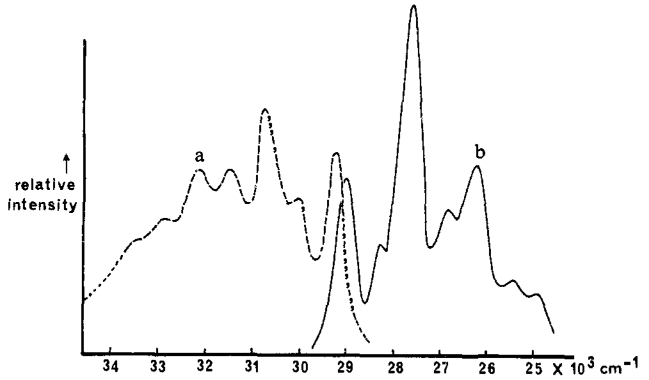

Figure 3. Electronic spectra of isobenzofuran: (a) absorption spectrum in hexane (broken line); (b) fluoresence spectrum at 77°K in isopentane–methylcyclohexane, 3:1 (solid line).

was characterized as its tetracyanoethylene adduct, **9**, mp 204°. The mass spectrum[18] of isobenzofuran showed a strong parent peak at m/e 118 (high resolution 118.04196; calcd for C_8H_6O, 118.04186) as well as major peaks at m/e 90 (P – CO, m* 68.6) and m/e 89 (90 – H, m* 88.2). The pmr spectrum (Figure 2) clearly supports the isobenzofuran structure, in which the downfield singlet is assigned to the furanoid protons. The pronounced downfield shift of these resonances (δ 8.40) compared with those found in cycloocta[*c*]furan (**12**) (δ 7.20),[19] implies the presence of a strong diamagnetic ring current, typical of other aromatic 10π planar systems.[20] The ultraviolet absorption spectrum (Figure 3) is very similar to that reported for isothianaphthalene.[3a] The lack of solvent dependence on the position of this absorption band, together with the mirror relationship of the fluorescence spectrum,[21] support the $\pi \rightarrow \pi^*$ character of the lowest singlet transition, which is again consistent with the oxygen n electrons being involved in the overall 10π system. It is not possible at this time to comment further on the significance of these results in terms of the aromaticity of isobenzofuran, particularly in view of the lack of model carbocyclic systems.

Acknowledgment. We thank the Australian Research Grants Committee for partial support of this work.

(18) We thank Dr. J. MacLeod and Mr. K. Goggin for the mass spectra (recorded on an AEI MS902 instrument, operated at 70 eV).

(19) E. Le Goff and R. B. LaCount, *Tetrahedron Lett.*, 2787 (1965).

(20) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, 1969, p 61.

(21) We thank Dr. B. K. Selinger and Mr. R. J. McDonald of this department for this measurement. For a description of the apparatus used see R. J. McDonald and B. K. Selinger, *Z. Phys. Chem. (Frankfurt am Main)*, **69**, 132 (1970).

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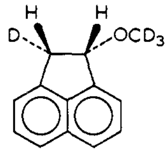
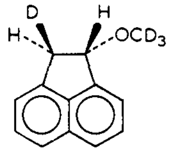
E1cB Reactions. Stereochemistry and the Counterion

Sir:

We wish to report observations on base-catalyzed elimination reactions of 1-methoxyacenaphthenes which appear to proceed with reversible formation of carbanionic intermediates.[1] Under the present conditions, elimination and hydrogen–deuterium exchange reactions were in close competition, and allowed observation of the stereochemical preferences of both processes. Both the elimination and exchange reactions changed from exclusive cis to preferential trans[2] stereoselectivity depending upon the nature of the cation in solution.



1



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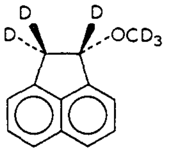

3

cis-1-Methoxy-d_3-2-deuterioacenaphthene (**1**) and *trans*-1-methoxy-d_3-2-deuterioacenaphthene (**2**)[3] (0.01–0.06 *M*) were treated in degassed sealed tubes as in Table I. The products of reaction were analyzed by vpc and mass and nmr spectrometry. For each set of conditions three reactions were run (10, 30, and 50% elimination) but only a representative run is included for each. While the recovered ethers were also analyzed for exchange, these results have been omitted for simplicity; exchange occurs predominantly at the 2 position.[4]

