passed through a hot tube maintained at 700 °C. The pyrolysate (0.23 g) was analyzed by GC/MS in addition to separation by preparative TLC on silica gel for unambiguous identification: benzophenone (51 mg, 36%; mp 46–48 °C), fluorene (46 mg, 36%; mp 114–116 °C), and *n*-butyl glyoxylate (48 mg, 47%). These products were formed in a ratio of 26:24:46 (the remaining 4% was starting material).

Pyrolysis of 2,5-Diphenyl-1,3-dioxolan-4-one. The dioxolanone (0.25 g, 1.04 mmol; cis/trans = 63/37)[7] was heated to 100 °C at 0.05 torr with the hot tube at 570 °C. The product (0.23 g) was analyzed by NMR as starting material (44%), benzaldehyde (40%), and stilbene oxide (16%, cis/trans = 16/84).

Pyrolysis of 2-(4-Methoxyphenyl)-5-phenyl-1,3-dioxolan-4-one. The dioxolanone (0.15 g, 0.55 mmol, cis/trans = 69/31) was vaporized at 130 °C at 0.005 torr through a hot tube at 570 °C to give 0.14 g of pyrolysate which analyzed by NMR to be benzaldehyde (44%), anisaldehyde (44%), and 1-phenyl-2-(*p*-methoxyphenyl)oxirane (12%, >95% trans) as well as a trace of starting material.

Pyrolysis of 2-(4-Nitrophenyl)-5-phenyl-1,3-dioxolan-4-one. The dioxolanone (0.15 g, 0.53 mmol; cis/trans = 55/45) was heated to 150 °C at 0.005 torr with the hot tube at 650 °C. The pyrolysate (0.13 g) was benzaldehyde (49%) and *p*-nitrobenzaldehyde (51%) as well as a trace of starting material by NMR.

Pyrolysis of 5-(4-Nitrophenyl)-2-phenyl-1,3-dioxolan-4-one. The dioxolanone (0.10 g, 0.35 mmol; cis/trans = 84/16) was heated to 130 °C at 0.05 torr with the hot zone at 570 °C to give 84 mg of a pale yellow wet solid. This analyzed by NMR to be *p*-nitrobenzaldehyde (27%), benzaldehyde (26%), 1-phenyl-2-(*p*-nitrophenyl)oxirane (34%, cis/trans = 30/70), and 13% starting material.

Proton-Transfer Reactions. 1. Partitioning of Carbanion Intermediates Generated by Reactions of Alkenes with Alkoxide Ions in Alcohol

H. F. Koch,* J. G. Koch, D. B. Donovan, A. G. Toczko,[1a] and A. J. Kielbania, Jr.[1b]

Contribution from the Department of Chemistry, Ithaca College, Ithaca, New York 14850.

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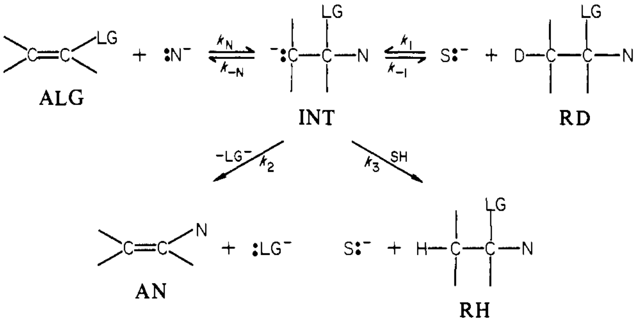
Abstract: Nucleophilic reactions with sodium alkoxide in alcohol have been studied with various *gem*-difluoroalkenes of general structure $C_6H_5CR{=}CF_2$. Rates and Arrhenius parameters [$k \times 10^3$ ($M^{-1}\ s^{-1}$), at −50 °C, $\Delta H^{\ddagger}$ (kcal mol^{-1}), and $\Delta S^{\ddagger}$, (eu)] are respectively: R = $-CF_3$ (II), 105, 9, and −23; $-CF_2Cl$ (III), 135, 10, and −19; $-CF_2CF_3$ (IV), 40.6, 9, and −23; $-CF_2H$ (V), 3.63, 11 and −19. Reactions proceed via carbanion intermediates, and the products from reaction with ~0.3 N sodium ethoxide in ethanol are: II, 85% vinyl ether and 15% saturated ether; III, 100% allylic ether; IV, 74% vinyl ether, 22% allylic ether, and 4% saturated ether; V, >98% allylic ether. The observed product distributions suggest the following order of leaving group ability for fluoride in different environments: $-CF_2H \gg -CF_2OR > -CF_2CF_3 \gg -CF_3$. Solvent protonation of the carbanion is apparently slower than fluoride ion ejection from all groups studied other than trifluoromethyl. Product isotope effects (PIE), k^H/k^D, for the protonation of the carbanion generated from II by reaction in ethanol are 1.50 (−78 °C) and 1.86 (20 °C) and by reaction in methanol are 1.22 (−78 °C).

Over the years our research efforts have gradually shifted from studies of nucleophilic reactions of alkenes[2] to proton exchange and elimination reactions,[3] and finally to an in-depth analysis of primary kinetic isotope effects applied to proton transfer occurring during dehydrohalogenation reactions.[4,5] The unifying theme of all our work has been the study of carbanion intermediates formed during the course of chemical reactions and the determination of products formed by the partitioning of these intermediates along alternate pathways. In order to study the partitioning of such intermediates, one must first be able to detect them directly or to design experiments whose results can best be interpreted by postulating the existence of a carbanion or the lack of one along the reaction pathway. A carbonion intermediate, INT, can be generated by the reaction of a nucleophile with an alkene, ALG, or by the base-catalyzed abstraction of hydrogen from a saturated carbon, RD, Scheme I. The intermediate can partition to form an alkene, AN, or to form the exchanged saturated compound, RH.

Scheme I



If the starting point of such investigations is the alkene, then the process will be the competition between a vinyl displacement reaction or the addition across a carbon–carbon double bond. On the other hand, if one starts with the saturated compound, then the reactions studied are elimination vs. exchange. However, if one considers the intermediate, both studies become a competition between the ejection of a leaving group, LG, and the proton transfer from a solvent molecule, SH. Problems can arise if reversible reactions are competitive with the forward process. For example, if N is a comparable or better leaving group than LG, a study of this reaction would not give a true measure of the rate of reaction of N with ALG, nor would it give the actual partitioning of the intermediate regarding all three alternatives. The study of elimination and exchange reactions is further complicated by the possibilities of a concerted mechanism becoming the low-energy pathway for elimination reactions.

The facile reaction of nucleophiles with a *gem*-difluoroethylene group, $=CF_2$, has been well documented in the literature, and the study of such systems is ideal for our purposes.[6] Miller et

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[1] (a) Supported by NSF-URP Grant GY-7413 during the summer of 1970; (b) supported by NSF-URP Grant GY-4287 during the summer of 1968.

[2] H. F. Koch and A. J. Kielbania, Jr., *J. Am. Chem. Soc.*, **92**, 729 (1970).

