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]

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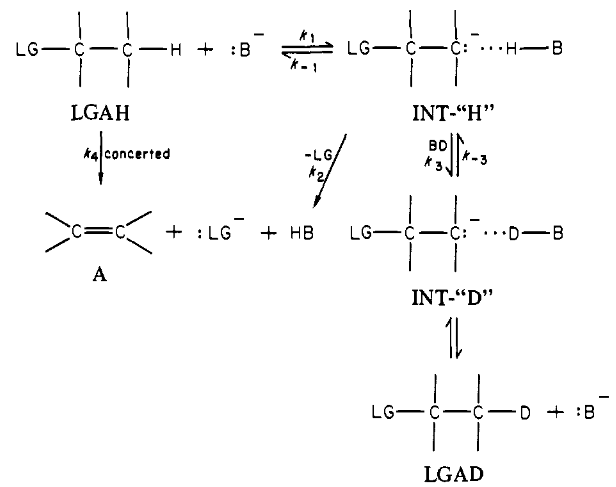
Abstract: Kinetics of alkoxide-promoted dehydrofluorination reactions are reported for the series $C_6H_5CH_2CH_2F$ (I), $C_6H_5CH_2CHF_2$ (II), $C_6H_5CH_2CF_3$ (III), and $C_6H_5CH_2CF_2CF_3$ (V). Rates and activation parameters [($k \times 10^3$ (M^{-1} s^{-1}) (50 °C), $\Delta H^{\ddagger}$ (kcal 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.

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.

Scheme I



To detect the otherwise unobservable internal return mechanism, Streitweiser 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).

0002-7863/81/1503-5423$01.25/0

Table I. Activation Parameters and Rate Constants for Alcoholic Alkoxide-Promoted Dehydrofluorination Reactions

compound	solvent[a]	k (50 °C), $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	temp range, °C
$PhCH_2CH_2F$ (I)	*t*-BuOH	1.88×10^{-4}	19.1 ± 0.1	−16.8 ± 0.2	50–90[b]
	EtOH	1.32×10^{-6}	25.6 ± 0.1	−6.5 ± 0.2	60–80[c]
$PhCH_2CHF_2$ (II)	*t*-BuOH	1.18×10^{-3}	20.3 ± 0.1	−9.3 ± 0.2	50–90[b]
	EtOH	5.28×10^{-7}	29.2 ± 0.3	3.0 ± 0.8	70–120
$PhCH_2CF_3$ (III)	*t*-BuOH	2.15×10^{-3}	22.1 ± 0.1	−2.4 ± 0.4	30–80[b]
	EtOH	3.45×10^{-7}	32.6 ± 0.3	12.5 ± 0.8	80–110
$PhCHClCF_3$ (IV)	EtOH	2.56×10^{-5}	29.3 ± 0.5	11.1 ± 1.5	70–110
$PhCH_2CF_2CF_3$ (V)	*t*-BuOH	3.93×10^{-2}	16.9 ± 0.5	−12.7 ± 1.7	25–50
	EtOH	5.41×10^{-5}	27.7 ± 0.1	7.6 ± 0.3	40–90
$PhCH_2CF_2Cl$ (VI)	EtOH	3.67×10^{-3}	21.0 ± 0.4	−4.9 ± 1.1	25–70
$PhCH(CF_3)CF_2OMe$	EtOH	1.60×10^{-3}	26.2 ± 0.3	9.6 ± 0.9	30–70[d]

[a] Potassium *tert*-butoxide (~0.2 N) was used in *t*-BuOH and sodium ethoxide (~0.3 N) was used in EtOH. [b] Data from ref 10 was included with our own. [c] Reference 13. [d] Reference 2.

as a good experimental probe. By measuring the rates of all three isotopes of hydrogen, one can in principle calculate the amount of internal return for each labeled compound, $a^L = k^L_{-1}/k_p$.[7,8] The Streitwieser treatment is for single-temperature measurements, and we have recently reported an analysis for the temperature dependence of primary kinetic isotope effects when an internal return mechanism is operating.[9] For systems with two equivalent hydrogens, the use of all three isotopes of hydrogen is often not feasible. In this paper we explore some experimental observations that could suggest an elimination reaction is occurring by a two-step mechanism with internal return. One observation is the high rate ratios when using potassium *tert*-butoxide in *tert*-butyl alcohol vs. sodium ethoxide in ethanol, and another the calculation of positive values for ΔS^*.

Discussion and Results

DePuy and Schultz[10] reported results from a study of dehydrofluorination reactions on the series $C_6H_5CH_2CH_2F$ (I), $C_6H_5CH_2CHF_2$ (II), and $C_6H_5CH_2CF_3$ (III). They used potassium *tert*-butoxide in *tert*-butyl alcohol at 50 °C and obtained the following data ($k \times 10^4\ M^{-1}\ s^{-1}$, k^H/k^D, and ρ) respectively for I (1.88, 4.50, and 3.2), II (11.8, 2.77, and 3.6), and III (22.8, --, and 4.0). No exchange occurred with solvent prior to elimination for I and II. Compound III was not subjected to this test. Their data was interpreted as being consistent with an E2 mechanism having a variable transition state with more carbanionic character for reaction of III than for reaction of I. The authors did not rule out the possibility of a two-step mechanism with internal return, but concluded that their data could not distinguish between the two possible mechanisms. The fact that II does not undergo exchange with solvent prior to elimination would not be surprising even if reaction proceeded by the formation of a carbanion since $C_6H_5\bar{C}(CF_2H)CF_2OEt$, generated by reaction of ethoxide with $C_6H_5C(CF_2H){=}CF_2$, preferentially ejects fluoride from the $-CF_2H$ group rather than protonates.[2]

Several things puzzles us about their results. The rate ratio of 12:1 for III:I seemed to be inconsistent with predictions made from results obtained in our laboratory. We reported that $C_6H_5CHClCF_3$ (IV) undergoes ethoxide-promoted dehydrofluorination 17 times faster than does I.[11,12] Therefore, IV should be only slightly more reactive than III; however, we measured a rate ratio of 350:1 for IV:III in ethanol at 100 °C. This latter rate ratio agreed with the rate ratio of 300:1 measured for $C_6H_5CCl{=}CF_2C_6H_5CH{=}CF_2$ undergoing nucleophilic reaction with ethoxide at 25 °C in ethanol.

Table II. Effects of Substituents Relative to Trifluoromethyl

	relative rates for R =				
reaction	CF_3	CF_2Cl	CF_2CF_3	CF_2H	temp, °C
$PhCR{=}CF_2 + EtO^-$ in EtOH[a]	1.0	1.3	0.39	0.035	−50
$PhCH_2R$ + *t*-BuO^- in *t*-BuOH (–HX)	1.0	(900)[b]	18.	0.55	50
$PhCH_2R + EtO^-$ in EtOH (–HX)	1.0	1.1×10^4	160.	1.5	50

[a] Data from ref 2. [b] Reaction too fast at 50 °C and therefore ratio is at 25 °C.

