic conclusions. For example, the leaving group effect criterion, often employed to distinguish an E2 from an $E1cB_I$ mechanism (only the former should exhibit a leaving group effect), especially in the case of eliminations from halides, has been recently questioned on the grounds that a halogen leaving group, by a hyperconjugative effect, might contribute to the stability of the intermediate carbanion.[7,8] This would lead to similar order of leaving group ability I > Br > Cl > F in E2 and $E1cB_I$ reactions.

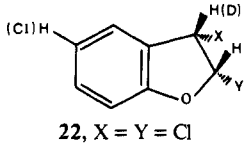
Our interest in the mechanism of elimination reactions has recently led us to investigate the elimination from 1,2-dihaloacenaphthenes.[3] Here the operation of a mechanistic dichotomy, syn eliminations occur by an $E1cB_I$ mechanism and anti eliminations by an E2 mechanism, has been suggested mainly on the basis of leaving group effect data.

It is seemed worthwhile to test the validity of these assignments by extending our investigation to the elimination from *cis*- and *trans*-2,3-dihalo-2,3-dihydrobenzofurans.[15] This system is structurally similar to the dihaloacenaphthene system but allows exploration of a larger range of structural variations and has the advantage that mechanistic criteria other than leaving group effects can be employed. Thus, since all substrates exhibit the same regioselectivity, both deuterium kinetic isotope and ring substituent effects can be conveniently measured as a function of the nature of the leaving group. Mechanistic conclusions should therefore rest on a firmer basis.

In this paper we present the results of a kinetic study of the syn and anti elimination reactions of *trans*-2,3-dihalo-2,3-dihydrobenzofurans, **1–21**, and *cis*-2,3-dihalo-2,3-dihydrobenzofurans, **22–31**, respectively, promoted by *t*-BuOK in *t*-BuOH and by EtOK in EtOH. Most of these compounds have been studied also in *t*-BuOK–*t*-BuOH in the presence of a crown ether. For compounds **1–3**, **10**, and **22**, the majority of kinetic data are taken from a previous investigation.[16b]



1-3, X = Y = Br
4–6, X = Br, Y = Cl
7-9, X = Cl, Y = Br
10–12, X = Y = Cl
13–15, X = Cl, Y = F
16–18, X = F, Y = Cl
19–21, X = Y = F



22, X = Y = Cl
23–25, X = Cl, Y = F
26–28, X = F, Y = Cl
29–31, X = Y = F

(12) Bordwell, F. G. *Acc. Chem. Res.* **1972**, *5*, 374–381.
(13) McLennan, D. J. *Quart. Rev.* **1967**, *21*, 490–506.
(14) Baciocchi, E. In "The Chemistry of Functional Groups. Supplement D"; Patai, S., Rappoport, Z., Eds.; Wiley: 1982; Chapter 23.
(15) Some eliminations from 2,3-dibromo- and 2,3-dichloro-2,3-dihydrobenzofuran had been previously investigated by us.[16] At that time an E2 mechanism had been assumed.
(16) (a) Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* **1980**, *45*, 827–830. (b) *Ibid.* **1979**, *44*, 28–31.

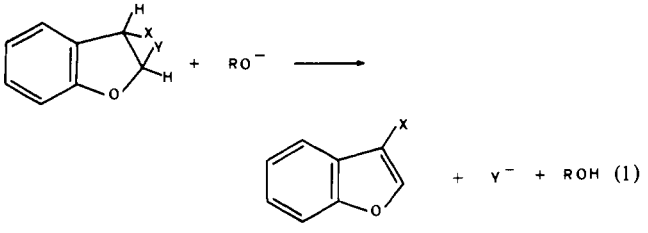
Table 1. Kinetic Data for the Elimination Reactions from *trans*- and *cis*-5-R-2-Y-3-X-3-L-2,3-dihydrobenzofurans in Different Base-Solvent Systems at 30 °C

	substrate				k_2, M^{-1} s^{-1}		
	R	X	Y	L	EtOK-EtOH[a]	*t*-BuOK-*t*-BuOH[b]	*t*-BuOK-*t*-BuOH-C(18C6)
1	H	Br	Br	H	4.63×10^{-2}	5.00[c]	770[c]
2	H	Br	Br	D	1.51×10^{-2}	2.48[c]	258[c]
3	Cl	Br	Br	H	5.38×10^{-1}	37.1[c]	11840[c]
4	H	Br	Cl	H	4.99×10^{-3}	1.49	50.8
5	H	Br	Cl	D	1.92×10^{-3}	4.31×10^{-1}	15.0
6	Cl	Br	Cl	H	8.90×10^{-2}	18.5	572
7	H	Cl	Br	H	1.22×10^{-2}	1.73	55.7
8	H	Cl	Br	D	2.78×10^{-3}	6.03×10^{-1}	18.4
9	Cl	Cl	Br	H	1.32×10^{-1}	12.4	856
10	H	Cl	Cl	H	1.52×10^{-3}	3.90×10^{-1} [d]	15.6[c]
11	H	Cl	Cl	D	5.78×10^{-4}	1.29×10^{-1}	5.50
12	Cl	Cl	Cl	H	3.14×10^{-2}	5.79	
13	H	Cl	F	H	6.93×10^{-4}	3.89	96.1
14	H	Cl	F	D	4.12×10^{-4}	1.35	32.2
15	Cl	Cl	F	H	3.22×10^{-2}	48.5	1459
16	H	F	Cl	H	no reaction	3.15×10^{-4}	1.96×10^{-2}
17	H	F	Cl	D		2.32×10^{-4}	1.08×10^{-2}
18	Cl	F	Cl	H		2.39×10^{-3}	1.48×10^{-1}
19	H	F	F	H	no reaction	1.50×10^{-4}	5.70×10^{-3}
20	H	F	F	D		1.01×10^{-4}	
21	Cl	F	F	H		7.12×10^{-3}	
22	H	Cl	Cl	H	33.9[c,e]	3380[c,f]	>200000[c]
23	H	Cl	F	H	5.28×10^{-2}	24.6	51460
24	H	Cl	F	D	2.87×10^{-2}	8.57	
25	Cl	Cl	F	H	2.22	312	
26	H	F	Cl	H	1.60×10^{-2}	5.01	2140
27	H	F	Cl	D	2.92×10^{-3}	8.05×10^{-1}	
28	Cl	F	Cl	H	1.47×10^{-1}	43.8	
29	H	F	F	H	6.20×10^{-6} [g]	5.01×10^{-3}	7.59
30	H	F	F	D		2.02×10^{-3}	
31	Cl	F	F	H		1.30×10^{-1}	

[a] [EtOK] = 2.7×10^{-1} M. [b] [*t*-BuOK] = 5×10^{-3} M. [c] Literature data.[16b] [d] In ref 16b k_2 is 3.49×10^{-1}. [e] [EtONa] = 1.1×10^{-1} M. [f] [*t*-BuOK] = 8×10^{-3} M. [g] Extrapolated from data at higher temperatures.

