Study of Olefin Proportions from E2 Reactions of Secondary Alkyl Bromides. Mechanistic Implications

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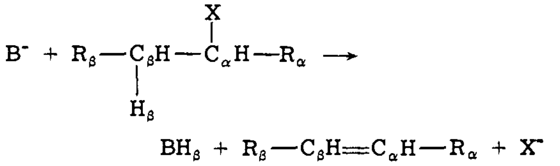
Abstract: The olfein proportions from E2 reactions of 2-butyl, 2-pentyl, 3-pentyl, 4-methyl-2-pentyl, and 2-methyl-3-pentyl bromides with Bu_4NBr in acetone, Et_4NF in acetone and DMF, *t*-BuOK in DMF and *tert*-butyl alcohol, and EtOK in ethanol have been determined. When the base in not ion associated with its counterion, the kinetic trans:cis ratios exceed their corresponding thermodynamic ratios. The trans:cis ratio of 4-methyl-2-pentene is higher when the reactant is 2-methyl-3-pentyl bromide than when the reactant is 4-methyl-2-pentyl bromide. In aprotic solvents, an increase in the strength of the base causes an increase in trans:cis ratios as well as in the relative proportion of the olefin with the less alkylated double bond. From these facts, we conclude that the departing bromine atom hinders the free rotation of the alkyl group on C_α; that the transition states of E2 reactions promoted by strong bases have better developed double bonds than those promoted by weak bases; and that the strength of the base is more important than the size of the base in controlling positional orientation. We suggest that the solvent type (i.e., protic or aprotic) may be more important than has been generally recognized.

The factors affecting olefin proportions in E2 reactions of alkyl halides (eq 1) have been extensively studied and reviewed.[1] Two types of orientation are of interest. Positional orientation refers to the proportion of an olefin with a less alkylated double bond (Hofmann rule olefin) relative to an olefin with a more alkylated double bond (Saytzeff rule olefin) when more than one isomer can be formed (i.e., 1- and 2-pentene from 2-pentyl bromide). Geometrical orientation refers to the relative proportions of trans and cis isomers of the same olefin. Studies of orientation in elimination reactions have most often been conducted with hydroxide and alkoxide bases in protic solvents.[2]


(1)

$$B^- + R_\beta-\underset{\underset{H_\beta}{|}}{C_\beta H}-\overset{\overset{X}{|}}{C_\alpha H}-R_\alpha \longrightarrow BH_\beta + R_\beta-C_\beta H{=}C_\alpha H-R_\alpha + X^- \qquad (1)$$

Surprisingly, a large variety of very weak bases, such as thiolate ions in alcohol solvents and halide ions in dipolar aprotic solvents, has been found to promote some elimination reactions faster than strong bases under comparable conditions.[3] Winstein and Parker[3d,4] have recently developed a theory to explain the ease with which weak bases can promote these reactions. Eliminations with the weak bases, according to the new theory, utilize transition states in which the base strongly interacts with C_α (see eq 1) but only weakly interacts with H_β. These reactions are labeled E2C.[4] Increasing the strength of the base causes a shift along the spectrum toward less interaction between the base and C_α and greater interaction between the base and H_β. Bases as strong as alkoxide ions interact, according to this theory, exclusively with H_β, as in the classical E2 mechanism. These eliminations are labeled E2H.[4] Thus, rates of elimination reactions depend on the carbon nucleophilicity as well as on the hydrogen nucleophilicity of a base.

The concept of nucleophilic participation at C_α by the weak bases is a modification of the merged mechanism of substitution and elimination.[3b,5,6] Bunnett has consistently disputed any interaction between the base and C_α and prefers to accommodate all data on E2 reactions within the framework of the variable transition state theory.[3c,7] This controversy, in our view, has not been conclusively decided,[8] and the intriguing question of how weak bases promote certain elimination reactions faster than strong bases remains unanswered.