The rate for the *tert*-butoxide-promoted elimination reaction of III in *tert*-butyl alcohol was over 6000 times faster than the rate we had measured using sodium ethoxide in ethanol. From previous work[13] one can calculate dehydrofluorination of I is 140 times faster in *t*-BuOH than in EtOH. DePuy et al.[14] had reported using *t*-BuOK (*t*-BuOH) and EtONa (EtOH) for dehydrobromination of substituted β-phenethyl bromides, and obtained ratios of 3–11 when comparing rates in *t*-BuOH vs. EtOH. It is generally believed that *tert*-butoxide is a stronger base than is ethoxide. Therfore, it is not surprising that reactions occur faster in *t*-BuOH vs. EtOH; however, what concerned us was the large variation of the rate ratios (*t*-BuOK/*t*-BuOH vs. EtONa/EtOH) for these elimination reactions. Since relative rates at a given temperature can be quite misleading when reactions have different temperature dependence characteristics, we decided to study the Arrhenius behavior of this series in both base/solvent systems and our results are tabulated in Table I.

The comparison of relative rates in *t*-BuOH with those obtained in ethanol clears up the discrepancy between our results and the rate ratios based on the DePuy and Schultz data. Relative rates for the series I:II:III in *t*-BuOH are 1:6:11 while they are 1:0.4:0.3 in EtOH. A close inspection of the activation parameters suggests that one should not even be comparing relative rates for this series since observed ΔS^* values are −17 (I), −9 (II), and −2 eu (III) in *t*-BuOH, and −7 (I), 3 (II) and 13 eu (III) in ethanol. Since there is a $\Delta\Delta S^*$ of −15 eu in *t*-BuOH between the slowest reaction (I) and the fastest (III), the faster compound actually has the highest observed ΔH^* (22 kcal mol^{-1}) and the slowest has the lowest ΔH^* (19 kcal mol^{-1}). Compound III does undergo some exchange with bulk solvent (8% deuterium incorporation was observed in recovered starting material after 40% reaction) during the *tert*-butoxide-promoted dehydrofluorination; however, with ethanolic sodium ethoxide the rate of exchange, $7 \times 10^{-5}\ M^{-1}\ s^{-1}$, is actually faster than is the rate of the elimination reaction, $2.81 \times 10^{-5}\ M^{-1}\ s^{-1}$, at 80 °C.

We have also included data for two other systems, $C_6H_5CH_2CF_2CF_3$ (V) and $C_6H_5CH_2CF_2Cl$ (VI), in Table I. These two compounds were included since we had data on the effects of C_2F_5 and CF_2Cl groups, relative to CF_3 and CF_2H, from our studies

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[7] Reference 5 does not include the formula to calculate a^H or a^D. This will appear in D. W. Boerth and A. Stretwieser, Jr., *J. Am. Chem. Soc.*, submitted for publication.

[8] The rate constant k_p refers to the product-forming step. In Scheme I it could represent either k_2 or k_3. Since the concentration of BH, when BD is used as solvent, would be extremely low, k_{-3} would not interfere with the kinetics other than to give a nonzero infinity point.

[9] H. F. Koch and D. B. Dahlberg, *J. Am. Chem. Soc.*, **102**, 6102–6107 (1980).

[10] C. H. DePuy and A. C. Schultz, *J. Org. Chem.*, **39**, 878–881 (1974).

[11] H. F. Koch, D. B. Dahlberg, A. G. Toczko, and R. L. Solsky, *J. Am. Chem. Soc.*, **95**, 2029–2030 (1973).

[12] The rate ratio II:V::1:17 is for 25 °C; this value is 1:20 at 50 °C.

[13] C. H. DePuy and C. A. Bishop, *J. Am. Chem. Soc.*, **82**, 2535–2537 (1960).

[14] C. H. DePuy, D. L. Storm, J. T. Frey, and C. G. Naylor, *J. Org. Chem.*, **35**, 2746–2750 (1970).

of nucleophilic reactions of alkenes. The effects of these groups relative to trifluoromethyl vary considerably depending on the reaction, Table II. Relative rates of this series in the alkene reactions should give an indication of the ability to stabilize a carbanion intermediate, and also for the way each group would affect the "acidity" of an adjacent carbon–hydrogen bond. The largest difference in relative rates arises in a comparison of CF_3 to CF_2Cl where the rate ratio of 1:1.3 for nucleophilic reactions of alkenes increases to 1:1 × 10^4 for dehydrohalogenation in ethanol. The difference between the alkene and alkane reactions suggests that the elimination reactions may not be a simple breaking of the C–H bond coupled with a leaving-group bond breaking.

Effects of $-CF_3$, $-CF_2Cl$, $-CF_2H$, and $-CF_2CF_3$. We feel that these discrepancies may be explained in part by the fact that the elimination reactions are proceeding by a two-step mechanism that has a varying amount of internal return. Since internal return is a competition between a reprotonation step, k_{-1}, and the ejection of halide, k_2, the use of fluoride ion as a leaving group from different environments could give large differences in observed experimental results. Large rate ratios for elimination of HF vs. HCl have been reported previously for ethoxide-promoted elimination of $C_6H_5CHClCF_3$ (IV):$C_6H_5CHClCF_2Cl$ (VII) = 1:1.3 × 10^5,[11] and for methoxide-promoted dehydrohalogenation of $CHCl_2CF_3$:$CHCl_2CF_2Cl$ = 1:~10^8.[15] For comparison, a similar rate ratio for the β-phenethyl halide series is $C_6H_5CH_2CH_2F$ (I):$C_6H_5CH_2CH_2Cl$ (VIII) = 1:70.[13]

When comparing rates of reaction of IV and VII, several factors must be considered. Ethoxide-catalyzed exchange of IV-*d* with ethanol occurs 10 times faster than does the ethoxide-promoted dehydrofluorination reaction.[11] Both reactions of IV occur with experimentally determined isotope effects near unity, k^H/k^D = 1.04 for elimination and 1.07 for exchange at 75 °C. This suggests that $k_{-1} \geq 10^3 \times k_3$ (or k_2). The ethoxide-promoted dehydrochlorination of VII occurs without prior exchange with ethanol and has a k^H/k^D = 3.06 at 25 °C. We concluded that reaction of VII proceeds via a carbanion intermediate.[16] The reason that exchange prior to elimination for VII is not observed could be that $k_2 >> k_3$ even though k_{-1} could be competitive with k_2. We therefore used IV as a model compound to predict the rate of exchange with solvent for VII since the substitution of a β fluorine by chlorine should not alter the rate significantly. The expected rate of exchange for VII is therefore slower by a factor of 10^4 than is the observed rate of dehydrochlorination, and this confirmed our suspicion that $k_2 >> k_3$ in this system.