Results

Base-promoted eliminations from *cis*- and *trans*-2,3-dihalo-2,3-dihydrobenzofurans (therefrom indicated, for the sake of brevity, as 2Y3XDBF, X and Y being the appropriate halogen) take place according to eq 1 always involving base attack at the



3-proton (see Experimental Section). As a consequence the 2- and 3-carbons of the benzofuran moiety are the α- and β-carbons, respectively, with reference to the β-elimination process, and the halogen in the 2-position is invariably the leaving group. We are therefore dealing with an elimination from a system which is β-aryl and β-halogen activated.

Kinetics have been carried out by monitoring the disappearance of the starting material at 288–320 nm, depending on the structure. For the eliminations from compounds **15**, **25**, and **28**, in *t*-BuOK–*t*-BuOH, and from compounds **4**, **6**, **7**, **9**, **13**, **15**, **23**, and **26**, in *t*-BuOK–*t*-BuOH in the presence of 18-crown-6 ether (18C6), reaction rates were so high to require the use of a stopped-flow apparatus. An excess of base was used in each case, and second-order rate constants, k_2, were calculated as usual from the first-order plots which always exhibited excellent linearity. Changes in the k_2 values with changes in base concentration, akin to those observed in the eliminations from 1,2-dihalo-

Table II. Deuterium Isotope Effect, Substituent Effect, and Leaving Group Effect in the Syn Elimination Reactions of *trans*-2-Y-3-X-2,3-dihydrobenzofurans with *t*-BuOK–*t*-BuOH at 30 °C

substrate		in the absence of 18C6			in the presence of 18C6		
X[a]	Y[b]	k_H/k_D	k_{5Cl}/k_H	leaving group effect	k_H/k_D	k_{5Cl}/k_H	leaving group effect
Br	Br	2.0	7.4	3.4[c]	3.0	15.4	15.1[c]
	Cl	3.4	12.4		3.4	11.2	
Cl	Br	2.9	7.2	4.4[c]	3.0	15.4	3.6[c]
	Cl	3.0	14.8	0.10[d]	2.8		0.16[d]
	F	2.9	12.5		3.0	15.2	
F	Cl	1.4	7.6	2.1[d]	1.8	7.5	3.4[d]
	F	1.5	47.5				

[a] β-Substituent. [b] Leaving group. [c] k_{Br}/k_{Cl}. [d] k_{Cl}/k_F.

Table III. Deuterium Isotope Effect, Substituent Effect, and Leaving Group Effect in the Syn Elimination Reactions of *trans*-2-Y-3-X-2,3-dihydrobenzofurans with EtOK in EtOH at 30 °C

substrate				leaving group effect
X[a]	Y[b]	k_H/k_D	k_{5Cl}/k_H	
Br	Br	3.1	11.6	9.3[c]
	Cl	2.6	17.8	
Cl	Br	4.4	10.8	8.0[c]
	Cl	2.6	20.6	2.2[d]
	F	1.7	46.5	

[a] β-Substituent. [b] Leaving group. [c] k_{Br}/k_{Cl}. [d] k_{Cl}/k_F.

Table IV. Deuterium Isotope Effect, Substituent Effect, and Leaving Group Effect in the Anti Elimination Reactions of *cis*-2-Y-3-X-2,3-dihydrobenzofurans with *t*-BuOK in *t*-BuOH and with EtOK in EtOH at 30 °C

substrate		*t*-BuOK–*t*-BuOH			EtOK–EtOH		
X[a]	Y[b]	k_H/k_D	k_{5Cl}/k_H	k_{Cl}/k_F	k_H/k_D	k_{5Cl}/k_H	k_{Cl}/k_F
Cl	Cl			137			642
	F	2.9	12.7		1.8	42	
F	Cl	6.2	8.7	1000	5.5	9.2	2580
	F	2.5	25.9				

[a] β-Substituent. [b] Leaving group.

acenaphthenes, were observed in both EtOK–EtOH and *t*-BuOK–*t*-BuOH. Therefore, in the present case too, only k_2 values obtained at the same base concentration are considered and discussed. All k_2 values are reported in Table I, whereas Tables II–IV display data concerning the deuterium kinetic isotope effect, k_H/k_D, the ring substituent effect, k_{5Cl}/k_H (which represents a measure of the carbanion character of the transition state), and the bromo:chloro and chloro:fluoro leaving group effect, k_{Br}/k_{Cl} and k_{Cl}/k_F, respectively, for the various reactions.

In the reactions of 3-deuterated *trans*-2F3ClDBF in *t*-BuOK–*t*-BuOH and EtOK–EtOH no significant incorporation of hydrogen in the unreacted substrate was observed (see Experimental Section).

Discussion

Syn Eliminations in *t*-BuOK-*t*-BuOH in the Presence of a Crown Ether. In this base–solvent system the results in Table II point to an $E1cB_I$ mechanism for the reactions of the 3-chloro substrates (*trans*-2Y3ClDBF, compounds, **7**, **10**, and **13**). In these reactions both k_H/k_D and k_{5Cl}/k_H are insensitive to the nature of the leaving group Y, thus showing that proton transfer is substantially uncoupled with the cleavage of the C–Y bond in the transition state of the reaction.[17] Furthermore, a concerted mechanism of elimination is also excluded by the observation that, among halogens, fluorine is the better leaving group, which is incompatible with a transition-state structure where the C_α–halogen bond breaking has made significant progress.

Interestingly, k_{Cl}/k_F leaving group effects smaller than 1 have also been observed in the syn eliminations from *trans*-1,2-dihaloacenaphthenes in *t*-BuOK–*t*-BuOH[3] and in the (presumably) anti eliminations from 9-halo-9,9′-bifluorenyls in MeOK–MeOH,[4] both suggested to occur by an $E1cB_I$ mechanism. It seems therefore that $k_{Cl}/k_F < 1$ is the general characteristic for $E1cB_I$ eliminations, which is not completely unexpected, since fluorine is much more electronegative than chlorine and should therefore be more effective in inductive stabilization of a β-halocarbanion.