We felt that a broad study of the olefins from E2 reactions of several alkyl bromides under a variety of reaction conditions would shed light on the structures of E2 transition states. Both Bunnett and Parker agree that transition states of weak base-promoted elimination reactions have better developed double bonds than those of strong base-promoted elimination reactions.[1b,3f,4,9] Our results, discussed below, lead us to doubt this hypothesis. We now present the olefin proportions formed upon treatment of five secondary alkyl bromides with Bu_4NBr in acetone, Et_4NF in acetone and dimethylformamide (DMF), *t*-BuOK in DMF and *tert*-butyl alcohol, and EtOK in ethanol.

Results and Discussion

Table I shows the olefin proportions from E2 reactions of 4-methyl-2-pentyl and 2-methyl-3-pentyl bromides; Table II shows the olefin proportions from 2- and 3-pentyl bromides; and Table III shows the olefin proportions from 2-butyl bromide. Equilibrium proportions are included in the tables for comparison.

Control experiments demonstrated the absence of olefin isomerization under our reaction conditions and work-up procedures. We also showed that unimolecular elimination did not compete with bimolecular elimination except in some of the reactions of 2-methyl-3-pentyl bromide. Corrections for these minor solvolytic olefin components were easily made[10] (see Experimental Section).

Before discussing the results, we must examine the role of two potential complications. It has recently been found that syn elimination[11] and the state of association of the base and its counterion[12] have profound effects on olefin proportions in elimination reactions. There is ample evidence that all of our reactions occur exclusively by anti elimination and can be, therefore, directly compared. For example, Závada, Krupička, and Sicher have shown that cycloalkyl bromides undergo anti elimination with EtOK in ethanol and *t*-BuOLi in DMF.[13] Parker has demonstrated the strong anti preference in elimination reactions of cycloalkyl chlorides and sulfonate esters with Bu_4NCl in acetone.[4a] Bartsch has shown that anti elimination is the favored pathway when 2-butyl bromide is treated with EtOK in ethanol, *t*-BuOK in *tert*-butyl alcohol and DMF, and Bu_4NF in DMF.[14]

Table I. Product Proportions from E2 Reactions of Methylpentyl Bromides at 60°

Expt	Base	Solvent	Isomer	% 4-Me-1-Pe	% 4-Me-2-Pe	% 2-Me-2-Pe	*trans:cis* 4-Me-2-Pe
1	Bu_4NBr	Acetone	4-Me-2-Pe	2	98		12
2	Et_4NF	Acetone	4-Me-2-Pe	11	89		17
3	Et_4NF	DMF	4-Me-2-Pe	14	86		21
4	*t*-BuOK	DMF	4-Me-2-Pe	55[a]	45[a]		25[a]
5	EtOK	EtOH	4-Me-2-Pe	34	66		12
6	*t*-BuOK	*t*-BuOH	4-Me-2-Pe	95	5		5
7	Bu_4NBr	Acetone	2-Me-3-Pe		3	97	32
8	Et_4NF	Acetone	2-Me-3-Pe		16	84	34
9	Et_4NF	DMF	2-Me-3-Pe		16	84	35
10	*t*-BuOK	DMF	2-Me-3-Pe		55[a]	45[a]	52[a]
11	EtOK	EtOH	2-Me-3-Pe		16	84	25
12	*t*-BuOK	*t*-BuOH	2-Me-3-Pe		44	56	17
	Equilibrium[b]			0.3	8	80	6

[a] 50°. [b] At 55° with *t*-BuOK in dimethyl sulfoxide. The remaining 12% is 2-methyl-1-pentene: A Schreisheim and C. A. Rowe, *J. Am. Chem. Soc.*, 84, 3160 (1962).