The roles of IV and VII can be reversed, and the latter can be used as a model compound to study proton-transfer steps for reactions of IV to form $C_6H_5\bar{C}ClCF_3$. By replacing the CF_3 by a CF_2Cl, the chloride could be an internal trap to detect carbanion formation. Therefore, one can conclude that $k_{-1} \geq 10^4 \times k_3$ when reaction occurs with IV and sodium ethoxide in ethanol. This result is in agreement with interpretations resulting from our studies on nucleophilic reactions of fluorinated alkenes.[2]

The presence of an α chlorine and two β fluorines should substantially increase the acidity of the benzylic hydrogen, and the 68 000-fold faster rate of dehydrochlorination of VII relative to VIII could be anticipated for a reaction that is initiated by attack of base on that hydrogen. What is surprising is that ethoxide-promoted dehydrofluorination of IV at 50 °C is only 20 times faster than elimination of HF from I, which in turn has a rate 3.8 times faster than III. The observed primary kinetic isotope effect, k^H/k^D = 1.04, for ethoxide-promoted dehydrofluorination of IV has been interpreted as evidence for extensive internal return from a strongly hydrogen-bonded carbanion intermediate. A trifluoromethyl group thus has two opposing effects for elimination reactions. It increases the acidity of the β hydrogen and stabilizes the corresponding carbanion, but it also decreases the leaving group ability of fluoride ion since the C–F bonds are stronger than those in less highly fluorinated groups.[17] The chlorodifluoromethyl group should have approximately the same effect as a CF_3 on a neighboring carbon,[18] but with a much better leaving group there is only a moderate amount of internal return.

The effects of a difluoromethyl group should not be as large for activating an adjacent C–H bond and in retarding fluoride as a leaving ion. The carbanion intermediate, $C_6H_5\bar{C}(CF_3)CF_2OR$, partitions in ethanol to give 80–85% vinyl ethers and 20–15% saturated ether. This represents a free-energy difference of ca. 0.8 kcal/mol between ejection of fluoride and protonation. Since $C_6H_5\bar{C}(CF_2H)CF_2OEt$ reacts in ethanol to give better than 98% allylic ether, the free–energy difference between ejection of fluoride from CF_2H vs. CF_2OEt would be 2 or 3 kcal/mol. One could thus predict a 3–4-kcal/mol free-energy difference between protonation of the carbanion and ejection of fluoride from CF_2H. In all cases we shall refer to protonation as the transfer of a hydrogen from a bulk solvent molecule to the carbanion intermediate.[19] We demonstrated that the observed product distribution from partitioning of the intermediate $C_6H_5\bar{C}(CF_3)CF_2OR$ is the same whether it is formed by reaction of ethoxide with $C_6H_5C(CF_3){=}CF_2$ in ethanol or by ethanolic ethoxide-catalyzed proton removal from $C_6H_5CH(CF_3)CF_2OMe$; however, internal return, k_{-1}, can be a faster reaction than the ejection of fluoride from $-CF_2OR$, k_2, or exchange with solvent, k_3.[2] In a similar manner, the low value for the isotope effect, k^H/k^D = 2.77, rported by DePuy and Schultz for the *tert*-butoxide-promoted dehydrofluorination of II at 50 °C in *t*-BuOH could come from a two-step mechanism with internal return even though that compound does not exchange with solvent prior to elimination.

The smallest difference in reactivity between groups for the three reactions listed in Table II is between difluoromethyl and pentafluoroethyl. The rate ratio CF_2H:C_2F_5 changes from 1:11 for ethoxide reaction with alkene, to 1:33 for *t*-BuOK-promoted elimination in *t*-BuOH, to 1:107 for the elimination using ethanolic sodium ethoxide. The leaving-group ability of fluoride ion was judged to be better from CF_2H than from C_2F_5 when determined by product studies of the alkene reactions.[2] However, the increase in rate ratios for the dehydrofluorination reactions suggests that the order of the two groups is reversed when internal return is considered. This could be due to different steric effects for the two systems and that the effect is not the same for internal return compared to a protonation from bulk solvent or the ejection of fluoride from a carbanion that is not strongly hydrogen-bonded. Caution must also be taken when attempting to justify rather small differences for reactions that have rather large differences in Arrhenius behavior. The $\Delta\Delta H^{\ddagger}$, $\Delta H^{\ddagger}{}_{II} - \Delta H^{\ddagger}{}_{V}$, is over 3 kcal/mol in *t*-BuOH which would represent a rate difference of 200 (V/II) rather than the observed 33. The compressing of rate difference comes from the fact that II has a slightly more favorable $\Delta S^{\ddagger}$ (−9 eu) compared to V (−13 eu). The $\Delta\Delta H^{\ddagger}$ is less in ethanol (1.5 kcal/mol) and would suggest a smaller difference for the rate ratio, but the observed ratio V/II increases to 107 and this is due to a reversal in the $\Delta S^{\ddagger}$ term which now favors V (7.6) over II (3.0).

Magnitude of Observed Entropy of Activation. We routinely carry out temperature-dependence behavior for kinetic studies, and have noted that larger values of $\Delta S^{\ddagger}$ are obtained for reactions thought to have greater amounts of internal return. For example, in the series $C_6H_5CHBrCF_2Br$ (X), $C_6H_5CHClCF_2Cl$ (VII), and $C_6H_5CHClCF_3$ (IV) methoxide-promoted dehydrobromination of X has $\Delta S^{\ddagger} = -1.5$ eu, while dehydrochlorination of VII results in $\Delta S^{\ddagger} = 2.5$ eu.[16] Observed values of $\Delta S^{\ddagger}$ are 10 and 11 eu for

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(15) (a) J. Hine, R. Wiesboeck, and O. B. Ramsay, *J. Am. Chem. Soc.*, **83**, 1222–1226 (1961); (b) J. Hine and P. B. Langford, *J. Org. Chem.*, **27**, 4149–4151 (1962).

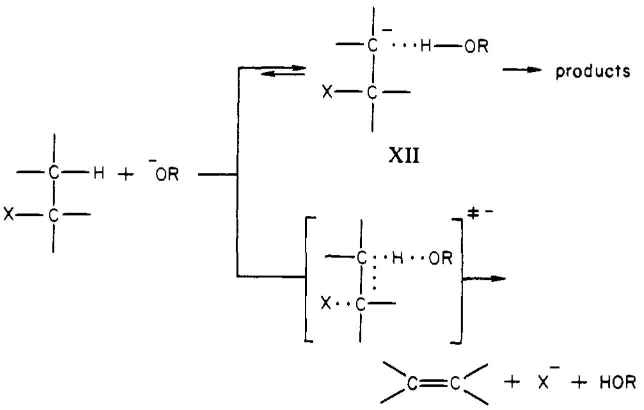
(16) H. F. Koch, D. B. Dahlberg, M. F. McEntee, and C. J. Klecha, *J. Am. Chem. Soc.*, **98**, 1060–1061 (1976).