The reactions of **1** and **2** were used to deduce the stereoselectivity of the elimination reactions. Analysis of the recovered acenaphthylenes allowed calculation of the amounts of acenaphthylene-d_0, -d_1, and -d_2[5] (see Table I). It is clear that the ratio of d_0 to d_1 varies widely and for discussion these results have been converted to $k_{\text{cis}}/k_{\text{trans}}$ elimination ratios in Table II. The conversion of the d_0/d_1 ratio to $k_{\text{cis}}/k_{\text{trans}}$ elimination involved extrapolation to zero time and the ratios changed by about 10% on extrapolation. Also included in Table II under the heading $k_{\text{cis}}/k_{\text{trans}}$ exchange are exchange results for 1-methoxy-d_3-1,2,2-trideuterioacenaphthene (**3**).[4]

In Table II under the heading ex/elim is a comparison of the relative amounts of total exchange of the ether and elimination based upon these and earlier results.[4] Comparison of the rates of elimination of **3** and of 1-methoxyacenaphthene yielded kinetic isotope effects for the reactions in *tert*-butyl alcohol with Cs$^+$, K$^+$, and K$^+$-crown ether[6] as cations. These fall in the range k_H/k_D = 1.6–1.8.[7] The observation of hydrogen–deuterium exchange requires the formation of carbanionic intermediates for the exchange reaction; it seems

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(1) For a recent discussion of types of E1cB reactions see F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5950 (1970).

(2) The terms cis and trans (rather than syn or anti) will be used throughout to designate the geometrical relationship of the proton (deuteron) to the methoxy group in both the exchange and elimination processes.

(3) Ether **1** was prepared *via* the alcohol from deuterioboration of acenaphthylene; ether **2** was prepared *via* the alcohol from $LiAlD_4$ reduction of 1,2-epoxyacenaphthene. Both ethers were ≥99% chemically pure and about 90% isotopically pure.

(4) D. H. Hunter and Y. T. Lin, *ibid.*, **90**, 5921 (1968).

(5) Acenaphthylene-d_2 exchange approximately 10^7 slower than **3**.

(6) (a) Dicyclohexyl-18-crown-6-ether kindly provided by H. K. Frensdorff, E. I. du Pont de Nemours and Co., Wilmington, Del.; (b) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(7) (a) *E.g.* D. J. McLennan, *Quart. Rev., Chem. Soc.*, **21**, 490 (1967); (b) R. Breslow, *Tetrahedron Lett.*, 399 (1964); (c) H. M. Walborsky and J. M. Motes, *J. Amer. Chem. Soc.*, **92**, 2445 (1970); (d) W. T. Ford, E. W. Graham, and D. J. Cram, *ibid.*, **89**, 4661 (1967).

Table I. Products of Elimination of Ether-**1** and Ether-**2**

Entry	Base[a]	Solvent	Base concn, M	Temp, °C	Time, min	Substrate	Acenaphthylene Mol %	Acenaphthylene % d_0	Acenaphthylene % d_1	Acenaphthylene % d_2	Ether mol %
1	$(CH_3)_4N^+$	*tert*-BuOH	0.10	45	90	**1**	8	1.6	6.3	0.1	92
2	K^{+b}	*tert*-BuOH	0.021	45	617	**1**	5	1.2	3.7	0.1	95
3	Cs^+	*tert*-BuOH	0.20	86	31	**1**	10.5	7.8	2.6	0.1	89.5
4	Cs^+	*tert*-BuOH	0.22	86	31	**2**	15	3	11.5	0.5	85
5	K^+	*tert*-BuOH	0.43	86	74	**2**	15	2.0	12.5	0.5	85
6	Li^+	*tert*-BuOH	0.14	152	462	**2**	25	2	22	1	75
7	K^+	CH_3OH	0.48	152	45	**1**	23	11	12		77

[a] Present as the alkoxide salt. [b] Complexed with 0.021 M dicyclohexyl-18-crown-6.