Table II. Product Proportions from E2 Reactions of Pentyl Bromides

Expt	Base	Solvent	Isomer	Temp, °C	% 1-pentene	% 2-pentene	*trans:cis* 2-pentene
13	Bu_4NBr	Acetone	2-Pentyl	60	2	98	5.3
14	Et_4NF	Acetone	2-Pentyl	60	11	89	5.6
15	Et_4NF	DMF	2-Pentyl	60	11	89	5.7
16	*t*-BuOK	DMF	2-Pentyl	50	29	71	5.8
17	EtOK	EtOH	2-Pentyl	60	23	77	3.9
18	*t*-BuOK	*t*-BuOH	2-Pentyl	60	70	30	1.8
19	Bu_4NBr	Acetone	3-Pentyl	60		100	5.4
20	Et_4NF	Acetone	3-Pentyl	60		100	5.7
21	Et_4NF	DMF	3-Pentyl	50		100	5.6[a]
22	Et_4NF	DMF	3-Pentyl	50		100	5.9[b]
23	Et_4NF	DMF	3-Pentyl	25		100	6.4[a]
24	Et_4NF	DMF	3-Pentyl	25		100	6.6[b]
25	*t*-BuOK	DMF	3-Pentyl	50		100	5.3
26	*t*-BuOK	DMF	3-Pentyl	25		100	6.1
27	EtOK	EtOH	3-Pentyl	60		100	4.0
28	*t*-BuOK	*t*-BuOH	3-Pentyl	60		100	1.9
	Equilibrium[c]			20	3	97	3.2

[a] Extraction method for isolating olefins (see Experimental Section). [b] Bubbling method for isolating olefins (see Experimental Section). [c] With a Ni(0)–HCN catalyst at 20° in benzene: B. Corain, *Chem. Ind. (London)*, 1465 (1971).

Table III. Product Proportions from E2 Reactions of 2-Butyl Bromide

Expt	Base	Solvent	Temp, °C	% 1-butene	% 2-butene	*trans:cis* 2-butene
29	Bu_4NBr	Acetone	50	2	98	3.4
30	Et_4NF	Acetone	50	10	90	3.4
31	Et_4NF	Acetone	25	10	90	4.0
32	Et_4NF	DMF	25	14	86	3.8[a]
33	Et_4NF	DMF	25	11	89	3.5[b]
34	*t*-BuOK	DMF	50	27	73	3.7
35	*t*-BuOK	DMF	25	24	76	4.4
36	EtOK	EtOH	50	18[c]	82[c]	3.2[c]
37	*t*-BuOK	*t*-BuOH	50	44[d]	56[d]	1.7[d]
	Equilibrium[e]		55	9	91	2.4

[a] Extraction method for isolating olefins (see Experimental Section). [b] Bubbling method for isolating olefins (see Experimental Section). [c] Reference 12b. [d] Reference 12b. These values are for 0.05 *M* *t*-BuOK and are dependent on the concentration of the base. [e] With *t*-BuOK in DMSO, ref 4b.

On the other hand, an ion-associated base, which favors the formation of a less alkylated double bond at the expense of a more alkylated double bond and lowers the trans:cis ratio, promotes reactions under at least one of our reaction conditions.[12] The dissociated forms of EtOK in ethanol[12a] and *t*-BuOK in DMF[12b] but the associated form of *t*-BuOK in *tert*-butyl alcohol[12] have been shown to be the active reagents in promoting elimination reactions of alkyl halides[12a] and tosylates.[12b]

Bu_4NCl is 38% dissociated in acetone at the concentrations used in our experiments.[15] Since ion association decreases with increasing ionic size in aprotic solvents,[16] Bu_4NBr in dimethylformamide is expected to be more than 38% dissociated. Dissociated Bu_4NBr, therefore, is probably promoting our elimination reactions since a base is more reactive in its dissociated state than in any of its associated states.[5e,12b,17]

Thus, reactions utilizing *t*-BuOK in *tert*-butyl alcohol can be compared with those utilizing EtOK in ethanol and *t*-BuOK in DMF to examine the effects of ion association. Experiments utilizing Bu_4NBr in acetone can be compared with those utilizing *t*-BuOK in DMF to examine the effects of base strength in aprotic solvents.