(17) See D. Holtz, *Progr. Phys. Org. Chem.*, **8**, 1–74 (1971), for a review of the effects of trifluoromethyl groups. A section on bond lengths and strengths is found on pp 16–21.

(18) (a) W. A. Sheppard, *Tetrahedron*, 945–951 (1971); (b) *J. Am. Chem. Soc.*, **87**, 2410–2420 (1965).

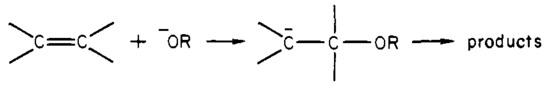
(19) Care must be taken to distinguish between two possible protonation reactions. Protonation that occurs by proton transfer from the unique alcohol molecule, which is formed by proton transfer from carbon to alkoxide, will be referred to as internal return; however, when the hydrogen transferred during a protonation reaction originated from bulk solvent, this will be referred to as the protonation reaction.

Scheme II



ethoxide-catalyzed exchange and dehydrofluorination of IV. The observed isotope effects become progressively smaller in this series, going from 4.0 for X to 2.4 for VII, to 1.07 and 1.04 for exchange and elimination of IV. The decrease in kinetic isotope effects can be attributed to an increasing amount of internal return for this series, X < VII << IV, and this would parallel increasing $\Delta S^\ddagger$ values. It should be noted that any activation parameters obtained from the Arrhenius equation are always observed values which may not be equal to the true parameters, especially for a two-step mechanism with internal return. Equations for observed "free energy" of activation in complex and reversible reactions have been treated by Kreevoy.[20] We have also carried out calculations that suggest good linear Arrhenius plots can be expected, but that the observed $\Delta H^\ddagger$ values may not equal the sum of individual $\Delta H^\ddagger$ for each step.[21] This means that observed $\Delta S^\ddagger$ values are also not a simple sum of the individual $\Delta S^\ddagger$ values since the observed $\Delta S^\ddagger$ must necessarily compensate for any differences between observed and true $\Delta H^\ddagger$.

Schaleger and Long[22] have discussed the study of $\Delta S^\ddagger$ in relation to mechanisms of reactions in solution, but it is difficult to attempt to predict expected $\Delta S^\ddagger$ values for bimolecular reactions in solution. We have data on $\Delta S^\ddagger$ for reactions of alkoxide ion with fluorinated alkenes in methanol and ethanol, and felt this might serve as a useful model reaction. For 14 temperature-dependence studies, $\Delta S^\ddagger$ values of −20 ± 3 eu were obtained with 11 of these values falling between −18 and −22 eu. The rate-limiting step for these reactions is believed to be the making of a carbon–oxygen bond with a breaking of the π bond to generate a carbanion intermediate:[2]

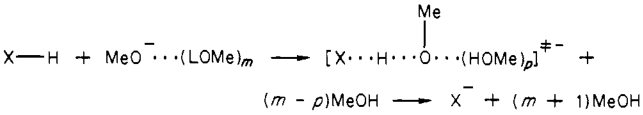


XI

The reaction is irreversible with product-forming steps not contributing to the observed rate or Arrhenius parameters. This is to be compared with two possible elimination mechanisms (Scheme II). Although XI and XII are formally depicted as carbanion intermediates, they are probably not the same since XI does not appear to have a unique strongly hydrogen-bonded alcohol molecule as does XII.[2] However, the two species are thought to have similar solvent shells surrounding them and therefore could have similar interactions with bulk solvent. Likewise, the transition state for the concerted pathway could have the same type of interaction with bulk solvent. All three processes could be considered to result from an interaction of a neutral species with an alkoxide ion leading to a transition state with charge delocalized from oxygen throughout the new network.

Desolvation of the attacking alkoxide ion may also contribute to the overall energetics of the reaction. One method to probe this effect is the study of kinetic solvent isotope effects (KSIE), $k^{\mathrm{ROD}}/k^{\mathrm{ROH}}$, for the various reactions. Effects of 2.2 to 2.4 were obtained for reaction of alkoxide with $C_6H_5CCl{=}CF_2$, and values of 2.3 to 2.8 were found for elimination and exchange reactions of our highly halogenated systems.[23,24] A KSIE of 1.9 was obtained[23] for methoxide-promoted dehydroiodination of $C_6H_5CL(CH_3)CH_2I$, a compound which is thought to react by an E2 mechanism.[25,26]

Gold and Grist[27] have analyzed possible origins for the KSIE in methanol and conclude that effects are due to a multiply solvated methoxide ion. The deuterium fractionation factor, $\phi_{\mathrm{OMe}} = 0.74$, implies that the equilibrium abundance of deuterium in the m hydrogen atoms of the solvated methoxide ion, $\mathrm{MeO^-\cdots(HOMe)}_m$, is 0.74 times that of bulk solvent. Calculation of the maximum KSIE in isotopically pure solvents can be done by using eq 1, and assuming that the molecules of solvation in the transition state will have a fractionation factor approximately equal to that of bulk solvent, $\phi^\ddagger = 1.0$. For $m = 3$ this gives a maximum value



$$\mathrm{X{-}H + MeO^-\cdots(LOMe)}_m \longrightarrow [\mathrm{X\cdots H\cdots \overset{Me}{O}\cdots(HOMe)}_p]^{\ddagger -} + (m-p)\mathrm{MeOH} \longrightarrow \mathrm{X^-} + (m+1)\mathrm{MeOH}$$

$$k^{\mathrm{OD}}/k^{\mathrm{OH}} = (\phi^\ddagger)^p/\phi_{\mathrm{OMe}}{}^m \qquad (1)$$

of the KSIE of 2.5. If the error in the fractionation factor for methoxide ion is 5%, then the maximum KSIE could be from 2.1 to 2.9. If $\phi^\ddagger$ is less than unity, the magnitude of KSIE would drop and now become dependent on the value of p. The transition state for an E2 elimination could still retain two solvent molecules bound to the methoxide ion, $p = 2$. A $\phi^\ddagger$ value between 0.85 and 0.90 could thus account for the observed $k^{\mathrm{OD}}/k^{\mathrm{OH}} = 1.9$ for reaction of $C_6H_5CL(CH_3)CH_2I$. Alternatively, the transition state could retain a single methanol of solvation, $p = 1$, which still has a $\phi_{\mathrm{OMe}} = 0.74$. The latter explanation seems less likely since an E2 transition state should have charge delocalized throughout the system. The fact that the KSIE for reaction of alkoxide with $C_6H_5CCl{=}CF_2$ and elimination and exchange reactions of our highly halogenated systems are close to the maximum effect predicted by theory suggests that any contribution to the observed activation parameters that can be attributed to a desolvation of alkoxide should be approximately the same for these reactions.