[3] H. F. Koch, D. B. Dahlberg, A. G. Toczko, and R. C. Solsky, *J. Am. Chem. Soc.*, **95**, 2029 (1973).

[4] H. F. Koch, D. B. Dahlberg, M. F. McEntee, and C. J. Klecha, *J. Am. Chem. Soc.*, **98**, 1060 (1976).

[5] H. F. Koch and D. B. Dahlberg, *J. Am. Chem. Soc.*, **102**, 6102 (1980).

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Table I. Activation Parameters and Rates (−50 °C) for Reaction of $PhCR{=}CF_2$ with Methanolic Sodium Methoxide

R	$k \times 10^3$, $M^{-1}\ s^{-1}$	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
CF_3 (II)[a]	105	8.7 ± 0.3	−23 ± 1
CF_2Cl (III)[a]	135	9.6 ± 0.1	−19 ± 1
CF_2CF_3 (IV)[a]	40.6	9.2 ± 0.2	−23 ± 1
CF_2H (V)[b]	3.63	11.2 ± 0.3	−19 ± 1

[a] Temperatures for rate constants were −55 and −77 °C.
[b] Temperature range studied was −20 to −55 °C. Rate constants were measured at five different temperatures.

Table II. Product Distribution from the Reaction:

$$C_6H_5CR{=}CF_2 + EtONa \xrightarrow{EtOH} C_6H_5CHRCF_2OEt\ (\text{satd}) + C_6H_5CR{=}CFOEt\ (\text{vinylic}) + C_6H_5\underset{\underset{\textstyle R}{\|}}{C}{-}CF_2OEt\ (\text{allylic})$$

R	temp, °C	% satd	% vinylic	% allylic
CF_3	−78	15 (34)[a]	85 (66)[a]	0 (0)[a]
CF_3	20	21 (44)[a]	79 (56)[a]	0 (0)[a]
CF_2Cl	−78	0	0	100[b]
CF_2CF_3	−78	4	74	22
CF_2H	−50	?	?	>98[b]
Cl	0	40 (49)[a]	60 (51)[a]	

[a] Values in parentheses are for reaction with MeONa in MeOH.
[b] Same product distribution observed for reaction with MeONa in MeOH.

al.[7] have reported the methoxide-catalyzed addition of methanol across the double bond of *unsym*-dichlorodifluoroethylene to give the saturated ether, $CH_3OCF_2CHCl_2$, as the only product. We find that by replacing one of the chlorines with a phenyl group, $PhCCl{=}CF_2$, the product distribution is altered to give both

$$CCl_2{=}CF_2 \xrightarrow[CH_3OH]{CH_3ONa} CHCl_2CF_2OCH_3$$

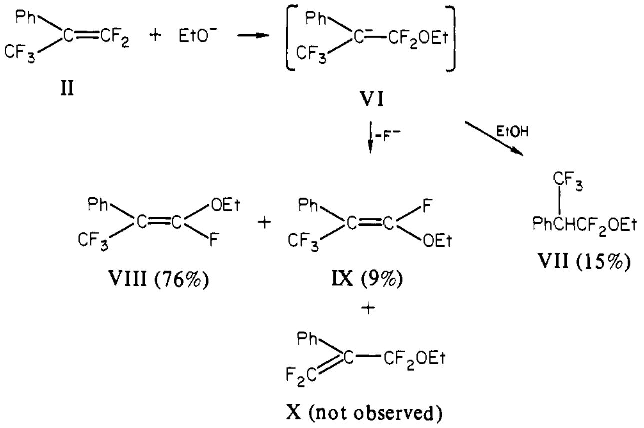
$$\underset{\textstyle I}{C_6H_5CCl{=}CF_2} \xrightarrow[CH_3OH]{CH_3ONa} \underset{49\%}{C_6H_5CHClCF_2OCH_3} + \underset{51\%}{C_6H_5CCl{=}CFOCH_3}$$

saturated and vinyl ethers. Although quantitative numbers are not available regarding the leaving-group ability of alkoxide vs. the halides, the experimental evidence suggests that even fluoride ion is a better leaving group than are aliphatic alkoxide ions.[8] This should eliminate the possibility that the unobserved reaction of the nucleophile acting as a competing leaving group complicates the interpretation of our results.

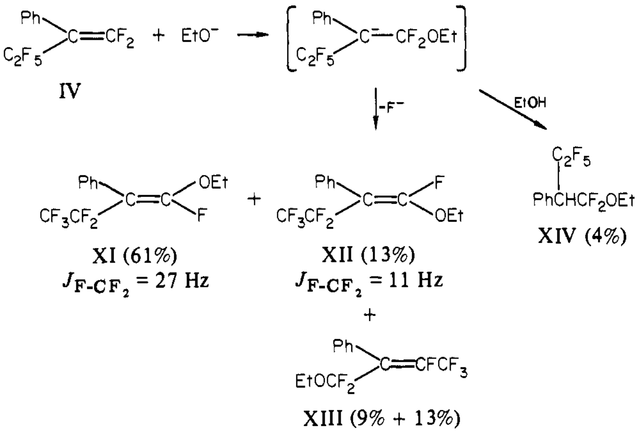
Results and Discussion

The reaction of I with alkoxide ion in alcohol results in a product distribution arising from a competition between the protonation of the carbanion intermediate and the ejection of a fluoride ion from the $-CF_2OR$ group. The leaving-group ability of fluoride from different environments can be investigated by using a series of compounds, $PhCR{=}CF_2$ where R = $-CF_3$ (II), $-CF_2CF_3$ (IV), or $-CF_2H$ (V), and chloride can also be included when R = $-CF_2Cl$ (III). Since nucleophilic attack always occurs at the $=CF_2$ position, the site of reaction remains constant, and groups leaving from the various R substituents can be compared with both the protonation reaction and the ejection of fluoride ion from $-CF_2OR$. Product analyses were carried out using gas chromatography and structures confirmed by ^{19}F NMR. Since the isomeric ethoxyvinyl ethers separate cleanly on our GC columns, the early kinetic studies and product analysis were carried out using sodium ethoxide in ethanol. Table I lists rates and Arrhenius parameters obtained in later studies using sodium methoxide in methanol. This latter system was found to give much better solvent behavior at the low temperatures required for good kinetic studies. Table II summarizes product distributions for these reactions.

Scheme II



Scheme III



Reaction of 2-phenylperfluoropropene (II) with sodium ethoxide in ethanol occurs rapidly at −78 °C to give the product distribution in Scheme II.[2] Reaction of II at −78 °C with methanolic sodium methoxide gives an increased yield of saturated ether (34%) at the expense of the vinyl ethers. The ratio of Z/E vinyl ethers remains the same as the ratio of VIII/IX and again no allylic ether is detected. Since kinetic studies are followed using a gas chromatographic analysis of alkene and an unreactive internal standard such as anisole, products can be monitored throughout the run. The product ratios remain constant during the course of a run, and this suggests that VIII and IX are formed directly from the intermediate, VI, rather than by a subsequent dehydrofluorination of VII. Studies of the ethanolic ethoxide-promoted elimination of VII confirmed this conclusion since reaction of II occurs six orders of magnitude faster than does the dehydrofluorination reaction.