Less is known about the ion association of Et_4NF. The proportions of the Saytzeff rule olefin and the trans:cis ratios which we observed with this base must, therefore, be considered minimum values. We suspect that fully dissociated Et$_4$NF is the active base for two reasons. First, when we varied the concentration of Et$_4$NF in acetone by a factor of 52 and in DMF by a factor of 23, there was no change in the ratio of trans:cis 2-pentene (±0.2) from 3-pentyl bromide. Increasing trans:cis ratios with decreasing base concentration has been used as a criterion for competing reactions of associated and free bases.[12b] Second, the olefin proportions from E2 reactions of the five alkyl bromides promoted by Et$_4$NF were not affected by changing the solvent from acetone (ϵ 20.5)[18] to DMF (ϵ 36.7).[18] It is most likely, then, that fully dissociated Et$_4$NF promoted our reactions in both acetone and DMF.

We will now analyze various aspects of our results along with our interpretation of their significance. We will discuss reactions in aprotic solvents first, covering geometrical and positional orientation separately. Then, we will briefly discuss the relationship between reactions in aprotic solvents and those in protic solvents.

Geometrical Orientation in Aprotic Solvents. In the absence of an unsymmetrical leaving group,[2e,f,11c,19,20] ion association (see above), and syn elimination (see above), eclipsing of the groups on the incipient double bond in the transition state leading to the cis olefin has been the only factor identified as important in determining trans:cis ratios.[2a,c,f,21] According to this theory, eclipsing strains, and hence trans:cis ratios, increase with increasing development of double bond character in the transition state. As the double bond character in the transition state approaches that of the product olefin, the kinetic trans:cis ratio should approach, *but never exceed*, the thermodynamic trans:cis ratio.[5b,10,22] Nevertheless, in all the reactions we studied, with the exception of those with *t*-BuOK in *tert*-butyl alcohol where the base and its counterion exist in an associated state, the observed trans:cis ratios are greater than the thermodynamic ratios by as much as a factor of 9 (expt 10 in Table I). This implies that the transition-state free-energy difference between trans and cis olefins is greater than the ground-state free-energy difference.[4b,10,22] Since the double bond is only partially developed in the transition state but fully developed in the ground state, an interaction other than eclipsing of the alkyl groups must be present.[4b,10,22a,e] An interaction proposed recently by Feit and Saunders provides a reasonable explanation. They suggested that a departing leaving group interferes with the free rotation of the alkyl group on C_α (R_α, eq 1) in the transition state.[20] Accordingly, the energy of those conformations that minimize eclipsing in the ground state of the cis olefin may be raised in the corresponding transition state. Eclipsing could now be more severe in the transition state than in the ground state resulting in a kinetic trans:cis ratio in excess of the thermodynamic ratio.

This eclipsing enhancement in the transition state also provides an explanation for the larger trans:cis 4-methyl-2-pentene ratios when the substrate is 2-methyl-3-pentyl bromide than when the substrate is 4-methyl-2-pentyl bromide under identical reaction conditions (see Table I). Eclipsing of the alkyl groups alone cannot cause this substrate dependence since a methyl and an isopropyl group are attached to the incipient double bond in both isomers. On the other hand, steric hindrance to rotation of R_α by the departing bromine atom, which leads to higher trans:cis ratios, is more sensitive to the size of the group at R_α than at R_β. Thus, the larger trans:cis ratios in E2 reactions of 2-methyl-3-pentyl bromide (R_α = *i*-Pr; R_β = Me) than of 4-methyl-2-pentyl bromide (R_α = Me; R_β = *i*-Pr) are in the expected direction.