The phenomenon is more marked in the syn ($k_{Cl}/k_F = 0.16$ and 0.42) than in the anti ($k_{Cl}/k_F = 0.79$) eliminations. No clear explanation for this finding is available since the presence of a crown ether in the reactions of *trans*-2Cl3ClDBF and *trans*-2F3ClDBF precludes the simple hypothesis of a stronger attraction for fluorine by the base counterion in the transition state of the syn process.[18] The different base–solvent systems used in the syn and anti reactions might be at the origin of the observed difference in the values of k_{Cl}/k_F. However, conformational factors and differences in the position of the transition state along the reaction coordinate might also play a role in making the inductive effect of fluorine and (or) chlorine different in the syn and anti eliminations.

Bromine is lost at a slightly greater rate than chlorine (compare *trans*-2Br3ClDBF and *trans*-2Cl3ClDBF), and a small but "normal" (>1) k_{Br}/k_{Cl} value is observed. This result, though, does not rule out an $E1cB_I$ mechanism since "normal" and small k_{Br}/k_{Cl} values have been found in elimination reactions which other evidence has suggested to occur by an $E1cB_I$ mechanism.[20] Probably, the observed k_{Br}/k_{Cl} values simply reflect fluctuations in the normal bromo inductive effect.[21] However, other effects, besides the inductive ones, could play a role in influencing the stability of the β-halocarbanion. Recently, it has been suggested that halogen hyperconjugation might be important in this respect.[7,8] However, the above suggestion can rationalize the observed k_{Br}/k_{Cl} values but is inconsistent with the values of k_{Cl}/k_F previously discussed. Unfortunately, the experimental determination of the halogen effect on the stability of a β-halocarbanion is very difficult.

An $E1cB_I$ mechanism should be assigned to the reaction of the β-bromo-substituted substrates (*trans*-2Y3BrDBF, compounds **1** and **4**) since in this case too k_{5Cl}/k_H and k_H/k_D are practically identical for Y = Cl and Br. However, the relatively high value of k_{Br}/k_{Cl} (ca. 15) is puzzling and may suggest an E2 mechanism, at least, for the dibromo compound. On the other hand, as chlorine and bromine should display a similar effect in stabilizing an α-halocarbanion,[23] a change in mechanism from $E1cB_I$ to E2 as we move from *trans*-2Br3ClDBF to *trans*-2Br3BrDBF is unlikely. We feel therefore than an unequivocal conclusion cannot be reached in this case.

Syn Elimination in *t*-BuOK–*t*-BuOH. Data of Table II allow us to assign an $E1cB_I$ mechanism to the eliminations from *trans*-2Cl3ClDBF and *trans*-2F3ClDBF: k_H/k_D and k_{5Cl}/k_H remain practically unchanged when the leaving group is changed from chlorine to fluorine and, moreover, as in the corresponding reactions in the presence of 18C6, k_{Cl}/k_F is significantly smaller than unity.

(17) A reviewer has pointed out that these results might also be compatible with an E2 mechanism if the change in leaving group is an insufficient perturbation to alter the transition-state structure. This possibility is, however, unlikely since, as we will see later, in EtOK–EtOH the same changes in leaving group significantly influence k_H/k_D and k_{5Cl}/k_H values.

(18) As previously discussed[3,19] also in the transition state of an $E1cB_I$ process, stabilizing interactions between the base counterions and the halogen leaving group can exist. The strength of this interaction, however, is not much different for chlorine and fluorine.

(19) Hunter, D. H.; Shearing, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 8333–8339.
(20) Bordwell, F. G.; Weinstock, J.; Sullivan, T. E. *J. Am. Chem. Soc.* **1971**, *93*, 4728–4735.

(21) In spite of the fact that the σ_I value of chlorine is larger than that of bromine there are reactions where the electron-attracting effect of bromine is larger than that of chlorine.[22]

(22) Taft, R. W.; Grob, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 1236–1238.
(23) Koch, H. F.; Dahlberg, D. E.; McEntee, M. F.; Klecha, C. J. *J. Am. Chem. Soc.* **1976**, *98*, 1060–1061.

The mechanistic assignment is more uncertain for the compound with the bromine leaving group (*trans*-2Br3ClDBF). Accordingly, on going from *trans*-2Cl3ClDBF to *trans*-2Br3ClDBF k_H/k_D does not change and k_{Cl}/k_H decreases to a significant extent. The former result is in line with an E1cB$_1$ mechanism, but the second suggests a concerted process, indicating a less carbanionic transition state for the substrate with the better leaving group.[24,25]

Similar difficulties are also experienced in the mechanistic assignments for the reactions of the two β-bromo-activated compounds: *trans*-2Br3BrDBF and *trans*-2Cl3BrDBF. As the leaving group is changed from bromine to chlorine, both k_H/k_D and k_{Cl}/k_H increase. In this case too the result is incompatible with the operation of the same mechanism, E1cB$_1$ or E2, for both substrates. In the former case similar values of k_H/k_D and k_{Cl}/k_H are expected, in the latter the increase in k_{Cl}/k_H should be accompanied by a decrease in k_H/k_D.[24-26]

A simple hypothesis might be that the mechanism is E2 for the dibromo compound and E1cB$_1$ for *trans*-2Cl3BrDBF, the change in leaving group determining the E2 → E1cB$_1$ mechanistic crossover. Perhaps, the contradictory results obtained in the eliminations from *trans*-2Br3ClDBF and *trans*-2Cl3ClDBF might be explained on the same grounds: E2 mechanism for the former substrate and E1cB$_1$ mechanism for the latter. It should also be considered that the interpretation of changes in k_{Cl}/k_H may become uncertain if the possibility of a change in mechanism, from E2 to E1cB$_1$, induced by the introduction of the 5-chloro substituent is considered. Some evidence for the occurrence of such a mechanistic shift is reported in the following discussion.

With β-fluorine activation the k_{Cl}/k_F leaving group effect returns to be normal (i.e., >1), even if very small, suggesting that an E2 mechanism might operate with *trans*-2Cl3FDBF (chlorine leaving group). However, we should be close to the borderline since the mechanism is likely to become E1cB$_1$ with the 5-chloro derivative of *trans*-2Cl3FDBF, which, accordingly, exhibits a k_{Cl}/k_F value of 0.33 (compare the 5-chloro derivatives of *trans*-2Cl3FDBF and *trans*-2F3FDBF).

The ring substituent effect, k_{Cl}/k_H, strongly increases when the chlorine leaving group is replaced by fluorine (*trans*-2F3FDBF); no variation in the k_H/k_D value (very small), though, is observed. As above, this finding makes unlikely that both *trans*-2Cl3FDBF and *trans*-2F3FDBF, react by a concerted mechanism. An E1cB$_1$ process is more likely for the difluoro compound, and this view is supported by the finding that *trans*-2F3FDBF is ca. 25 000-fold less reactive than *trans*-2F3ClDBF. This factor, which represents the effect of replacing β-fluorine by β-chlorine, is of the same order of magnitude as that observed in other reactions supposed to occur by an E1cB$_1$ mechanism[3] and is consistent with the much greater ability of the latter halogen to stabilize a planar α-halocarbanion.[27] On the other hand, if an E2 → E1cB$_1$ mechanistic crossover may be induced in this system by the introduction of a 5-chloro substituent, it is reasonable that the same shift may also take place when the leaving group is changed from chlorine to fluorine.