3-Chloro-2-phenylperfluoropropene-1 (III) reacts at a similar rate and has the same Arrhenius behavior as does II. This suggests that the rate-limiting step in both reactions is the attack of alkoxide on $=CF_2$ to generate a carbanion intermediate. Since chloride is a much better leaving group than is fluoride, it is not surprising that the intermediate from reaction of III would preferentially eject a chloride ion to form the allylic ether, X. The allylic ether will rearrange on standing to form a mixture of vinyl ethers, VIII (47%) and IX (53%).[9] To ensure that X was not formed during

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(6) An excellent review of this area was made by R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, **4**, Chapter 3, 50 (1965).

(7) W. T. Miller, Jr., E. W. Fager, and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

(8) C. J. M. Stirling, *Acc. Chem. Res.*, **12**, 198 (1979).

(9) A similar rearrangement of $CH_3OCF_2CF{=}CF_2$ has been reported by B. L. Dyatkin, L. S. German, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **114**, 320 (1957).

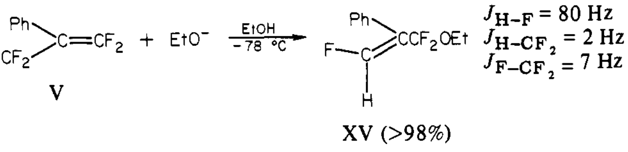
Table III. Comparison of Observed Products from Carbanion Partitioning When Generated from Saturated Ether or or Alkene at 40 °C

reaction	$PhC(CF_3)=CFOR$, VIII + IX, %	$PhCD(CF_3)CF_2OR$, VII-*d*, %	$\frac{\text{VIII + IX}}{\text{VII-}d}$
$PhCH(CF_3)CF_2OMe \xrightarrow[EtOD]{EtONa}$	20[a]	3.2-2.4[b]	6-8
$PhC(CF_3)=CF_2 \xrightarrow[EtOD]{EtONa}$	85	15	6

[a] The relative rates for reaction with EtONa are 1.0 (VII), 1.2 (IX), and 1.4 (VIII). An accurate ratio of VIII:IX formed during the course of reaction was therefore not obtained. Initial values for VIII/IX were >2:1, and this value dropped until IX > VIII in later stages of reaction. [b] Reactions were run to 20% elimination to form VIII and IX. Unreacted starting material was isolated and analyzed for deuterium content by mass spectral analysis. A 3% deuterium incorporation represents 2.4% VII-*d*, and 4% deuterium content is 3.2% VII-*d* formed during the reaction.

the reaction of II, a series of runs with II and with III were carried out and immediately analyzed under identical conditions. The three unsaturated ethers are cleanly separated from each other and from the saturated ether on a 10-ft SE-30 column. No detectable amount of X was observed from reaction of II, and no VIII or IX were observed in the analysis of reaction with III. Direct displacement of chloride by an S_N2 reaction was ruled out since this type of reaction is quite slow with a $-CF_2X$ group.[10]

Although no allylic ether was formed by reaction of II, 2-phenylperfluorobutene-1 (IV) reacts with sodium ethoxide in ethanol to form 96% unsaturated ethers which include a mixture of both isomeric allylic ethers XIII (Scheme III). The major products (74%) are again the vinyl ethers, and the amount of saturated ether is reduced to only 4% of the total products. On the other hand, 3-hydro-2-phenylperfluoropropene-1 (V) reacts to give better than 98% of the allylic ether XV.



The observed products from these alkenes suggest that several reactions can occur at a faster rate than does the protonation of a carbanion intermediate generated in alcohol. Ejection of chloride ion and fluoride ion from a $-CF_2H$ group clearly wins the competition with protonation of the respective intermediates generated from III and V. Since vinyl ethers are the major products from ethoxide reaction of II (85%) and IV (74%), apparently fluoride ion is a better leaving group from $-CF_2OEt$ by factors of 5.7 (II) and 19 (IV) than is the protonation of these intermediates. Ejection of fluoride from $-CF_2CF_3$ is also faster than protonation, and it is only the loss of fluoride from a trifluoromethyl group that cannot compete favorably with the protonation reaction.

When carbanions are generated by a base-promoted removal of hydrogen, the mode of intermediate formation shifts to the right-hand side of Scheme I. Questions can now arise regarding a concerted elimination reaction, the possibility of the unobserved internal-return reaction, and whether or not the "same" carbanionic species is generated by approach from either side. In an attempt to answer these questions, the exchange and elimination of $PhCH(CF_3)CF_2OCH_3$ (VII–OMe) were studied in ethanol-*O-d* at 40 °C. The methoxy ether was chosen for ease of synthesis and purification, and also to check for a possible methanol elimination competing with the expected dehydrofluorination reaction. The elimination of methanol would result in the formation of I which under these conditions would rapidly react with ethoxide to give a mixture of VII, VIII, and IX. None of these compounds were observed in our GC analysis. When the ethoxide-promoted dehydrofluorination was stopped at 20% reaction, unreacted VII-OMe was isolated by preparative GC and found to contain 3-4% deuterium incorporation (by mass spectral analysis) into the benzylic position (Table III).

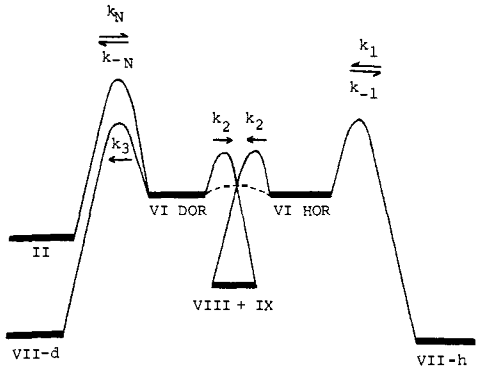
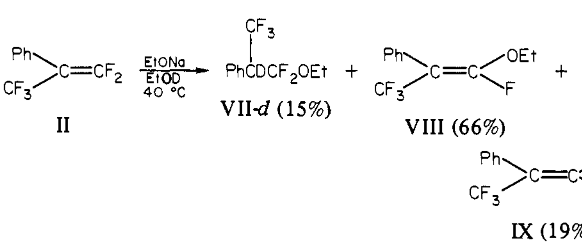
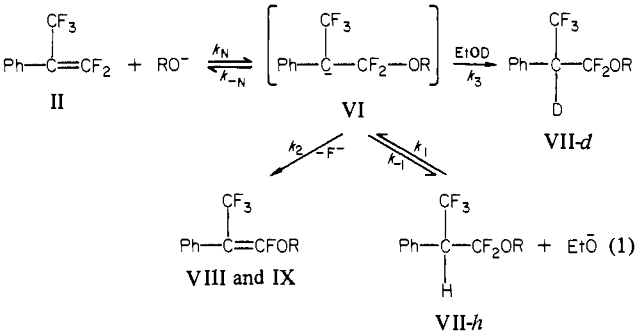


Figure 1. Possible free-energy diagram for reaction of II and VII with sodium ethoxide in ethanol. Numbering of rate constants is consistent with eq 1.