Both 2-pentyl bromide (R_α = Me; R_β = Et) and 3-pentyl bromide (R_α = Et; R_β = Me) give the same trans:cis 2-pentene ratios under the same reaction conditions (see Table II). Apparently, the difference in hindrance to rotation when R_α is changed from methyl to ethyl is too small to be experimentally discernible in these reactions.

The effect of base strength on the trans:cis ratios we observed when aprotic solvents were used casts doubt on the generally accepted hypotheses that weak base-promoted elimination reactions utilize transition states with better developed double bonds than strong base-promoted elimination reactions (see above). With only one minor exception,[23] the change to a stronger base caused either no change or an increase in the trans:cis ratio. This trend is best observed in the reactions of methylpentyl bromides (Table I). As noted in previous studies,[11b] olefin proportions from methylpentyl derivatives show more clear-cut variations with changes in reaction conditions than unbranched derivatives (Tables II and III) and thus allow conclusions to be drawn that might otherwise be obscured. In their study of 2-butyl halides, for example, Bartsch et al.[24] found that trans:cis ratios are, within experimental error, invariant with base strength.

Winstein and Parker[4b] claim that *trans:cis* 2-butene ratios *decrease* on changing the base from Br$^-$ to either F$^-$ or *t*-BuO$^-$ in E2 reactions of 2-butyl bromide. This trend is presented as further evidence that weak base-promoted E2 reactions have transition states with well-developed double bonds.[4b] We have repeated this experiment under rigorously controlled reaction conditions and work-up procedures and find that the ratio of trans:cis 2-butene remains constant when the base is changed from Br$^-$ to F$^-$ (compare expt 29 with 30) but *increases* when the base is changed to *t*-BuO$^-$ (compare expt 33 with 35). This trend is consistent with the trends found for the other alkyl bromides we examined.

The trans:cis olefin ratio is considered to be a measure of double-bond character in the transition state of an E2 reaction.[2a,c,f,21a,b,25] The general trend toward increasing trans:cis ratios with increasing base strength implies, therefore, *greater* double-bond development in transition states of E2 reactions promoted by strong bases than those promoted by weak bases.

Furthermore, both Parker and Winstein[4b,26] and Bunnett[7b] have found that conjugation between the developing double bond and a phenyl group at R_β is less important in an E2 reaction that is promoted by a weak base than one that is promoted by a strong base. They attribute this phenomenon to the lack of coplanarity between the developing double bond and the phenyl group in the transition states of weak base-promoted E2 reactions. This explanation seems doubtful since dehydrotosylation of 4-cyclohexenyl tosylate is only slightly faster than dehydrotosylation of cyclohexyl tosylate with Bu$_4$NCl in acetone.[3f] Dehydrotosylation of 4-cyclopentenyl tosylate is actually slower than that of cyclopentyl tosylate with Bu$_4$NCl in acetone.[3f] Thus, conjugation of the developing double bond and an already existing double bond with which coplanarity is ensured is also insignificant in an E2 reaction promoted by a weak base. Ring strain in another to explain the same phenomenon, we suggest that the lack of conjugation between the developing er than invoke lack of coplanarity in one case and ring strain in another to explain the same phenomenon, we suggest that the lack of conjugation between the developing double bond and an already existing π system in the transition state of an E2 reaction promoted by a weak base is due to the poorly developed double bonds in the transition states of these reactions.

Positional Orientation in Aprotic Solvents. There is a regular increase in the proportion of the less substituted (Hofmann rule) olefin along the series of bases Br$^-$ < F$^-$ < *t*-BuO$^-$ in aprotic solvents. The increase in the proportion of the Hofmann rule olefin in elimination reactions promoted by increasingly branched alkoxide ions has been attributed to either the size[2d,27] or strength[2b,f,28] of the base and has been the subject of considerable debate. The evidence for both points of view is necessarily indirect since increased branching leads to an increase in both the size and strength of an alkoxide base in alcohol solution. Froemsdorf,[29] Feit and Saunders,[11b] and Bartsch[30] have recently presented more quantitative evidence to support the greater importance of the strength, relative to the size, of the base.