An average $\Delta S^\ddagger$ of −8.2 ± 1.7 eu can be calculated from 16 temperature-dependence studies on alkoxide-promoted dehydrohalogenation reactions of $C_6H_5CL(CH_3)CH_2Br$,[28] $C_6H_5CL_2CH_2Br$,[29] $C_6H_5CL_2CH_2Cl$,[30a] $C_6H_5CL_2CL(CH_3)Cl$,[30b] and $C_6H_5CL(CH_3)CH_2I$.[30c] Since these reactions are thought to proceed by a concerted mechanism,[25] this value of $\Delta S^\ddagger$ could be a model for an elimination reaction that can have no internal return. Reference 16 contains $\Delta S^\ddagger$ values from 16 temperature-dependence studies, which have an average value of −1.1 ± 2.5 eu, for dehydrohalogenations thought to proceed by a two-step mechanism with internal return. We have also completed 18 temperature-dependence studies on alkoxide-catalyzed exchange and dehy-

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(20) M. M. Kreevoy in "Technique of Organic Chemistry", Vol. 8, Part II, 2nd ed., A. Weissberger, Ed., Wiley-Interscience, New York, 1963, pp 1371–1374.

(21) D. B. Dahlberg, unpublished results.

(22) L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, **1**, 1–33 (1963).

(23) Values for KSIE for alkoxide reaction with $C_6H_5CCl{=}CF_2$ at 0 °C are 2.28 for methanol and 2.44 for ethanol.[24a] For methoxide-promoted dehydrohalogenations in methanol the following were observed: $C_6H_5CLClCF_2Cl$, 25 °C, 2.83 (H), 3.02 (D), and 2.77 (T);[24b] $C_6H_5CLBrCF_2Br$, 0 °C, 3.06 (H) and 3.17 (D);[24b] $C_6H_5CL(CH_3)CH_2I$, 50 °C, 1.83 (H), 1.86 (D), and 1.86 (T).[24c]

(24) (a) S. B. Kelemen, unpublished results; (b) M. F. McEntee, unpublished results; (c) W. Tumas, unpublished results.

(25) Reference 4, p 377.

(26) H. F. Koch, J. G. Koch, W. Tumas, D. J. McLennan, B. Dobson, and G. Lodder, *J. Am. Chem. Soc.*, **102**, 7955–7956 (1980).

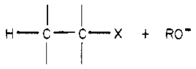
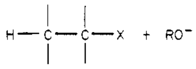
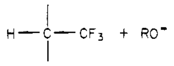
(27) V. Gold and S. Grist, *J. Chem. Soc. B*, 2282–2285 (1971).

(28) (a) V. J. Shiner, Jr., and M. C. Smith, *J. Am. Chem. Soc.*, **83**, 593–598 (1961); (b) V. J. Shiner, Jr., and B. Martin, *Pure Appl. Chem.*, **8**, 371–378 (1964).

(29) W. H. Saunders and D. H .Edison, *J. Am. Chem. Soc.*, **82**, 138–142 (1960).

(30) (a) S. K. Sweinberg, unpublished results; (b) H. F. Koch, unpublished results; (c) N. H. Koch, W. Tumas, unpublished results.

Table III. Observed Values of $\Delta S^{\ddagger}$ for Reactions with Alcoholic Alkoxides

reactants[a]	type of reaction	$\Delta S^{\ddagger}$,[b] eu	k^H/k^D	KSIE k^{OD}/k^{OH}
alkene + RO⁻	addition and substitution	−20 ± 3		2.2–2.4
 $\mathrm{H{-}C{-}C{-}X + RO^-}$	E2 elimination	−8.2 ± 1.7	>6	1.9
 $\mathrm{H{-}C{-}C{-}X + RO^-}$	E1cb elimination	−1.1 ± 2.5	2–4	2.3–2.8
 $\mathrm{H{-}C{-}CF_3 + RO^-}$	E1cb elimination and exchange	12 ± 3	1.04–1.21	2.3–2.8

[a] RO⁻ is either CH_3O^- or $C_2H_5O^-$. [b] The number of systems studied and references are found in text.

drofluorination reactions of $C_6H_5CLClCF_3$ and $C_6H_5CL(CF_3)_2$, and an average $\Delta S^{\ddagger}$ value of 11.6 ± 2.9 was obtained. Primary kinetic isotope effects for this latter series were found to be between 1.04 and 1.21 for k^H/k^D at 25 °C, and we feel this is consistent with a reaction that has extensive amounts of internal return.

Comparing the ΔS^* values reported in Table I to those in Table III, ethoxide-promoted elimination of $C_6H_5CH_2CH_2F$ (−6.5 eu) falls in the same category as the other β-phenethyl halides. Therefore dehydrofluorination of this compound could proceed by a concerted pathway. At the other extreme, $C_6H_5CH_2CF_3$ (12.5 eu) fits rather well with the other trifluoromethyl compounds to which we have attributed extensive amounts of internal return. The other compounds, $C_6H_5CH_2CHF_2$ (3.0 eu), $C_6H_5CH_2C_2F_5$ (7.6 eu), and $C_6H_5CH(CF_3)CF_2OCH_3$ (9.6 eu), could have varying amounts of internal return; however, there are clearly not enough substrates with different structural features to attempt to equate the magnitude of ΔS^* with the amount of internal return. We have not studied the nucleophilic reactions of alkenes with potassium *tert*-butoxide in *tert*-butyl alcohol and therefore do not have a ΔS^* value for that solvent system. The spread in ΔS^* values observed in *t*-BuOH listed in Table I is similar to that for ethoxide-promoted reactions.

***t*-BuOK/*t*-BuOH: EtONa/EtOH Rate Ratios.** Because of the properties of liquid *t*-BuOH, it is often difficult to obtain good kinetic data over a range sufficient to calculate $\Delta S^{\ddagger}$ values for *tert*-butoxide-promoted elimination reactions. However, several systems have been studied using both potassium *tert*-butoxide in *tert*-butyl alcohol (*t*-BK) and sodium ethoxide in ethanol (ENa). Results from eliminations that are carried out with *t*-BK have more negative $\Delta S^{\ddagger}$ values than those using ENa. For example, the following values of $\Delta S^{\ddagger}$ have been obtained for the two base–solvent systems (*t*-BK; ENa, eu): $C_6H_5CH_2CH_2Br$ (−25; −7),[14] $C_6H_5CH_2CH(CH_3)Br$ (−23; −9),[14] $C_6H_5CH_2CH(CH_3)Cl$ (−19; −10),[30b] $C_6H_5CH_2N(CH_3)Cl$ (−21; −12),[31] and $C_6H_5CH(CH_3)CH_2I$ (−19; −10).[24c] The average value for *t*-BK reactions, −21 ± 3 eu, is 10 eu more negative than the average value for ENa reactions, 10 ± 2 eu.