Syn Elimination in EtOK–EtOH. In this base–solvent system eliminations from the 3-chloro-activated compounds exhibit different behaviors than in *t*-BuOK–*t*-BuOH and *t*-BuOK–*t*-BuOH–18C6 (Table III). In EtOK–EtOH k_{Cl}/k_H rises and k_H/k_D decreases as the nucleofugal ability of the leaving group decreases. This trend is that expected in E2 reactions[24] and a concerted mechanism can be suggested for the eliminations from *trans*-2Br3ClDBF and *trans*-2Cl3ClDBF. In line with this conclusion small, but "normal" k_{Br}/k_{Cl} and k_{Cl}/k_F values are observed.

Table V. *t*-BuOK–*t*-BuOH:EtOK–EtOH Reactivity Ratios (*t*-BK:EK) in the Elimination Reactions of Some *trans*- and *cis*-2-Y-3-X-2,3-dihydrobenzofurans

substrate		*t*-BK:EK	
X[a]	Y[b]	syn elimination	anti elimination
Br	Br	108	
	Cl	298	
Cl	Br	142	
	Cl	257	99.7
	F	5613	466

[a] β-Substituent. [b] Leaving group.

The reaction of the dichloro compound, however, is close to the borderline since an E1CB$_1$ mechanism may be operating with the 5-chloro derivative of *trans*-2Cl3ClDBF, which exhibits a slightly smaller rate than the 5-chloro derivative of *trans*-2F3ClDBF ($k_{Cl}/k_F = 0.98$).

The E1cB$_1$ mechanism probably holds for *trans*-2F3ClDBF since k_H/k_D and k_{Cl}/k_H values for the syn eliminations from this compound are nearly identical with those of the anti eliminations from the cis isomer (Table IV). This situation has been observed in other processes suggested to take place by an E1cB$_1$ mechanism;[20] in contrast, syn and anti E2 reactions from isomeric cyclic derivatives generally exhibit transition states with different carbanion character and different degrees of C–H bond breaking.[24]

The observation of a faster rate for the anti elimination does not contrast with the conclusion of an E1cB$_1$ mechanism for both anti and syn reactions of 2F3ClDBF since anti elimination might be favored over the syn by less steric hindrance to the approach of the base and steric relief of both eclipsing strain and dipolar repulsions of the two cis halogen atoms.[28] Conformational factors favoring proton abstraction from the cis form might also be present.

For the β-bromo-activated derivatives the changes in k_{Cl}/k_H and k_H/k_D as the leaving group is changed from bromine to chlorine are similar to those observed with the 3-chloro compounds; hence an E2 mechanism is also suggested for the eliminations from *trans*-2Br3BrDBF and *trans*-2Cl3BrDBF.

The above data might also be consistent with a stepwise mechanism of elimination by assuming that in EtOK–EtOH, different than in *t*-BuOK–*t*-BuOH, the formation of the carbanion is reversible and the return step competes with the loss of the leaving group. Since the importance of the return step increases as the leaving group becomes poorer, k_H/k_D should decrease and k_{Cl}/k_H *might* increase[29] as the leaving group is changed from bromine to fluorine.

The additional hypotheses are required that the return step is internal and that the carbanion expels the leaving group at a faster rate than that of reprotonation by the solvent, E1cB$_{ip}$ mechanism. This because no hydrogen deuterium isotope exchange with the solvent has been observed in the elimination from *trans*-2F3ClDBF. The carbanion from this substrate should have the greatest tendency to revert back to reactants.

Recently Koch and co-workers have suggested that an E1cB$_{ip}$ mechanism with variable internal return should be characterized by large (>130) reactivity ratios between reactions in *t*-BuOK–*t*-BuOH and EtOK–EtOH (*t*-BK:EK), since there is a greater amount of internal return from EtOH than there is from *t*-BuOH.[5,30] In our eliminations *t*-BK:EK values between 110 and 5000 are observed (Table V) and this would suggest an E1cB$_{ip}$ mechanism at least for those substrates where chlorine or fluorine is the leaving group.

(24) Saunders, W. H., Jr.; Cockerill, A. F. "Mechanisms of Elimination Reactions"; Wiley: New York, 1973; Chapter 2.
(25) Winey, D. A.; Thornton, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 3102–3108.
(26) Of course, we reasonably assume that the proton is, in each case, more than half transferred to the base in the transition state. Thus, as the extent of C–H bond breaking increases (a consequence of the increase in carbanion character), the k_H/k_D value is expected to decrease.
(27) Stretwieser, A.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444–2445; Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley-Interscience: New York, 1974; p 189.
(28) LeBel, N. A. *Adv. Alicycl. Chem.* **1971**, *3*, 195–290.
(29) This cannot be established ā priori since it depends on the relative weight of the contrasting effects that a substituent will exert on the equilibrium constant for the carbanion formation and on the rate of leaving group ejection from the carbanion itself.
(30) Actually, ref 5 suggests a *t*-BuOK–*t*-BuOH:EtOK–EtOH reactivity ratio of >200 as indicative of an E1cB$_1$ mechanism. Since in our systems EtOK is ca. 1.5-fold more reactive than EtONa,[16b] the above ratio should correspond to a *t*-BK:EK value of ca. 130.

Table VI. Summary of Suggested Mechanistic Attributions for the Elimination Reactions of *trans*- and *cis*-2,3-Dihalogeno-2,3-dihydrobenzofurans

β-substituent	leaving group	stereochemistry	base–solvent	suggested mechanism
Br	Br	syn	*t*-BuOK–*t*-BuOH–18C6	?
			t-BuOK–*t*-BuOH	E2
			EtOK–EtOH	E2
	Cl		*t*-BuOK–*t*-BuOH–18C6	$E1cB_I$
			t-BuOK–*t*-BuOH	$E1cB_I$
			EtOK–EtOH	E2
Cl	Br	syn	*t*-BuOK–*t*-BuOH–18C6	$E1cB_I$
			t-BuOK–*t*-BuOH	E2
			EtOK–EtOH	E2
	Cl		*t*-BuOK–*t*-BuOH–18C6	$E1cB_I$
			t-BuOK–*t*-BuOH	$E1cB_I$
			EtOK–EtOH	E2
		anti	*t*-BuOK–*t*-BuOH	E2
			EtOK–EtOH	E2
	F	syn	*t*-BuOK–*t*-BuOH–18C6	$E1cB_I$
			t-BuOK–*t*-BuOH	$E1cB_I$
			EtOK–EtOH	$E1cB_I$
		anti	*t*-BuOK–*t*-BuOH	$E1cB_I$
			EtOK–EtOH	$E1cB_I$
F	Cl	syn	*t*-BuOK–*t*-BuOH	E2
		anti	*t*-BuOK–*t*-BuOH	E2
			EtOK–EtOH	E2
	F	syn	*t*-BuOK–*t*-BuOH	$E1cB_I$
		anti	*t*-BuOK–*t*-BuOH	E2
			EtOK–EtOH	E2