The product distribution from reaction of II with ethanolic sodium ethoxide changes slightly at elevated temperatures. At 20 °C more saturated ether, 21%, is formed and the ratio of VIII:IX changes from 76:9 to 60:19. Therefore, reaction of II with sodium ethoxide was carried out at 40 °C in EtOD to allow comparison with the results obtained by reaction of VII–OMe in EtOD. Since the two experimental results appear to be in agreement regarding the ratio of vinyl ethers vs. deuterated product, one is tempted to conclude that the observed products are coming from the same intermediate which can be generated from either alkene or the saturated ether (eq 1) (Figure 1).





The main feature of this free-energy diagram is that the energy barrier for fluoride ejection, k_2, should be about 0.8 kcal mol^{-1} less than the barrier for a transfer of proton from alcohol to the carbanion, k_3. This would represent the product split of 15% saturated ether vs. 85% vinyl ether. We have arbitrarily shown a rather small barrier for the exchange of the alcohol generated by proton transfer from carbon to oxygen with that of a bulk solvent alcohol. This would mean that the exchange with bulk solvent, which is often thought to be a diffusion-controlled process, occurs faster than the ejection of fluoride; however, the extent of this exchange cannot be observed since loss of fluoride is five to six times faster than the step that forms the carbon-hydrogen bond. If this representation is correct, one could expect to measure

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(10) W. T. Miller, Jr., and A. H. Fainberg, *J. Am. Chem. Soc.*, 79, 4164 (1957).

Table IV. Activation Parameters and Rates (25 °C) for Dehydrofluorination of $PhCL(CF_3)CF_2OMe$ with Ethanolic Sodium Ethoxide

L	$k \times 10^5$, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	temp range, °C
H	4.84	26.2 ± 0.3	9.6 ± 0.9	30-70
D	7.89	25.9 ± 0.3	9.7 ± 0.8	30-70

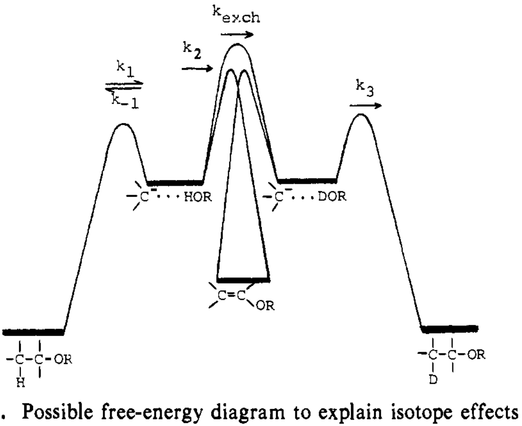
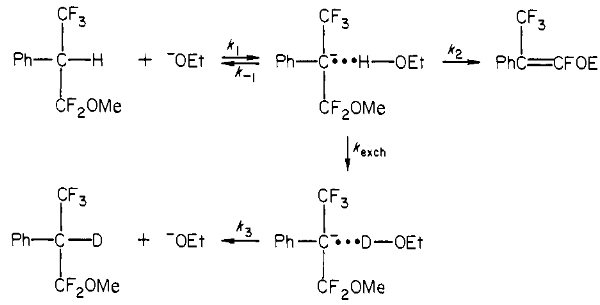


Figure 2. Possible free-energy diagram to explain isotope effects and exchange observed during the ethoxide-promoted dehydrofluorination of $C_6H_5CH(CF_3)CF_2OCH_3$, eq 2.

a sizable isotope effect during the ethoxide-promoted dehydrofluorination of VII–OMe.

The ethoxide-promoted elimination of VII–OMe has a primary kinetic isotope effect, k^H/k^D, of only about 1.3 at 40 °C,[11] and this suggests that a rather large amount of internal return may be occurring during the dehydrofluorination reaction,[12] eq 2. This



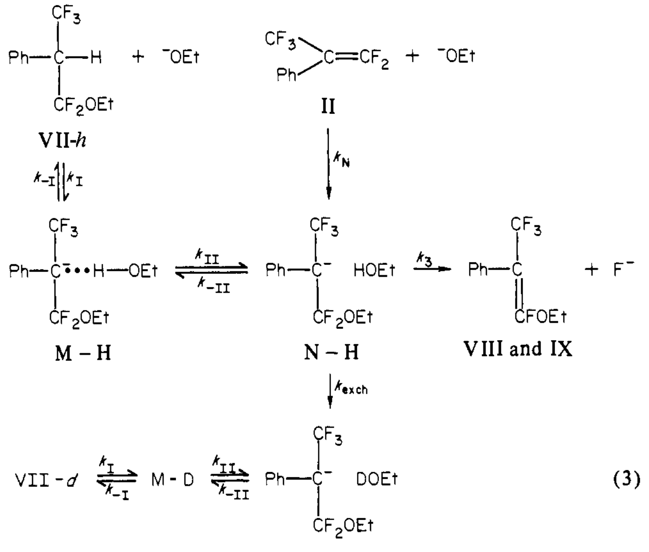
(2)

would mean that the fastest reaction of the carbanion intermediate (formed during the elimination and exchange reaction) is reprotonation by the specific alcohol molecule generated from the initial proton-transfer step, k_{-1} (Figure 2). Since the actual proton-transfer step now has a lower energy barrier than that for the loss of fluoride ion, k_2, this free-energy diagram could not describe the carbanion intermediate generated by the reaction of alkene with alkoxide. The barrier for exchange with bulk solvent must now be about 0.8 kcal mol^{-1} greater than the barrier for ejection of fluoride ion.

A free-energy diagram similar to the one in Figure 2 is also consistent with our observed equilibrium isotope effects for both exchange and elimination reactions of two model compounds $C_6H_5CLClCF_3$ and $C_6H_5CL(CF_3)_2$.[13] Formation of a stable hydrogen-bonded intermediate in an equilibrium step, k_1/k_{-1}, is followed by rate-limiting steps for both exchange and elimination.[3] Since fluoride appears to be a poorer leaving group from $-CF_3$ than from $-CF_2OR$, the rate of exchange, k_{exch}, would now be faster than that for ejection of fluoride, k_2, in the model compounds.

Observation of equilibrium isotope effects for exchange reactions normally occurs with carbanions that are quite localized on one carbon atom. Kresge[14] has discussed the behavior of phenylacetylene and chloroform where the charge must remain on a specific carbon. These two substrates and various polyfluorobenzenes[15] result in equilibrium isotope effects when undergoing exchange with bulk solvent. Little information can be obtained about the energies of the actual proton-transfer step when it occurs in an equilibrium process prior to a rate-limiting step. Many substrates used in exchange studies form highly delocalized carbanions, and it is for these substrates that the actual exchange process is thought to be diffusion controlled. We feel that the carbanions formed in our systems are quite localized on the benzylic carbon since the presence of fluorine substituents can greatly stabilize a localized carbanion. Fluorine attached to carbon adjacent to the negative charge is thought to stabilize that charge by a field effect rather than by no-bond hyperconjugation,[16] and Streitwiesser et al.[17] have interpreted their recent calculations to support this view.