Our results show conclusively that it is the strength and not the size of the base that is important. With two of the bases in our series, the order of increasing base strength ($Br^- < F^-$) is different from the order of size ($F^- < Br^-$). Since the order of increasing proportion of Hofmann rule olefin corresponds to the order of increasing base strength, we conclude that the strength of the base must be more important than the size.

Protic vs. Aprotic Solvents. The positional orientation obtained with the strong base EtOK in the protic solvent ethanol is intermediate between the positional orientation obtained with the strong bases Et_4NF and *t*-BuOK in the aprotic solvents. The trans:cis ratios, on the other hand, are smaller with EtOK in ethanol than with any of the bases, including the weak base Bu_4NBr, in an aprotic solvent. It is important to note that it is the solvent type that influences orientation. With a common base within a series of either protic[11b,21b,31] or aprotic solvents (compare reactions with Et_4NF in acetone and DMF), a change in solvent causes negligible changes in olefin proportions as long as the state of ion association of the base is not changed. When ion association is encouraged, as in our reactions in *tert*-butyl alcohol, an increase in the relative proportions of the less substituted olefin and a decrease in trans:cis ratios are observed, as has been previously reported.[12]

The mechanistic differences between E2 reactions promoted by weak bases and by strong bases have been discussed mainly in terms of the nature of the base. We suggest that the role of the solvent may be more important than is generally considered.[7b,21b]

Experimental Section

Materials. 2-Butyl and 2-pentyl bromides were obtained from Baker and Aldrich, respectively, and were distilled. The method of Wiley et al.[32] was used to prepare 3-pentyl and 4-methyl-2-pentyl bromides. They had bp 60-62° (115 mm), $n^{8.5}$D 1.4487 and bp 80-82° (132 mm), n^{11}D 1.4463, respectively. The method of Arain and Hargreaves[33] was used to prepare 2-methyl-3-pentyl bromide, bp 67-69° (73 mm), n^{20}D 1.4496. Analysis by GC, ir, and bromide ion titration was used to demonstrate the purity of the alkyl bromides and especially the absence of olefinic impurities.

Tetrabutylammonium bromide was obtained from Eastman and had mp 113-116° (lit.[34] mp 115.5-116°).

Anal. Calcd for $C_{16}H_{36}NBr$: Br, 24.78. Found: Br, 24.87.[35]

Tetraethylammonium fluoride (Eastman) and potassium *tert*-butoxide (MSA Research Corp.) were used without further purification. Acetone and DMF were of reagent grade quality and were dried over molecular sieve. Karl Fischer titration showed less than 0.2% H_2O. Alcohol solvents were purified and alkoxide solutions were prepared as previously described.[20]

General Procedure. Five or ten milliliters of a solution of an alkyl bromide (0.003-0.16 *M*), Bu_4NBr (0.005-0.16 *M*), and excess lutidine in acetone was heated in a tightly sealed stainless steel tube[36] for 64-432 hr in a thermostated oil bath at the temperatures indicated in the tables. The reaction mixture was then added to 25 ml of H_2O. The aqueous mixture was extracted with CS_2 (2 × 5 ml), and the extracts were washed with H_2O (2 × 10 ml). The CS_2 solution was then examined by GC.

In the reactions with *t*-BuOK in DMF, the olefins were bubbled out of solution with N_2 as they were formed in order to prevent isomerization.[2g] The olefins were collected in CS_2 at −78°. After a reaction time of about 15 min, the CS_2 solutions were washed with water and analyzed by GC. The *t*-BuOK concentrations were 0.04-0.46 *M*, while the alkyl bromide concentrations were 0.01-0.14 *M*.