However, this possibility is unlikely in the light of the previous observation that the anti and syn eliminations from 2F3ClDBF exhibit nearly identical k_H/k_D and k_{5Cl}/k_H values. Accordingly, if an $E1cB_{ip}$ mechanism is operating this finding would indicate that both the syn and anti eliminations are characterized by the same extent of internal return. Such a conclusion is not reasonable since the carbanion formed from the cis compound (anti elimination) has the lone pair ideally situated for the expulsion of the leaving group and should therefore have less probability to undergo internal return than the carbanion formed from the trans compound (syn elimination). If internal return is unlikely for *trans*-2F3ClDBF, it should also be excluded for the other dihalides for the reasons given above. On the other hand, the high *t*-BK:EK values reported in Table V can be easily discussed within our mechanistic conclusions. In the first place *t*-BK:EK values for *trans*-2Br3ClDBF and *trans*-2Br3BrDBF are close to the borderline and may be consistent with the E2 mechanism previously suggested for these compounds. If this conclusion is correct, the higher *t*-BK:EK ratios for the other substrates can be simply due to the different leaving group effects in the two base–solvent systems, consequence of the operation of different reaction mechanisms. Thus, k_{Br}/k_{Cl} is larger in EtOK–EtOH, where the mechanism is E2 for the 2-bromo and 2-chloro compounds, than in *t*-BuOK-*t*-BuOH where the mechanism is E2 for the former and $E1cB_I$ for the latter. Hence, *t*-BK:EK is significantly higher for the substrates with the chlorine leaving group than for those with the bromine leaving group. Likewise, k_{Cl}/k_F is larger in EtOK–EtOH than in *t*-BuOK–*t*-BuOH since the mechanism is E2 for 2Cl3ClDBF and $E1cB_I$ for 2F3ClDBF in the former base–solvent system but is $E1cB_I$ for both compounds in the latter. Therefore, still larger *t*-BK:EK values for the 2-fluoro compound are observed.

If the foregoing discussion is correct, an interesting conclusion is that high *t*-BK:EK ratios can also be due to the operation of different mechanisms in the two base–solvent systems, other than to the operation of a stepwise mechanism with variable internal return.

Anti Elimination in *t*-BuOK–*t*-BuOH. When chlorine is the β-substituent, normal and significant k_{Cl}/k_F leaving group effects are observed (Table IV). This suggests an E2 mechanism for the eliminations from *cis*-2Cl3ClDBF. However, the mechanism probably becomes $E1cB_I$ when fluorine is the leaving group since anti eliminations from *cis*-2F3ClDBF exhibit values of k_{5Cl}/k_H and k_H/k_D almost identical with those of the syn eliminations from the trans isomer. As discussed earlier this finding suggests a stepwise mechanism for both isomeric substrates. It should also be noted that an $E1cB_I$ mechanism had been already assigned to the syn eliminations from *trans*-2F3ClDBF in *t*-BuOK–*t*-BuOH.

When fluorine is the β-substituent, a large k_{Cl}/k_F value is again observed and an E2 mechanism for *cis*-2Cl3FDBF is a plausible possibility. The same mechanism probably also holds for *cis*-2F3FDBF as k_H/k_D and k_{5Cl}/k_H values are significantly different from those observed for the syn elimination from the trans-difluoro compound previously suggested to occur by an $E1CB_I$ mechanism. Moreover, if *cis*-2F3FDBF, like *cis*-2F3ClDBF, reacted by an $E1cB_I$ mechanism, the difference in reactivity between these two compounds should be significantly larger than observed (ca. 5000). As previously mentioned, in $E1cB_I$ reactions the replacement of a β-fluorine with a β-chlorine should enhance the rate by a factor of ca. 2×10^4.

Anti Eliminations in EtOK–EtOH. A very large k_{Cl}/k_F can be calculated from data for the β-chloro-substituted compounds (Table IV). This points to an E2 mechanism for the reaction of *cis*-2Cl3ClDBF. An $E1cB_I$ mechanism has been already assigned to *cis*-2F3ClDBF.

An E2 mechanism is suggested for *cis*-2Cl3FDBF, always on the grounds of a large k_{Cl}/k_F leaving group effect. The mechanism is probably the same for *cis*-2F3FDBF as an E2 process has been considered likely for the eliminations from this compound in *t*-BuOK–*t*-BuOH. In EtOK–EtOH too the difference in reactivity between *cis*-2F3FDBF and *cis*-2F3ClDBF (β-F → β-Cl replacement) is less than the expected if both compounds reacted by an $E1cB_I$ mechanism.

It should finally be noted that k_{Cl}/k_F values reported in Table IV are substantially larger than those observed in the phenethyl halides series.[31] The phenomenon cannot be accounted for by invoking a different transition-state structure for the E2 reactions of the two systems since this should lead to the opposite result. Accordingly, smaller leaving group effects are expected for the reactions of the dihalodihydrobenzofuran system which should exhibit a transition state with a greater carbanion character. A tentative explanation might be that the steric interactions between the two cis halogens and the oxygen lone pair are larger in the chlorofluoro than in the difluoro compound, thus favoring the leaving group explusion from the former compound.

General Conclusions. The mechanistic assignments discussed above are summarized in Table V as a function of the nature of the β-halogen, the leaving group, and the base–solvent system as well as the reaction stereochemistry. Among these assignments those concerning the syn eliminations from compounds with bromine as the leaving group in *t*-BuOK–*t*-BuOH are probably the more uncertain, in view of the contradictory k_H/k_D and k_{5Cl}/k_H values. The application of other mechanistic criteria would be certainly desirable in these cases. Additional evidence could also be useful for the mechanism of the reactions of difluoro compound which was assigned on the basis of the β-halogen effect only. Much less doubt should instead exist for the other cases, especially when structural effects on the reaction parameters, k_{5Cl}/k_H and k_H/k_D (the structure–reactivity interaction coefficients, according to the Jencks discussion[1,2]) have given unequivocal indications.