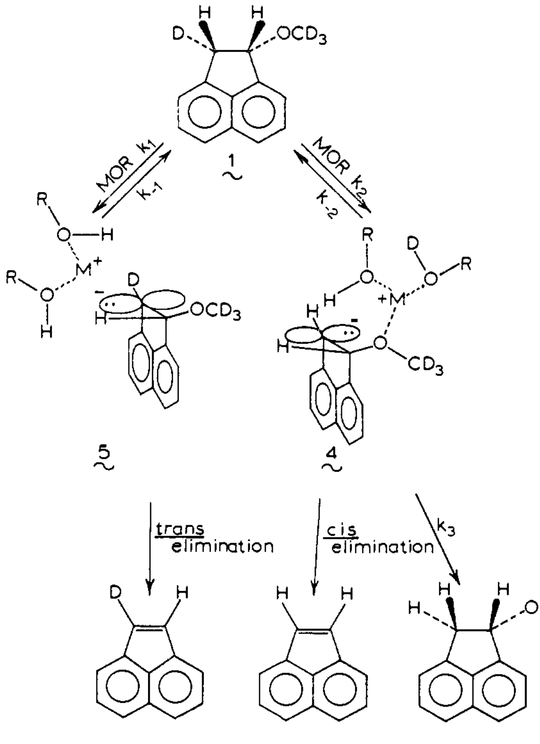
Table II. Effect of Cation on Relative Exchange and Elimination Rates

Entry	Base[a]	Ex/elim	Exchange k_{cis}/k_{trans}	Elimination k_{cis}/k_{trans}
8	$Li^+\bar{O}C(CH_3)_3$	0.4	≥ 16	≥ 13
9	$K^+\bar{O}C(CH_3)_3$	1.3	2.2	≥ 7
10	$Cs^+\bar{O}C(CH_3)_3$	2.1	0.9	≥ 5
11	$(CH_3)_4N^+\bar{O}C(CH_3)_3$	3.2	0.5	0.3
12	$K^+\bar{O}C(CH_3)_3{}^b$	3.2	0.6	0.3
13	$K^+\bar{O}CH_3$	5.1	1.0	0.6
14	$K^+\bar{O}CH_3{}^b$	3.4	1.0	

[a] Solvent is the conjugate acid. [b] Complexed with dicyclohexyl-18-crown-6-ether.

most reasonable to interpret the elimination reaction also in terms of carbanionic intermediates (E1cB).

As the results of Table II show, the ratio of cis/trans for both the exchange and elimination reactions varies by a factor of at least 30 (entries 8 and 11) from exclusive cis to dominant trans. The exchange and elimination stereoselectivity parallel each other closely except for Cs+ and K+ which show a greater cis to trans preference in elimination than in exchange.



Lithium cation shows a strong preference for cis reactions which can be interpreted in terms of a strong coordination between Li+ of the base ion pair (or agglomerates) and the ether oxygen of substrate. This is shown in the simplified reaction scheme for **1**. The formation of **4** is greatly preferred over **5** with Li+ present.

With K+ and Cs+, the coordinating ability is progressively reduced until **4** and **5** are produced in nearly equal amounts. However, from the elimination results it appears the cations enhance the decomposition into olefin and methoxide of **4** relative to **5**. The formation of a cation–methoxide ion pair from **4** seems to be an important factor in eliminations in *tert*-butyl alcohol.

In the absence of a coordinating cation (entries 11–14), intermediates **4** and **5** become near degenerate. A dramatic demonstration of this change is the large decrease in cis elimination and exchange when dicyclohexyl-18-crown-6-ether[6b] was added to potassium *tert*-butoxide (entries 9 and 12) and with tetramethylammonium cation.[8] In contrast, when dicyclohexyl-18-crown-6-ether is added to the already dissociated potassium methoxide in methanol (entries 13 and 14), there is no alteration in the stereochemistry of exchange.

These observations imply that there can be a significant role for cations in designing and interpreting elimination reactions in low polarity solvents.

Acknowledgment. The authors wish to thank the National Research Council of Canada for financial assistance.

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[8] W. H. Saunders, D. G. Bushman, and A. F. Cockerill, *J. Amer. Chem. Soc.*, **90**, 1775 (1968).

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Hypofluorous Acid

Sir:

We have synthesized hypofluorous acid, HOF, by the reaction of fluorine with liquid or solid water in a Kel-F vessel. It is a volatile compound, stable enough to be transferred at room temperature under vacuum or in a gas stream.

Although the preparation of oxyacids of fluorine was reported in the early 1930's,[1,2] these results were soon

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[1] L. M. Dennis and E. G. Rochow, *J. Amer. Chem. Soc.*, **54**, 832 (1932).

[2] L. M. Dennis and E. G. Rochow, *ibid.*, **55**, 2431 (1933).