An alternate explanation for these results could be that two types of carbanion intermediates are formed along the reaction pathway, eq 3. One intermediate, M, could be a carbanion that



(3)

is stabilized by a hydrogen bond, which is much stronger than might be anticipated,[18] while the other intermediate, N, might be a carbanion which is surrounded by a shell of rather loosely attracted alcohol molecules. Internal return may be the low-energy pathway for M, but internal return from N would only occur if the unique alcohol molecule is still in the best position to reprotonate the carbanion. The exchange with bulk solvent could be a diffusion-controlled process and not require the rather large energy barrier pictured in Figure 2. Reaction of II with ethoxide would lead directly to N, which can partition between ejection of fluoride and formation of M. Once M is formed, the lowest energy pathway would be a proton-transfer reaction to form the

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(11) The actual k^H was measured in EtOH and k^D was measured in EtOD. We corrected the ratio for a kinetic solvent isotope effect of 2.0 for k^{OD}/k^{OH}. Results are shown in Table IV.

(12) D. J. Cram, "Fundamentals of Carbanion Chemistry", Acadamic Press, New York, 1965, pp 27-29.

(13) $C_6H_5CLClCF_3$ and $C_6H_5CL(CF_3)_2$ have been studied using sodium ethoxide for exchange where L is H (EtOD), D (EtOH), and T (both EtOH and EtOD), and elimination where L is H (EtOH) and D (EtOD). $C_6H_5CL(CF_3)_2$ has also been studied in the same manner using sodium methoxide in the appropriate MeOL. All isotope effects were corrected for a kinetic solvent isotope effect measured by using the tritium compounds in both ROH and ROD, and range from k^H/k^D = 1.04 to 1.21.

(14) A. J. Kresge, *Acc. Chem. Res.*, **9**, 354 (1975).

(15) A. Streitwieser, Jr., J. A. Hudson, and F. Mares, *J. Am. Chem. Soc.*, **90**, 648 (1968).

(16) D. Holtz in "Progress in Physical Organic Chemistry", Vol. 8, A. Streitwieser, Jr., and R. W. Taft, Eds., Wiley-Interscience, New York, 1971.

(17) A. Streitwieser, Jr., C. M. Berke, G. W. Schriver, and J. B. Collins, *Tetrahedron Suppl.*, 37, No. 9, 345 (1981).

(18) L. L. Ferstandig, *J. Am. Chem. Soc.*, 84, 3553 (1962), experimentally demonstrated that neutral carbon is a good hydrogen-bonding base and suggested that carbanions should be excellent in that capacity.

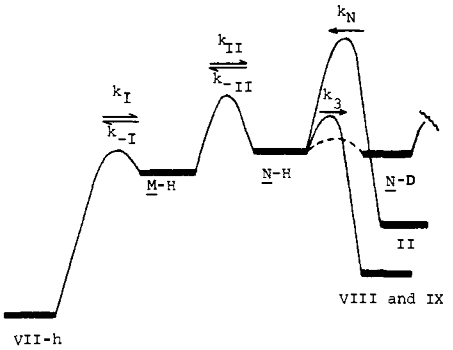

Figure 3. Possible free-energy diagram for reaction of II and VII with sodium ethoxide in ethanol, eq 3.

saturated ether. A partial free-energy diagram is shown in Figure 3.

The two-intermediate mechanism also appears to be a good working model to explain the observed product isotope effects (PIE)[19,20] for reaction of II with alcoholic alkoxide. The kinetic solvent isotope effect, $k^{EtOD}/k^{EtOH} = 1.9$ at −78 °C, measured for reaction of II with sodium ethoxide, is quite normal.[21] The amount of saturated ether formed in EtOD (13%) is slightly less than is formed in EtOH (15%), and similar results come from reaction with methoxide in MeOD (32% VII–OMe-*d*) and in MeOH (34% VII–OMe) at −78 °C. At 20 °C the amount of saturated ether formed increases and there is a larger difference between VII-*d* formed in EtOD (15%) and VII-*h* formed in EtOH (21%). A similar trend is observed with methoxide where 38% VII–OMe-*d* is observed in MeOD vs. 44% VII–OMe in MeOH. Results are summarized in Table V.

To confirm these results, II was treated with a 1:1 mixture of EtOH–EtOD, and VII was isolated and subjected to mass spectral analysis. Saturated ether from the −78 °C reactions analyzed as a 60:40 ratio of H:D, while product from 20 °C runs gave a 65:35 ratio. These ratios allow calculation of a product isotope effect (PIE) $k^H/k^D = 1.50$ (−78 °C) and 1.86 (20 °C). Using a 1:1 mixture of MeOH–MeOD at −78 °C resulted in PIE equal to 1.22 which represented a 55:45 H:D content of VII–OMe. The rather small values for PIE are qualitatively consistent with the free-energy diagram shown in Figure 3, but we have no explanation for the small, but real, increase in PIE with increasing temperature.

For a two-intermediate mechanism, any isotope effect for the actual proton-transfer step from oxygen to carbon could not be observed since it would occur after the rate-limiting step of formation of the hydrogen-bonded intermediate. The isotope effect associated with the latter step is expected to be quite small. A model for this could come from work reported by Gold and Grist[21] on possible origins for kinetic solvent isotope effects of alcohols. They conclude that these effects are due to a multiple solvated methoxide ion which has a deuterium fractionation factor, $\phi_{OMe} = 0.74$. This fractionation factor implies that the equilibrium abundance of deuterium in the *m* hydrogen atoms of the solvated methoxide ion, $MeO^- \cdot\cdot\cdot (LOMe)_m$, is 0.74 times that of bulk solvent. Therefore, MeOH molecules rather than MeOD will preferentially solvate the methoxide ion.

The fact that α-chloro-β,β-difluorostyrene (I) reacts with methanolic sodium methoxide to give a mixture of saturated (49%) and vinyl (51%) ethers made this an interesting system since we could study the partitioning of carbanion intermediates along alternate pathways. Although the results for *unsym*-dichlorodifluoroethylene (XVI), which reacts to give only the saturated ether, differ from those obtained with I, they are in agreement with exchange and dehydrofluorination studies on $CHCl_2CF_2OCH_3$ (XVII). Hine et al.[22] reported that XVII-*d* undergoes exchange with methanol 10^4 times faster than methoxide-promoted dehydrofluorination of XVII-*h*. This is consistent with the fact that the carbanion, $CH_3OCF_2\bar{C}Cl_2$, preferentially abstracts a proton from solvent rather than ejecting fluoride ion to give a vinyl ether. Although we have not studied $C_6H_5CHClCF_2OCH_3$, the results reported above for reactions of II and VII also have an internal consistency when comparing carbanions generated from an alkene (sp^2 carbon) and an alkane (sp^3 carbon). Data are summarized in Table VI.