The rate ratios (*t*-BK/ENa) for these five systems are between 2 and 11, and appear to come from the enthalpy term favoring *t*-BK more than the entropy term favors ENa. The reactions cited are examples of dehydrohalogenations thought to proceed by the E2 mechanism, and one could consider the reported ΔS^* values and *t*-BK/ENa ratios as "normal" for this reaction type. Ethoxide ion is thought to be more highly solvated by ethanol than is *tert*-butoxide ion by *t*-BuOH. If the transition state for these elimination reactions has loosened the alcohols of solvation from the alkoxide ion, then the more favorable entropy term for ENa reactions could be due to this phenomenon. However, weakening the solvent bonds would cost energy and thus the enthalpy term favors *t*-BK reactions. Listed in Table IV are *t*-BK/ENa rate ratios for the series of compounds we have been studying.

In our series, the largest *t*-BK/ENa, 6200, is for $C_6H_5CH_2CF_3$ (III), and the lowest, 140, is for $C_6H_5CH_2CH_2F$ (I). Experimental $\Delta S^{\ddagger}$ values for I are consistent with those for compounds thought to proceed by the concerted mechanism, and the values obtained for III suggest extensive amounts of internal return prior to fluoride ion ejection. If the varying *t*-BK/ENa ratios result from the enhancement of fluoride as a leaving group, then one might predict that ethanol would be of greater assistance than *t*-BuOH. The smaller alcohol molecule should have much less steric interaction when placing alcohols of solvation around the developing fluoride ion. Ethanol has a larger dielectric constant, 24.3, than *t*-BuOH, 10.9, and this should make it a better solvent for fluoride ion. Differences in rates between ENa and methanolic sodium methoxide (MNa) are smaller, but the rate ratios follow the same trend noted for *t*-BK/ENa. Therefore, calculated ENa/MNa values are smaller for $C_6H_5CH(CH_3)CH_2I$ (3.8)[30c] than for $C_6H_5CH(CF_3)_2$ (22).[32] Solvation properties and a dielectric constant of 32.6 should favor methanol over ethanol if solvation and stabilization of fluoride ion were of great importance in the rate-limiting step.

Table IV. Rate Ratios and Differences in Activation Parameters for *t*-BuOK/*t*-BuOH: EtONa/EtOH Promoted Dehydrohalogenations of $C_6H_5CH_2R$ (50 °C)

R	elim reaction	*t*-BuOK/*t*-BuOH / EtONa/EtOH	$\Delta\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta\Delta S^{\ddagger}$,[a] eu
$-CF_3$	HF	6,200	11	15
$-CHF_2$	HF	2,200	9	12
$-CF_2CF_3$	HF	730	11	20
$-CF_2Cl$	HCl	400[b]	–	–
$-CH_2F$	HF	140	7	10
$-N(CH_3)Cl$[c]	HCl	35[d]	5[d]	9[d]
$-CH(CH_3)Cl$[e]	HCl	9	4	9
$-CH(CH_3)Br$[f]	HBr	5	6	17
$-CH_2Br$[g]	HBr	11	7	18

[a] Defined for EtOH–*t*-BuOH values. [b] $PhCH_2CF_2Cl$ was too reactive with *t*-BuOK so we could only obtain a value at 25 °C. [c] Data from ref 31. [d] This is reported for MeONa/MeOH vs. *t*-BuOK/*t*-BuOH. [e] Data from ref 30a. [f] Data from ref 14. [g] Data from ref 13.

The relative rates of ethoxide-promoted dehydrofluorination of III increase slightly when the gegenion is changed from Li^+ (1) to Na^+ (5) to K^+ (10). These differences are normally considered to arise from a greater amount of ion pairing for the smaller lithium ion relative to the larger potassium ion. If the gegenion played a major role in helping fluoride ion as a leaving group, then one might expect the reverse order of $Li^+ > Na^+ > K^+$ since the smaller cation would form a stronger attraction for the small fluoride ion. We have observed similar behavior for alkoxide reactions with alkenes. When varying the gegenion, the relative rates for nucleophilic reactions of alkoxides with alkenes are similar to those obtained for the dehydrofluorinations, but the product ratios of unsaturated to saturated ethers remain constant and therefore appear to be independent of the gegenion.[32] Our conclusion is that the ejection of fluoride ion receives little help from either the gegenion in solution or from the solvent. If there

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(31) R. A. Bartsch, B. R. Cho, *J. Am. Chem. Soc.*, **101**, 3587–3591 (1979)

(32) A. G. Toczko, unpublished results.

is a solvation effect, it appears to be lost in the compensating effect believed to arise from internal return.

Our working model to explain the large *t*-BK/ENa rate ratios is that there is a greater amount of internal return from an ethanol molecule than there is from *t*-BuOH. If the results obtained from the compounds believed to proceed by an E2 pathway can be used as a model for the initial proton-transfer step from carbon to oxygen, then we would predict that reactions in *t*-BK favor carbanion formation slightly over reactions in ENa. Since the *t*-BuOH molecule formed by this proton-transfer step is bulkier than the corresponding ethanol molecule, it could be farther away from the negative carbon and thus be in a less favorable position to return the proton back to carbon. Protonation reactions are apparently better in ethanol than in *t*-BuOH[19] since the rate of exchange for III with bulk solvent is three times faster than is the dehydrofluorination reaction with ENa while the reverse is true in *t*-BK. After 40% elimination of III in *t*-BuOH-*O-d*, the recovered III had only 8% deuterium incorporation and this gives a 8:1 rate ratio for elimination:exchange.

The compounds listed in Table III that have *t*-BK/ENa rate ratios of 400 or larger are systems we feel proceed by a two-step mechanism with varying amounts of internal return. The compounds with ratios under 20 are thought to proceed by a concerted pathway. The odd compound is I which has a *t*-BK/ENa of 140, yet from other experimental data is though to belong to the E2 group. Schlosser and co-workers[33-35] have observed *t*-BK/ENa rate ratios for 20 dehydrochlorination or dehydrobromination reactions of aliphatic or substituted β-phenethyl halides thought to proceed by an E2 mechanism. Their values range from 0.3 to 50, and this means that the range could be extended to cover I.

Modena et al.[36] have observed large *t*-BK/MNa rate ratios for alkoxide-promoted eliminations of *Z*-ArCH=CHX, where X = Cl or Br, and report values of 3000 to 30000. If the ENa/MNa rate ratios for their compounds are between 10 to 20, then the *t*-BK/ENa rate ratios could be from 300 to 3000 and fall within the range of results for reactions thought to proceed with internal return. They report primary kinetic isotope effects of 1.6 to 4.6, which are higher in *t*-BK than in MNa for any given compound, and variable Element effects, k^{Br}/k^{Cl}, which range from 35 to 313. These experimental results and the lack of hydrogen–deuterium exchange prior to elimination were interpreted as being consistent with an E2 mechanism having a variable transition state with a great deal of carbanionic character. Their results could also be consistent with a two-step pathway featuring different amounts of internal return, but further experimental work is required to differentiate between alternate explanations.