In spite of the above reservations, data of Table V provide significant information with respect to structural and solvent effects on the mechanism of a β-elimination and allow the following considerations to be made.

In the first place, 2,3-dihalo-2,3-dihydrobenzofuran is an extraordinarily flexible system where also small changes in structure and reaction conditions may induce a mechanistic change. Evidently, the stability of the intermediate carbanion is so low that

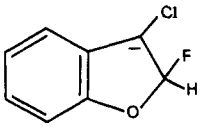
(31) De Puy, C. H.; Bishop, C. H. *J. Am. Chem. Soc.* **1960**, *82*, 2535–2537.

even subtle structural modifications can lead to the disappearance of its lifetime, which should enforce, as suggested by Jencks,[1,2] the crossover from a stepwise to a concerted reaction.

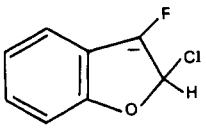
The structural situation with the chlorine β-substituent and the fluorine leaving group is certainly the most favorable for the occurrence of an $E1cB_1$ mechanism of elimination, which is accordingly observed, regardless of stereochemistry, in *all base–solvent systems* examined.

The reverse situation, the fluorine β-substituent and the chlorine leaving group, strongly favors the E2 process which takes place in both EtOK–EtOH and *t*-BuOK–*t*-BuOH; a shift to an $E1cB_1$ elimination seems however induced by the introduction of a 5-chloro substituent.

These conclusions are reasonable since the carbanion **32** derived from 2F3ClDBF is expected to be much more stable than the carbanion **33** formed from 2Cl3FDBF. As previously stated



32



33

chlorine is much more effective than fluorine in stabilizing an α-halocarbanion; moreover, since chlorine is also a better leaving group than fluorine, **33** is less stable than **32** with respect to leaving group expulsion.

The stability of both **32** and **33** should be increased by the introduction of a chlorine atom in the 5-position (a meta-type position with respect to the reaction center), thus favoring the E2 → $E1cB_1$ shifts mentioned above.

The data of Table V provide information on the role played by the base–solvent system and the reaction stereochemistry. The ability of the base–solvent system to induce a stepwise mechanism of elimination decreases in the order *t*-BuOK–*t*-BuOH–18C6 > *t*-BuOK–*t*-BuOH > EtOK–EtOH, which is the order of decreasing medium basicity. The data obtained for *trans*-2Cl3ClDBF and *trans*-2Br3ClDBF are the first clear example of a mechanistic crossover induced by a change from *t*-BuOK–*t*-BuOH to EtOK-EtOH. Probably, as the medium basicity decreases, the lifetime of the carbanion with respect to the reprotonation process also decreases.

An $E1cB_1$ mechanism is favored by a syn stereochemistry of reaction. Accordingly, with 2Cl3ClDBF and 2F3FDBF the mechanism becomes stepwise as the stereochemistry changes from anti to syn. The reasons that can make the lifetime of the syn carbanion greater than that of the anti one have been already discussed here and elsewhere.[3]

The mechanistic dichotomy (E2 anti eliminations and E1cB syn eliminations) exhibited by the dihaloacenaphthenes is not confirmed by the present data since cases of stepwise anti eliminations (*cis*-2F3ClDBF) and concerted syn eliminations (*trans*-2Cl3FDBF) have been found. Clearly, structural factors can become more important than the stereochemical ones in determining the reaction mechanism. In particular, it is noteworthy that anti elimination of HF from *cis*-1-chloro-2-fluoroacenaphthene occurs by an E2 mechanism,[3] whereas the corresponding elimination from *cis*-2F3ClDBF is suggested to take place by an $E1cB_1$ mechanism. A tentative explanation is that fluorine behaves as a worse leaving group in the latter system owing to the effect of the α-oxygen atom.

Experimental Section

All melting points were measured with a Koffler electrothermal apparatus and are uncorrected. ^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 a MAT 311A spectrometer. Kinetic experiments were carried out on a Beckman DB-GT spectrophotometer and, for very high reaction rates, on a Durrum-Gibson D110 stopped-flow spectrophotometer.

Materials. Benzofuran (Fluka), a commerical sample, was distilled under vacuum (15 mmHg). 3-Deuteriobenzofuran and 5-chlorobenzofuran were prepared as previously described.[16b] Silver fluoride (Merck) was a commercial sample dried under vacuum (0.5–1 mmHg) at 40–50 °C in the dark for about 2 h immediately before use.

***trans*-2,3-Dibromo- (1), *trans*-2,3-dibromo-3-deuterio- (2), and *trans*-2,3-dibromo-5-chloro-2,3-dihydrobenzofuran (3)** were prepared by bromine addition in CS_2 at ca. −10 °C on the corresponding benzofuran as previously described.[16b]

***trans*-3-Bromo-2-chloro- (4), *trans*-3-bromo-2-chloro-3-deuterio- (5), and *trans*-3-bromo-2,5-dichloro-2,3-dihydrobenzofuran (6)** were prepared by monopyridine bromine(I) chloride addition in CCl_4 at room temperature on the corresponding benzofuran. The details of the procedure and the characteristics of **4** are reported elsewhere.[32] The properties of the other compounds are as follows. **5**: mp 61–63 °C; ^1H NMR (CCl_4) δ 6.52 (1 H, s, 2-H), 6.82–7.50 (4 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 233 (M^+, 100), 235 (133), 237 (30); UV (EtOH) 292 nm. **6**: mp 79–81 °C; ^1H NMR (CCl_4) δ 5.40 (1 H, s, 3-H), 6.52 (1 H, s, 2-H), 6.80–7.45 (3 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 266 (M^+, 100), 268 (157), 270 (71), 272 (10); UV (EtOH) 303 nm.

***trans*-2-Bromo-3-chloro- (7), *trans*-2-bromo-3-chloro-3-deuterio- (8), and *trans*-2-bromo-3,5-dichloro-2,3-dihydrobenzofuran (9)** were obtained by bromine chloride addition in CH_3NO_2 at ca. 0 °C on the corresponding benzofuran. The details of the procedure and the characteristics of **7** are reported elsewhere.[32] The properties of the other compounds are as follows. **8**: mp 64–66 °C; ^1H NMR (CCl_4) δ 6.65 (1 H, s, 2-H), 6.80–7.55 (4 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 233 (M^+, 100), 235 (130), 237 (35); UV (EtOH) 286 nm. **9**: mp 81–83 °C; ^1H NMR (CCl_4) δ 5.53 (1 H, s, 3-H), 6.65 (1 H, s, 2-H), 6.80-7.50 (3 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 266 (M^+, 100), 268 (160), 270 (75), 272 (9); UV (EtOH) 297 nm.