Hine et al.[22] report a more detailed study using $CHCl_2CF_3$ (XVIII) which could be a model compound for product formation from reactions of XVI, and we have studied $C_6H_5CHClCF_3$ (XIX) which could serve as a model compound for reactions of I. Exchange of XVIII-*d* with methanolic sodium methoxide occurs 10^7 times faster than does methoxide-promoted dehydrofluorination of XVIII.[23] We find that XIX-*d* undergoes exchange with ethanolic sodium ethoxide only ten times faster than dehydrofluorination. The differences between XVIII and XIX are quite striking with regard to the rate ratios for exchange/dehydrofluorination for what appears to be a relatively minor substitution of a phenyl group for a chlorine. Rates of alkoxide-promoted dehydrofluorination at 70 °C are 1.9×10^{-5} M^{-1} s^{-1} for $CHCl_2CF_3$ in methanol and 4.1×10^{-4} M^{-1} s^{-1} for $C_6H_5CHClCF_3$ in ethanol. A correction is necessary to compare the two base/solvent systems,[24] and after this is made, the rates are within a factor of 8 of each other. On the other hand, rates of exchange with bulk solvent for the two deuterated analogues at 20 °C are 1.0×10^{-2} M^{-1} s^{-1} for $CDCl_2CF_3$ in methanol and 4.0×10^{-6} M^{-1} s^{-1} for $C_6H_5CDClCF_3$ in ethanol.[25] After correction is made for different base/solvent systems used for the two studies, the halogenated aliphatic compound exchanges its hydrogen with bulk solvent over 10^4 times faster than does the halogenated phenethyl derivative.

Whenever such large differences in relative rates for two similar reactions are observed, one must question which case is normal for that system and which one is abnormal. Since exchange occurs faster than elimination for both systems, it is reasonable to assume that both reactions proceed via formation of carbanion intermediates. Comparison of two other reactions in this series might be helpful. Dehydrochlorination reactions at 0 °C in methanol have been reported for the corresponding chloro compounds, and the ratio of these rates is about 70 for $CHCl_2CF_2Cl$, 4.5×10^{-2} M^{-1} s^{-1},[26] vs. $C_6H_5CHClCF_2Cl$, 6.6×10^{-4} M^{-1} s^{-1}.[4] Since they observe no exchange with bulk solvent prior to elimination, Hine and Langford speculate that the dehydrochlorination of $CHCl_2CF_2Cl$ proceeds by a concerted E2 mechanism. The fact that this dehydrochlorination reaction proceeds 55 times faster than does the exchange with bulk solvent for $CHCl_2CF_3$ was also considered consistent with their interpretation. We do not observe exchange with bulk solvent prior to elimination, but still interpret our experimental results for the elimination of $C_6H_5CHClCF_2Cl$ as being consistent with a two-step process rather than a concerted mechanism. Our conclusions are largely based on a temperature-independent primary kinetic isotope effect, $k^H/k^D = 2.35$,[4] and almost identical ρ values for this series of reactions.[27] The similarity of behavior between $C_6H_5CHClCF_2Cl$ and $CHCl_2CF_2Cl$

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(19) This term is used by Eaborn et al.[20] when they study the protonation of carbanions generated in isotopically mixed solvents such as MeOH and MeOD.

(20) (a) C. Eaborn, D. R. M. Walton, and G. Seconi, *J. Chem. Soc., Perkin Trans. 2* 1857 (1976); (b) D. Macciantelli, G. Seconi, and C. Eaborn, *ibid.*, 834 (1978); (c) R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Chem. Soc.*, 2342 (1963).

(21) V. Gold and S. Grist, *J. Chem. Soc. B*, 2282 (1971).

(22) (a) J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *J. Am. Chem. Soc.*, **83** 1219 (1961); (b) J. Hine, R. Wiesboeck, and O. B. Ramsay, *ibid.*, **83**, 1222 (1961).

(23) The data reported in ref 22 must be extrapolated to obtain the 10^7 rate differences. Studies on the exchange reaction were carried out at 0 and 20 °C, and kinetics of elimination were run at 55 and 70.5 °C.

(24) We find that both elimination and exchange rates are normally a factor of 10–25 faster when using EtONa in EtOH rather than MeONa in MeOH. See Table VI for actual values used.

(25) Our studies were carried out at six temperatures between 45 and 82.2 °C and extrapolated to 20 °C.

(26) J. Hine and P. B. Langford, *J. Org. Chem.*, 27, 4149 (1962).

(27) Reference 3 cites ρ values: dehydrofluorination of $XC_6H_5CHClCF_3$ (3.7), detritiation of $XC_6H_4CTClCF_3$ (3.9), dehydrochlorination of $XC_6H_4CHClCF_2Cl$ (3.9), and nucleophilic reactions of $XC_6H_4CCl{=}CF_2$ (3.9). All reactions used X = H, *m*-CH, *p*-CH, *m*-Cl, and *p*-Cl, and were carried out in ca. 0.3 N sodium ethoxide in ethanol.

Table V. Isotope Effects on Product Distribution

$$\mathrm{PhC(CF_3){=}CF_2 \xrightarrow[ROL]{RONa} PhCL(CF_3)CF_2OR + PhC(CF_3){=}CFOR}$$

ROL[a]	temp, °C	PhCL(CF$_3$)-CF$_2$OR, %	PIE,[b] k^H/k^D
C_2H_5OH	−78	15	1.50
C_2H_5OD	−78	13	
C_2H_5OH	20	21	1.86
C_2H_5OD	20	15	
CH_3OH	−78	34	1.22
CH_3OD	−78	32	
CH_3OH	20	44	
CH_3OD	20	38	

[a] Solutions made by reaction of sodium with ROL. [b] Product isotope effect (PIE) as defined in ref 20.

Table VI. Comparison of Phenyl vs. Chlorine Substituent on Reactions with Alkoxides in Alcohol

reaction	second-order rate constants, M^{-1} s^{-1}		(k^{Cl}/k^{Ph})[i]
	R = Cl[a]	R = C_6H_5	
$RCCl{=}CF_2$ + CH_3ONa in MeOH at 0°[b]	3.0×10^{-2}	8.1×10^{-3}	3.7
$RCHClCF_2Cl$ + CH_3ONa in MeOH at 0°[c]	4.5×10^{-2}	6.6×10^{-4}	68
$RCHClCF_3$ + CH_3ONa in MeOH at 70°[d]	1.9×10^{-5}	(4.1×10^{-4})[f]	~1
$RCDClCF_3$ + CH_3ONa in MeOH at 20°[e]	1.0×10^{-2}	(4.0×10^{-6})[g,h]	~3 × 10^4