For a similar system, *Z*-$C_6H_5CH{=}CFBr$, we find a *t*-BK/ENa rate ratio of 600 for alkoxide-promoted dehydrobromination, and k^H/k^D values below 1.5 at 50 °C in both base–solvent systems.[37] Dehydrochlorination of (*Z*)-$C_6H_5CH{=}CFCl$ using *t*-BK gives a $k^{Br}/k^{Cl} = 130$ at 30 °C, and a $k^H/k^D = 1.1$ at 50 °C. Unfortunately, there is a competitive nucleophilic attack when (*Z*)-$C_6H_5CH{=}CFCl$ reacts with ENa; however, a crude *t*-BK/ENa of over 600 can be estimated from the rate data. We are continuing studies on these systems and will report results at a later date.

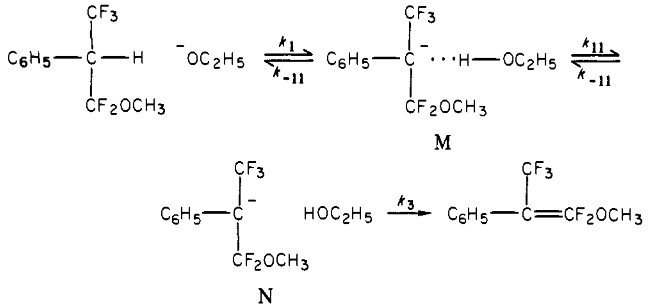
Conclusions

Internal return, k_{-1}, can have a profound effect on observed reaction rates. For example, $C_6H_5CLClCF_3$ (IV) exhibits measured kinetic isotope effects near unity for both elimination and exchange reactions in ethanol. This suggests that carbanion formation occurs in a preequilibrium step for both processes and that the overall kinetics are dominated by $k_{-1} > 10^3$ times k_2 or k_3 for the kinetic expression of a two-step mechanism with internal return: $k_{obsd} = k_1k_2/(k_{-1} + k_2)$ or $k_1k_3/(k_{-1} + k_3)$. Therefore, if one wishes to predict carbanion formation by using the observed rate constants for exchange reactions, the prediction could be off by a rate factor greater than 10^3 and a free energy of >4 kcal mol^{-1}. Although necessary documentation is still incomplete, $C_6H_5CH_2CF_3$ (III) appears to behave in a similar experimental manner as does IV. The fact that elimination rates are greatly enhanced when using *t*-BK instead of ENa therefore suggests that there is less internal return occurring in *t*-BuOH than in ethanol. Likewise there appears to be less internal return in ethanol than in methanol.

The effect of an internal-return mechanism on the observed $\Delta S^{\ddagger}$ values is more difficult to interpret, but a comparison can be made with *t*-BK/ENa. For the series $C_6H_5CH_2CH_nF_{3-n}$, there is an increase in $\Delta S^{\ddagger}$ values when *n* goes from 2 to 0. This seems to parallel *t*-BK/ENa ratios which are highest for *n* = 0 and lowest for *n* = 2. Close analysis of the activaton parameters shows that $\Delta H^{\ddagger}$ favors reactions in *t*-BK while $\Delta S^{\ddagger}$ favors reactions in ENa.

An experimental method commonly used to detect the existence of a carbanion intermediate along the reaction pathway is to trap it by a reaction with ROD; however, we have demonstrated that both chloride and fluoride can be ejected from such an intermediate faster than a proton can be transfered from a solvent molecule to neutralize the carbanion.[2] An alternative experimental method to distinguish a concerted elimination from a stepwise process might be the measurement of *t*-BK/ENa for the elimination. Values of *t*-BK/ENa less than 100 appear to be consistent with an E2 mechanism, while values over 200 suggest that an E1cb mechanism may be occurring.

In the preceding paper,[2] we proposed that the ethoxide-promoted dehydrofluorination of $C_6H_5CH(CF_3)F_2OCH_3$ proceeded by a reaction pathway that included two types of carbanion intermediates (eq 2). Carbanion M is stabilized by a strong hydrogen bond to the alcohol molecule formed by a proton transfer reaction from carbon to oxygen, while carbanion N is stabilized by a solvent shell of alcohol molecules. We have assumed as a working model that better leaving groups such as chloride and bromide can readily be ejected from M, while a fluoride leaving from CF_3 or CF_2OR can be efficiently ejected only from a "naked" carbanion, N. An explanation for the large *t*-BK:ENa values could be that it is easier to form N with *t*-BK since *t*-BuOH will not form a hydrogen bond as readily as EtOH.



Many questions still remain unanswered regarding both elimination and exchange reactions, and we are continuing studies in an attempt to find answers.

Experimental Section

Materials. Compounds II, III, V, and VI were synthesized using a procedure similar to that reported by DePuy and Schultz.[10] All melting points and boiling points are uncorrected. Proton NMR spectra were recorded using a Varian T-60 spectrometer and ^{19}F NMR were run using a Varian HA-60IL.

Preparation of Fluorinated Acetophenones and Propiophenone. The ketones were prepared via the reaction of phenylmagnesium bromide (Aldrich) with the appropriate carboxylic acids (Aldrich and Pierce) in ether using the modification of Bergmann et al.[38] on the procedure for

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(33) Ph.D. Theses of G. Jan (University of Lausanne, 1974), E. Byrne (University of Lausanne, 1974), and C. Tarchini (Ecole Polytechnique Federale Lausanne, 1978).

(34) A private communication from Professor Schlosser, which expands on previously reported work,[35] reports that they have measured a *t*-BK/ENa of 3600 for (*E*)-$C_6H_5CH{=}CHCl$. They believe that this system proceeds via an internal-return mechanism.

(35) M. Schlosser and V. Ladenberger, *Chem. Ber.*, **104**, 2873–2884 (1971).

(36) G. Marchese, F. Naso, N. Tangari, and G. Modena, *J. Chem. Soc. B*, 1196–1198 (1970).

(37) K. B. Gundlach, unpublished results.

Dishart and Levine.[39] **α,α-Difluoroacetophenone**: bp 61–62 °C (8 mm); 50% yield. **α,α,α-Trifluoroacetophenone**: bp 43–44 °C (14 mm); 60% yield. **α,α-Difluoro-α-chloroacetophenone**: bp 57–59 °C (6 mm); 72% yield. **$\alpha,\alpha,\beta,\beta,\beta$-Pentafluoropropiophenone**: bp 58–59 °C (18 mm); 60% yield.

Preparation of Fluorinated Phenylethanols and Corresponding Tosylates. The ketones were reduced with sodium borohydride (Aldrich) in 90% aqueous dioxane as described by Depuy and Schultz.[10] The tosylates were prepared by reacting the alcohols with *p*-toluenesulfonyl chloride (Aldrich, recrystallized from petroleum ether–chloroform) in pyridine (Fisher, distilled). Reaction times were rather long (up to a week). **2,2-Difluoro-1-phenylethanol**: bp 97–99 °C (9 mm); 67% yield. **Tosylate**: mp 86–87 °C; 82% yield. **2,2,2-Trifluoro-1-phenylethanol**: bp 66–67 °C (5 mm); 86% yield. **Tosylate**: mp 114–115 °C; 85% yield. **2,2,3,3,3-Pentafluoro-1-phenyl-1-propanol**: bp 65–67 °C (3 mm); 73% yield. **Tosylate**: mp 58–58.5 °C; 67% yield. **2,2-Difluoro-2-chloro-1-**phenylethanol: bp 71–72 °C (3 mm); 80% yield. **Tosylate**: mp 111–112 °C; 80% yield.