***trans*-2,3-Dichloro- (10), *trans*-2,3-dichloro-3-deuterio- (11), and *trans*-2,3,5-trichloro-2,3-dihydrobenzofuran (12)** were prepared by chlorine addition in Et_2O at ca. −5 °C on the corresponding benzofuran as previously reported.[16a,33]

***trans*- (13) and *cis*-3-chloro-2-fluoro- (23), *trans*- (14) and *cis*-3-chloro-3-deuterio-2-fluoro- (24), and *trans*- (15) and *cis*-3,5-dichloro-2-fluoro-2,3-dihydrobenzofuran (25)** were obtained by AgF addition at ca. 0 °C to a solution of **7**, **8**, and **9**, respectively, in 9:1 C_6H_6–CH_3CN. The details of the procedure and the characteristics of **13** and **23** are reported elsewhere.[32] The properties of the other compounds are as follows. **14**: ^1H NMR (CCl_4) δ 6.13 (1 H, d, $^2J_{HF}$ = 60 Hz, 2-H), 6.80–7.50 (4 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 173 (M^+, 100), 175 (32); UV (EtOH) 280 nm. **24**: mp 47.5–48.5 °C; ^1H NMR (CCl_4) δ 6.09 (1 H, d, $^2J_{HF}$ = 62 Hz, 2-H), 6.80–7.45 (4 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 173 (M^+, 100), 175 (33); UV (EtOH) 280 nm. **15**: ^1H NMR (CCl_4) δ 5.10 (1 H, d, $^3J_{HF}$ = 15 Hz, 3-H), 6.12 (1 H, d, $^2J_{HF}$ = 60 Hz, 2-H), 6.75–7.45 (3 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 206 (M^+, 100), 208 (67), 210 (11), UV (EtOH) 294 nm. **25**: mp 74.5–75.5 °C; ^1H NMR (CCl_4) δ 5.30 (1 H, dd, $^3J_{HF}$ = 21 Hz, $^3J_{HH}$ = 5.2 Hz, 3-H), 6.10 (1 H, dd, $^2J_{HF}$ = 62 Hz, $^3J_{HH}$ = 5.2, 2-H), 6.75–7.40 (3 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 206 (M^+, 100), 208 (64), 210 (10); UV (EtOH) 289 nm.

***trans*- (16) and *cis*-2-chloro-3-fluoro- (26), *trans*- (17) and *cis*-2-chloro-3-deuterio-3-fluoro- (27), and *trans*- (18) and *cis*-2,5-dichloro-3-fluoro-2,3-dihydrobenzofuran (28)** were obtained by AgF addition at ca. −5 °C to a solution of **4**, **5**, and **6**, respectively, in 9:1 C_6H_6–CH_3CN. The details of the procedure and the characteristics of **16** and **26** are reported elsewhere.[32] The properties of the other compounds are as follows. **17**: ^1H NMR (CCl_4) δ 6.30 (1 H, d, $^3J_{HF}$ = 15 Hz, 2-H), 6.85–7.50 (4 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 173 (M^+, 100), 175 (33); UV (EtOH) 282 nm. **27**: ^1H NMR (CCl_4) δ 6.32 (1 H, d, $^3J_{HF}$ = 9.9 Hz, 2-H), 6.75–7.50 (4 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 173 (M^+, 100), 175 (30); UV (EtOH) 282 nm. **18**: ^1H NMR (CCl_4) δ 5.79 (1 H, d, $^2J_{HF}$ = 56 Hz, 3-H), 6.31 (1 H, d, $^3J_{HF}$ = 15 Hz, 2-H), 6.75–7.50 (3 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 206 (M^+, 100) 208 (65), 210 (12); UV (EtOH) 292 nm. **28**: mp 63–65 °C; ^1H NMR (C_6D_6) δ 4.90 (1 H, dd, $^2J_{HF}$ = 57 Hz, $^3J_{HF}$ = 5.2 Hz, 3-H), 5.45 (1 H, dd, $^3J_{HF}$ = 9.9 Hz, $^3J_{HH}$ = 5.2 Hz, 2-H), 6.10–6.90 (3 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 206 (M^+ 100), 208 (66), 210 (10); UV (EtOH) 292 nm.

***trans*- (19) and *cis*-2,3-difluoro- (29), *trans*- (20) and *cis*-3-deuterio-2,3-difluoro- (30), and *trans*- (21) and *cis*-5-chloro-2,3-difluoro-2,3-dihydrobenzofuran (31)** were obtained by AgF addition at ca. 0 °C to a solution of **1**, **2**, and **3**, respectively, in 9:1 C_6H_6:CH_3CN. The details of the procedure and the characteristics of **19** and **29** are reported elsewhere.[34] The properties of the other compounds are as follows. **20**:

(32) Perugini, R.; Ruzziconi, R.; Sebastiani, G. V. *Gazz. Chim. Ital.*, in press.

(33) Baciocchi, E.; Clementi, S.; Sebastiani, G. V. *J. Heterocycl. Chem.* **1977**, *14*, 359–360.

^{1}H NMR (CCl_4) δ 6.10 (1 H, dd, $^2J_{HF}$ = 58.5 Hz, $^3J_{HF}$ = 11.4 Hz, 2-H), 6.80-7.50 (4 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 157 (M^+); UV (EtOH) 278 nm. **30**: ^{1}H NMR (CCl_4) δ 5.98 (1 H, dd, $^2J_{HF}$ = 61.2 Hz, $^3J_{HF}$ = 2.9 Hz, 2-H), 6.70-7.45 (4 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 157 (M^+); UV (EtOH) 278 nm. **21**: ^{1}H NMR (CCl_4) δ 5.64 (1 H, dd, $^2J_{HF}$ = 54.7 Hz $^3J_{HF}$ = 11.5 Hz, 3-H), 6.08 (1 H, dd, $^2J_{HF}$ = 58 Hz, $^3J_{HF}$ = 11.5 Hz, 2-H), 6.70-7.40 (3 H, m, ArH); MS (70 eV), *m/e* (relative intensity) 190 (M^+, 100), 192 (32); UV (EtOH) 286 nm. **31**: mp 82.5-83.5 °C; ^{1}H NMR (C_6D_6) δ 4.89 (1 H, ddd, $^2J_{HF}$ = 54 Hz, $^3J_{HF}$ = 14.2 Hz, $^3J_{HH}$ = 5.2 Hz, 3-H), 5.27 (1 H, ddd, $^2J_{HF}$ = 60.8 Hz, $^3J_{HF}$ = 2.9 Hz, $^3J_{HH}$ = 5.2 Hz, 2-H), 6.15-7.10 (3 H, m, ArH); MS (70 eV) *m/e* (relative intensity), 190 (M^+ 100), 192 (34); UV (EtOH) 286 nm.