[a] Data from ref 22 and 26. [b] Nucleophilic reaction leading to vinyl substitution and/or addition of methanol across the double bond. [c] Dehydrochlorination. [d] Dehydrofluorination. [e] Exchange. [f] Rates measured using EtONa in EtOH and therefore need correction (÷22) to obtain k^{Cl}/k^{Ph} ratio. [g] Rates measured using EtONa in EtOH and therefore need correction (÷12) to obtain k^{Cl}/k^{Ph} ratio. [h] Rate extrapolated. See ref 25. [i] Ratios have been corrected for solvent differences as noted in footnotes *f* and *g*.

suggests that $CHCl_2CF_2Cl$ might also be proceeding via an Elcb mechanism with elimination faster than exchange.[28]

Although they have different product distributions, the two alkenes react with sodium methoxide in methanol at quite similar rates at 0 °C $CCl_2{=}CF_2$, 3×10^{-2} M^{-1} s^{-1},[22b] and $C_6H_5CCl{=}CF_2$, 8.1×10^{-3} M^{-1} s^{-1}. It appears that the generation of a carbanion intermediate by either proton transfer from carbon to oxygen (alkoxide-promoted elimination of HF and HCl) or by the reaction of alkoxide with the corresponding alkene occurs at comparable rates for the two systems. Therefore, the substitution of chlorine by a phenyl group seems to have the largest effect on the proton-transfer reaction from a bulk solvent molecule to the carbanion intermediate. This could account for the difference in product distribution from the two alkenes and the large difference in rates of exchange with bulk solvent for $CDCl_2CF_3$ and $C_6H_5CDClCF_3$.

A qualitative comparison between reaction of II and an aliphatic analog, $CF_3CF{=}CF_2$, gives results similar to, but not as striking as, those for I vs. XVI. Perfluoropropene reacts faster than II with sodium ethoxide in ethanol at −78 °C to give better than 95% saturated ether, $CF_3CHFCF_2OC_2H_5$; however, evidence for small amounts of vinyl and allyl ethers were observed in gas-phase infrared spectra and GC analysis.[29] Andreades[30] reported rates for methanolic sodium methoxide catalyzed exchange of CF_3CDFCF_3 that are slightly faster than rates we have measured for $C_6H_6CD(CF_3)_2$.[31] Although rates of elimination were not measured for CF_3CHFCF_3, evidence for dehydrofluorination was observed during the exchange studies.[32] The model compound for II, $C_6H_5CH(CF_3)_2$, has an observed rate of exchange only four times faster than the rate of elimination.

Results presented in this paper suggest that the fundamental reaction of carbanion protonation by bulk solvent molecules can vary dramatically depending on the structure of that carbanion. The actual transfer of a proton from oxygen to carbon is thought to be very fast;[14] however, the proton donor and acceptor must be in the proper configuration for this to occur. Protonation of a carbanion that has been generated by reaction of alkoxide with alkene has been shown to be slow relative to other chemical processes such as ejection of chloride or fluoride. We assume that leaving-group ability of fluoride ion from various environments remains constant regardless of the other groups attached to that carbanion. However, the rate of protonation of that carbanion by solvent can vary depending on the other groups and bulk of the alcohol. Therefore, the competition of ejection of fluoride from $-CF_2OCH_3$ with the protonation changes from 100% protonation of $\bar{C}Cl_2CF_2OCH_3$ to 34% protonation of VI–OCH_3. Intermediate values are obtained for $CF_3\bar{C}FCF_2OCH_3$ (~98% protonation) and $C_6H_5\bar{C}ClCF_2OCH_3$ (49% protonation). Ethanol is less favorable in protonation than methanol for VI (15%) vs. VI–OCH_3 (34%) and $C_6H_5\bar{C}ClCF_2OC_2H_5$ (40%) vs. $C_6H_5\bar{C}ClCF_2OCH_3$ (49%).

When the carbanion is formed by a base-catalyzed proton abstraction reaction, an additional step must occur prior to protonation by bulk solvent. The solvent molecule generated by a proton transfer from carbon to oxygen, $\bar{C}\cdots H{-}OR$, must first exchange with bulk solvent, $\bar{C}\cdots D{-}OR$, prior to proton transfer from oxygen to carbon. Very little is known about the energetics of this process, and in the accompanying paper and future papers we will address this problem.

Experimental Section

Materials. Compounds I,[33] II,[34] IV,[34] and V,[34] were synthesized as reported in the literature. The saturated ethers, VII, VII-*d*, VII–OMe, and VII–OMe–*d* were synthesized by a room-temperature reaction of II with the appropriate 0.5–1.0 N solution of sodium alkoxide in the appropriate alcohol. Reaction was allowed to proceed for 1-5 min prior to killing with dilute aqueous HCl and extracting organic products with carbon tetrachloride. The solvent was stripped off and a crude separation was obtained by vacuum distillation. When pure ethers were required, the distilled fractions were purified by preparative gas chromatography using a $^3/_4$-in. 10-ft SE-30 column.[35] Alcoholic alkoxide solutions were made from a reaction of sodium with alcohol. The small chunks of freshly cut sodium were washed with alcohol prior to placing them into the reaction solution. Nuclear magnetic resonance spectra were recorded using a Varian HA-60IL spectrometer.

Kinetics. Kinetics were carried out under pseudo-first-order conditions with ratios of alkoxide:alkene of better than 10:1. Initial kinetic runs used a series of single point kinetic runs;[2] however, we found that using standard sampling techniques gave more consistent results. A 50-mL Erlenmeyer was charged with 30–40 mL of a ~0.3 N alcoholic alkoxide solution, capped with a serum stopper, and allowed to reach temperature in a constant-temperature bath. The reactant, ca. 150 μL, and a suitable standard, 75–100 μL, were mixed and then injected into the reaction Erlenmeyer by means of a 1-cm^3 glass Luer-lok syringe with a 4-in. stainless steel needle. To assure mixing, the syringe was pumped 10–20 times and this was taken as $T = 0$; 5-mL disposable glass syringes fitted with a 4-in. needle were used to take 3–4-mL aliquots which were immediately syringed into ca. 100 mL of dilute aqueous HCl kill solution.

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(28) Although they do not report isotope effects for the exchange of $CHCl_2CF_3$ with methanol, Hine et al. do report a k^H/k^D of 1.3 for the exchange reaction in aqueous medium. This isotope effect was not corrected for a possible kinetic solvent isotope effect, and the low value could arise from extensive amounts of internal return. The exchange rates could be interpreted as consistent with an Elcb mechanism for $CHCl_2CF_2Cl$.

(29) H. F. Koch, unpublished results.

(30) S. Andreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964).

(31) Reference 30 reports a value of 1.25×10^{-3} M^{-1} s^{-1} for CF_3CDFCF_3 rates in MeOH at 20 °C and we obtain 1.04×10^{-3} M^{-1} s^{-1} for $C_6H_5CD(CF_3)_2$. Their results for CF_3CHFCF_3 (4.50×10^{-3} M^{-1} s^{-1}) can compare to our value for $C_6H_5CH(CF_3)_2$ (3.04×10^{-3} M^{-1} s^{-1}) in MeOD.