Preparation of Phenylethanes. The desired fluorinated phenylethanes were obtained by hydrogenolysis of the tosylates using palladium on carbon (Alfa Products) in ethyl acetate (Fisher) under an atmosphere of hydrogen in an apparatus similar to that described by Depuy and Schultz.[10] **2,2-Difluoro-1-phenylethane (II)**: bp 58–59 °C (18 mm); 65% yield; NMR (CCl_4) δ 7.2 (s, 5 H), 5.8 (tt, 1 H, J_{HH} = 5.0 Hz, J_{HF} = 58.0 Hz), 3.1 (tt, 2 H, J_{HH} = 5.0 Hz, J_{HF} = 17 Hz). **2,2,2-Trifluoro-1-phenylethanol (III)**: bp 59–61 °C (49 mm); 63% yield; NMR (CCl_4) δ 7.3 (s, 5 H), 3.4 (q, 2 H, J_{HF} = 10.0 Hz). **2,2,3,3,3-Pentafluoro-1-phenylpropane (V)**: bp 47–49 °C (20 mm); 73% yield; NMR (CCl_4) δ 7.3 (s, 5 H), 3.3 (t, 2 H, J_{HF} = 18 Hz). **2,2-Difluoro-2-chloro-1-phenylethane (VI)**: bp 40–41 °C (10 mm); 85% yield; NMR (CCl_4) δ 7.2 (s, 5 H), 3.4 (t, 2 H, J_{HF} = 13.8 Hz).

Preparation of 2-Fluoro-1-phenylethane. 2-Fluoro-1-phenylethane (I) was prepared by the reaction of cesium fluoride (Alfa) in dimethylformamide with β-phenethyl tosylate (mp 39–40 °C) which was prepared in the usual manner from β-phenethyl alcohol (Aldrich). To a dry 100-mL three-neck creased round-bottom flask equipped with a Trubore stirrer, condenser, and stopper were charged 10 g of β-phenethyl tosylate (0.036 mol), 8.2 g of cesium fluoride (0.054 mol), and 40 mL of dimethylformamide (Aldrich, distilled and dried over molecular sieves). This was heated to 100 °C with a sand bath and stirred at that temperature for ca. 8 h, after which NMR analysis of an aliquot revealed that reaction was complete. The reaction mixture was worked up by pouring the contents of the flask into 300 mL of ice water (a dark oil separated). Extraction with pentane (5 × 75 mL) gave an organic layer which was washed with water (2 × 150 mL) and dried over magnesium sulfate. After removal of solvent by distillation through a 20-cm Vigreux column, the residue was vacuum distilled yielding 2.4 g (54%) of 99% pure β-phenethyl fluoride (bp 50–51 °C (8 mm)): NMR δ 7.2 (s, 5 H), 4.4 (dt, 2 H, J_{HH} = 6.0 Hz, J_{HF} = 48 Hz), 2.8 (dt, 2 H, J_{HH} = 6.0 Hz, J_{HF} = 24 Hz). Approximately 20% styrene was also formed, presumably by fluoride ion acting as a base in elimination of the tosylate. The distillation sufficed in separating this from the desired product.

Kinetics. Ethanolic ethoxide solutions were prepared by dissolving cleaned sodium metal in ethanol as previously described.[2]

Potassium *tert*-butoxide solutions were prepared by two methods. First, potassium metal which had been washed in *t*-BuOH was dissolved in *t*-BuOH (Aldrich) which had been distilled from potassium under a nitrogen atmosphere. The second procedure involved purifying the potassium metal by the procedure of Pearson and Keaton[40] in *tert*-amyl alcohol prior to dissolving it in *t*-BuOH which had been distilled twice from potassium metal (81 °C). The resulting solution was maintained under an inert atmosphere. These solutions were stable for several weeks after which they would become yellow in color. The kinetics run in *t*-BuOK/*t*-BuOH were identical for both methods of preparation.

The kinetic procedure has been described in the preceding paper.[2] The isotopic exchange studies were performed in EtOH-*O-d* (Aldrich Gold Label) and *t*-BuOH-*O-d* (Aldrich). A sufficient amount of either sodium or potassium was dissolved in their respective deuterated alcohols for preparation of the desired alkoxide solutions. Substrate (200 μL) was added via syringe to a 25-mL Erlenmeyer containing 20 mL of alkoxide/alcohol which was equilibrated to the desired temperature. The reaction was permitted to proceed to approximately 1 half-life and then quenched by charging the contents into a 125-mL separatory funnel containing 75 mL of 1 N HCl and CCl_4. The extent of elimination was determined by GLC. The starting material was recovered via preparatory GLC and the extent of deuterium incorporation was determined by mass spectrometry. A rate constant for exchange of III in ethanol-*O-d* was measured by sampling five points through 2 half-lives of elimination and analyzing the samples of starting material, which were isolated by preparative GLC, for deuterium content.

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Extended Unsaturated Carbenes. Novel Silicon-, Germanium-, and Tin-Functionalized Cumulenes, $R_2C{=}C{=}C{=}CHMR'_3$, via Insertion of Alkadienylidenecarbenes into Group 4 Hydrides[1]

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Abstract: Interaction of alkadienylidenecarbenes, $R_2C{=}C{=}C{=}C{:}$, with group 4 hydrides results in the formation of novel Si, Ge, and Sn functionalized tetratrienes $R_2C{=}C{=}C{=}CHMR^1_3$. The reaction is general for alkyl- and aryl-substituted carbenes with isolated yields of 26–88%. The parent systems are too unstable to isolate, although IR evidence clearly indicates their formation. All cumulenes show a molecular ion with proper isotope distribution in the mass spectra, an intense IR absorption between 2015 and 2055 cm^{-1}, and a highly characteristic ^{13}C NMR with the two central sp-hybridized cumulenic carbons between 158 and 173 ppm and the two sp^2 olefinic carbons between 98 and 140 ppm. All new cumulenes are stable, isolable, but moderately oxygen-sensitive compounds that rearrange or polymerize upon prolonged standing at room temperature. No [4]radialene dimers were observed upon reaction with $CuOSO_2CF_3$, nor was isomerization to the terminally substituted enynes observed upon reaction with *t*-BuOK. Deuterium incorporation occurs in the presence of *t*-BuOD/*t*-BuOK. These results are discussed in detail.

Cumulenes are of considerable theoretical, structural, and synthetic interest.[2] The simplest cumulenes are allenes, first reported in 1888.[3] Although a large amount of research has been done on allene chemistry,[4] considerably less is known about the