A variety of conditions were used in the reactions promoted by Et_4NF. For comparisons with Bu_4NBr-promoted reactions, 5-10 ml of a solution of the alkyl bromide (0.003-0.076 *M*), Et_4NF (0.003-0.16 *M*), and 2,6-lutidine in acetone was placed in a stainless steel tube and heated at the temperatures indicated in the tables. After periods ranging from 1 to 48 hr, the reaction mixtures were worked up the same way as the Bu_4NBr-promoted reactions. There was no variation in product proportions with varying reaction times.

For comparison with the *t*-BuOK-promoted reactions, Et_4NF-promoted reactions were conducted in DMF the same way as in acetone. Tightly stoppered volumetric flasks were used in addition to the stainless steel tubes. The method of bubbling the olefins out of DMF solutions (see above) was also applied to the Et_4NF-promoted reactions. No substantial differences in olefin proportions were observed for the different types of reaction vessels or the olefin isolation method.

The reaction conditions for the reactions in alcohol solvents were as previously described.[20]

Control Experiments. The absence of competition from E1 reactions for the butyl and pentyl bromides was demonstrated by the absence of olefins found after maintaining 2-butyl bromide in acetone or 3-pentyl bromide in DMF at the conditions used in the base-promoted reactions. In addition, no variation in the *trans:cis* 2-pentene ratio was observed in reactions of 3-pentyl bromide with a greater than tenfold variation in the concentration of each base used in the aprotic solvents. A fourfold variation in the concentration of MeOK in methanol or EtOK in ethanol has previously been found to cause no variation in olefin proportions in E2 reactions of 2-butyl bromide at 50°.[12b] A tenfold variation in the concentration of *t*-BuOK in *t*-BuOH causes a small variation in olefin proportions in E2 reactions of 2-butyl bromide at 50°, but this has been attributed to base-cation association and not to a competing E1 reaction.[12b]

When 2-methyl-3-pentyl bromide was heated at 100° for 80 hr in DMF and at 135° for 18 hr in ethanol, significant amounts of olefins were detected. In the olefin mixture, 17% 2-methyl-1-pentene in DMF and 15% in ethanol were observed. This olefin is the result of a rearrangement of the intermediate carbonium ion in an E1 reaction and cannot be formed in a concerted elimination.[10] Thus, the rearranged olefin is a probe for an E1 component when a base is present. Since we never observed more than 1.6% 2-methyl-1-pentene under any of our reaction conditions, we conclude that less than 11%[10] of the olefins were due to an E1 process under any of our reaction conditions. Since only 2 and 7% of the olefins from these solvolytic reactions in DMF and ethanol, respectively, were 4-methyl-2-pentene, the correction[10] of the *trans:cis* 4-methyl-2-pentene ratio from the base-promoted reactions was negligible. The correction[10] of the relative proportions of 4-methyl-2-pentene and 2-methyl-2-pentene was never more than 1 percentage unit. Since ethanolysis of 4-methyl-2-pentyl bromide is four times slower than ethanolysis of 2-methyl-3-pentyl bromide,[37] the olefins we observed from the former bromide cannot have come from an E1 reaction to any significant extent.

We also demonstrated the absence of olefin isomerization under our reaction conditions. No other olefins were formed after treatment of *cis*-2-pentene with Et_4NF in acetone at 65° for 2 days. Neither the ratio of *trans:cis* 2-pentene nor the relative proportions of 4-methyl-1-pentene, *cis*- and *trans*-4-methyl-2-pentene, and 2-methyl-2-pentene changed after adding known mixtures of the 2-pentenes and the methylpentenes, respectively, to 0.4 *N* *t*-BuOK in DMF at 50° and bubbling them into CS_2 at −78° with N_2.

The stability of the olefins to the reaction conditions used with the alcohol solvents has been previously demonstrated.[20]

GC Analysis. The isomeric butenes were analyzed on a 10 ft × 0.25 in. column of 10% adiponitrile at room temperature. The separation of the isomeric pentenes and methylpentenes has been previously described.[20] A Perkin-Elmer 900 gas chromatograph with a flame ionization detector was used.

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