(32) Andreades in a private communication mentioned that CF_3CDFCF_3 eliminates faster relative to exchange than does $CF_3(CF_2)_6D$, which undergoes exchange 200 times faster than dehydrofluorination.[30]

(33) D. J. Burton, A. L. Anderson, R. Takei, H. F. Koch, and T. L. Shih, *J. Fluorine Chem.*, **16**, 229–235 (1980).

(34) F. E. Herkes and D. J. Burton, *J. Org. Chem.*, **32**, 1311–1318 (1967).

(35) Reference 34, p 1316, gives a description of various gas chromatographic columns useful for the analysis or purification o these compounds.

The kill solution and 0.25 cm^3 of CCl_4 were contained in a 125-mL separatory funnel which had a Teflon stopcock. After vigorous shaking for about 1 min, the solutions were allowed to separate, and the CCl_4 layer was carefully removed and analyzed by gas chromatography.[35] A run usually consisted of eight to nine points plus an infinity sample.

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Proton-Transfer Reactions. 2. Effects of Internal Return on Reactivity Difference between Alkoxide-Promoted Eliminations in *tert*-Butyl Alcohol and Ethyl Alcohol[1a]

H. F. Koch,* W. Tumas,[1b] and R. Knoll[1c]

Contribution from the Department of Chemistry, Ithaca College, Ithaca, New York 14850.

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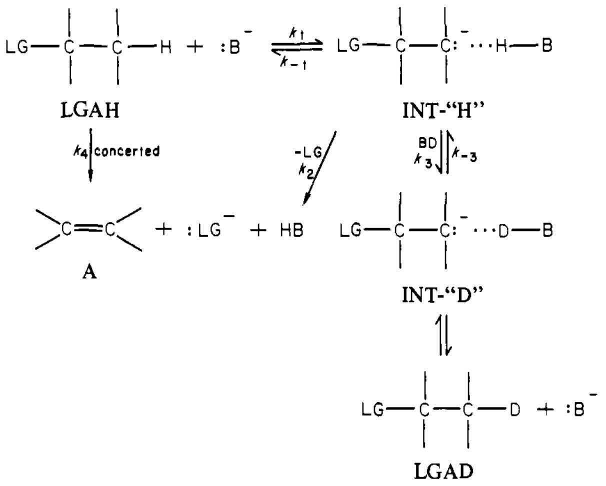
Abstract: Kinetics of alkoxide-promoted dehydrofluorination reactions are reported for the series $C_6H_5CH_2CH_2F$ (I), $C_6H_5CH_2CHF_2$ (II), $C_6H_5CH_2CF_3$ (III), and $C_6H_5CH_2CF_2CF_3$ (V). Rates and activation parameters [($k \times 10^3$ (M^{-1} s^{-1}) (50 °C), $\Delta H^{\ddagger}$ (kcal mol^{-1}), and $\Delta S^{\ddagger}$, (eu)] are respectively: (a) using potassium *tert*-butoxide in *tert*-butyl alcohol, I (1.88×10^{-4}, 19.1, −16.8), II (1.18×10^{-3}, 20.3, −9.3), III (2.15×10^{-3}, 22.1, −2.4), V (3.93×10^{-2}, 16.9, −12.7); and (b) using sodium ethoxide in ethanol, I (1.32×10^{-6}, 25.6, −6.5), II (5.28×10^{-7}, 29.7, 3.0), III (3.45×10^{-7}, 32.6, 12.5), V (5.41×10^{-5}, 27.7, 7.6). The variation in *tert*-butoxide:ethoxide ratios of 140 (I), 2200 (II), 6200 (III), and 730 (V) are discussed in terms of a two-step mechanism with varying amounts of internal return for II, III, and V. Differences in reactivity for groups attached to the benzylic carbon ($-CF_3$, $-CF_2Cl$, $-CHF_2$, $-CF_2CF_3$) and variation of $\Delta S^{\ddagger}$ values for these reactions are also discussed in terms of a two-step mechanism.

We have been interested in studying the fate of carbanions generated as intermediates when alcohols are used as reaction solvents. In the preceding paper[2] we dealt with the partitioning of carbanions formed by a nucleophilic attack of alkoxide ion on *gem*-difluoroalkenes. In this paper, we deal with carbanions generated by an alkoxide-promoted hydrogen abstraction from LGAH, Scheme I. After an intermediate, INT-"H", is formed, it can proceed along alternate pathways: (i) it can collapse to regenerate LGAH and $B^{(-)}$, k_{-1}; (ii) it can exchange BH with bulk solvent, BD, to form INT-"D", k_3; and (iii) it can eject LG to form A, k_2.

Scheme I



When a carbanion is generated by reaction of an alkene with alkoxide in alcohol, several reactions occur at a rate faster than does the protonation of the intermediate by a solvent molecule.[2] Carbanions formed by alkoxide-promoted removal of a hydrogen have an additional step, the actual exchange with bulk solvent in going from INT-"H" to INT-"D" that must occur prior to an observable "protonation" reaction. Internal return, k_{-1}[3] an unobserved no-reaction process, competing with forward reactions, k_2 or k_3, can complicate matters. Although hydrogen-exchange reactions have received a great deal of attention in the literature, little is known about the detailed mechanism or the energetics of the specific step, k_3, in which the new protonated base is replaced by a bulk solvent molecule. In an effort to learn more about the exchange step, we have made use of elimination reactions where a leaving group can act as an internal trap for the carbanion, $k_2 >> k_3$. When elimination reactions are used for this purpose, an additional complication arises, namely, the possibility of a concerted process, k_4, as a lower energy pathway to the alkene. This would completely avoid formation of the desired intermediate.[4] The lack of exchange with bulk solvent is often cited as evidence against carbanion formation along the reaction pathway for an elimination; however, our results from alkene reactions suggest that there are several leaving groups that can be ejected from a carbanion faster than the actual protonation step.

To detect the otherwise unobservable internal return mechanism, Streitwieser et al.[5] have suggested that deviations from the Swain–Schaad equation,[6] $k^H/k^D = (k^D/k^T)^{2.344}$, could be used

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[1] (a) Presented in part at the IUPAC Fourth International Symposium on Physical Organic Chemistry, York, England, Sept 4-8, 1978; (b) supported by NSF-URP Grant SMI76-83152 during the summer of 1979; (c) supported by NSF-URP Grant SMI76-83152 during the summer of 1978.

[2] H. F. Koch, J. G. Koch, D. B. Donovan, A. G. Toczko, and A. J. Kielbania, Jr., preceding paper in this issue.

[3] D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, pp 27-29.

[4] F. G. Bordwell, *Acc. Chem. Res.*, **5**, 374-381 (1972), gives a compact table (p 375) of the mechanistic classification of elimination reactions. He also advises that: "In view of the plethora of symbols required for these mechanistic descriptions it is questionable whether their usage should be encouraged."

[5] A. Streitwieser, J.r, W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmaka, C. J. Chang, and T. C Kruger, *J. Am. Chem. Soc.*, **93**, 5096-5102 (1971).

[6] C. G. Swain, E. C. Stivers, J. F. Reuwer, J.r., and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885-5893 (1958).

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