3-Bromo-,[16b] **3-bromo-5-chloro-**,[16b] **3-chloro-**,[16b] **3,5-dichloro-**,[16a] **3-fluoro**,[31] **and 5-chloro-3-fluorobenzofuran** were prepared by dehydrohalogenation of **1**, **3**, **10**, **12**, **29**, and **31**, respectively, with *t*-BuOK in *t*-BuOH. The 5-chloro-3-fluoro derivative showed the following spectroscopic characteristics: ^{1}H NMR (CCl_4) δ 7.20-7.50 (3 H, m, ArH), 7.48 (1 H, d, $^3J_{HF}$ = 4.5 Hz, 2-H); MS (70 eV), *m/e* (relative intensity) 170 (M^+, 100), 172 (35); UV (EtOH) 287, 294 nm.

18-Crown-6 ether (18C6), a commercial material (Fluka), was purified by crystallizing from *n*-hexane (mp 38.5-39.5 °C).

Base-Solvent Solution. *tert*-Butyl alcohol and ethyl alcohol (Erba RPE) were purified and dried as previously described.[16b] Solutions of alkoxide were obtained by reaction, under nitrogen, of freshly cut potassium with alcohol.

Product Analysis. A known amount of the dihalide was added, under strong stirring, to a 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 time with petroleum ether. After the mixture was dried and the solvent evaporated, the crude reaction product was analyzed by ^{1}H NMR and GLC (1.5 × 0.002 m column packed with 1:1 15% bentone-didecylphthalate at 120 °C). In all the cases the corresponding 3-halogenobenzofuran was the exclusive final product from comparison with the authentic specimen.

(34) Ruzziconi, R.; Sebastiani, G. V. *J. Heterocycl. Chem.* **1980**, *17*, 1147-1148.

Kinetic Studies. Kinetic experiments were carried out by following spectrophotometrically the disappearance of the substrate at 288-320 nm. In all the cases the kinetic runs were carried out at a wavelength where no appreciable absorbance is exhibited by the final product. 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 swiftly 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 288-320 nm especially in the presence of the crown ether. The concentration of the substrate was in the range (4.5-9) × 10^{-4} M, and the base concentration was 5 × 10^{-3} M for *t*-BuOK in *t*-BuOH and 2.7 × 10^{-2} M for EtOK in EtOH. At the end of each kinetic run it was checked that the UV spectrum of the reaction mixture was identical with that of the expected olefin.

H-D Exchange Experiments. A solution of ROK in ROH was added to a known amount of the dihalide **17** (the base-solvent molar ratio was 0.5). When the reaction was completed, the mixture was poured into water and the solution extracted with petroleum ether. The crude product, after the solvent evaporation, was analyzed by ^{1}H NMR. In the spectrum in CCl_4, besides the multiplet relative to the final product and to the unreacted substrate, only a doublet at δ 6.15 ($^2J_{HF}$ = 60 Hz) of 2-H aliphatic proton of this substrate was observed, this showing no hydrogen incorporation at C-3 in the deuterated starting material.

Acknowledgment. The financial support of the Italian National Council of Research (C.N.R.) and the Ministero della Pubblica Istruzione is gratefully acknowledged. Thanks are also due to Dr. R. A. More O'Ferrall for communicating a manuscript in advance of publication.

Registry No. 1, 58863-52-8; **2**, 68051-08-1; **3**, 68051-09-2; **4**, 86324-77-8; **5**, 86324-78-9; **6**, 86324-79-0; **7**, 86324-80-3; **8**, 86324-81-4; **9**, 86324-82-5; **10**, 63361-57-9; **11**, 70749-80-3; **12**, 72360-51-1; **13**, 86324-83-6; **14**, 86324-84-7; **15**, 86324-85-8; **16**, 86324-86-9; **17**, 86324-87-0; **18**, 86324-88-1; **19**, 75446-91-2; **20**, 86324-89-2; **21**, 86324-90-5; **22**, 63361-58-0; **23**, 86324-91-6; **24**, 86324-92-7; **25**, 86324-93-8; **26**, 86324-94-9; **27**, 86324-95-0; **28**, 86324-96-1; **29**, 66946-74-5; **30**, 86324-97-2; **31**, 86324-98-3; deuterium, 7782-39-0.

Absolute Rate Constants for Reactions of Cumyloxy in Solution[1]

A. Baignée,[2] J. A. Howard,* J. C. Scaiano,* and L. C. Stewart[2]

Contribution from the Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1A 0R9. *Received March 16, 1983*

Abstract: Rate constants have been measured for reaction of α-cumyloxy with 10 substrates including cumene and di-α-cumyl peroxide and for β-scission of α-cumloxy in solution by using laser flash photolysis techniques in conjunction with high-performance liquid chromatographic determination of product yields. Hydrogen atom abstraction from cumene and di-α-cumyl peroxide by α-cumyloxy proceeds with E_x (kcal mol^{-1}) = 2.4 and 5.7 and log A_x (M^{-1} s^{-1}) = 8.1 and 9.4, respectively. The rate constant for β-scission of α-cumyloxy obeys the equation log k_β (s^{-1}) = $[(12.36 \pm 0.64) - (8.60 \pm 0.45)]/\theta$, where $\theta = 2.303RT$ kcal mol^{-1}.

Alkoxys (RO·), formed by decomposition of alkyl peroxides (ROOR), alkyl hydroperoxides (ROOH), and self-reaction of alkylperoxys (RO_2·), are important transients in many biological[3] and atmospheric[4] oxidations. *tert*-Butoxy, because of its ease of generation, has been the most thoroughly studied alkoxy in the gas and liquid phases. Higher homologues have, however, received some attention and studies on α-cumyloxy have been of particular importance because of its involvement in cumene autoxidation.[5]

Walling and co-workers[6] were the first to study cumyloxy kinetics and obtained values of the rate constant ratio k_x/k_β, where

(1) Issued as NRCC No. 22461.
(2) NRCC summer student 1982.
(3) Pryor, W. A. "Free Radicals in Biology"; Academic Press: New York, 1976; Vol. 3, Chapter 1.
(4) (a) Demerjian, K. L.; Kerr, J. A.; Calvert, J. G. *Adv. Environ. Sci. Technol.*, **1974**, *4*, 1-262. (b) Pitts, J. N.; Finlayson, B. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 1-15.
(5) Howard, J. A.; Bennett, J. E.; Brunton, G. *Can. J. Chem.* **1981**, *59*, 2253-2260.
(6) (a) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593-1597. (b) Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 3368-3375.

0002-7863/83/1505-6120$01.50/0 Published 1983 by the American Chemical Society