Effect of Base and Solvent on Orientation in *E*2 Reactions of Quaternary Ammonium Salts

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A CHANGE from ethoxide ion in ethanol to t-butoxide ion in t-butyl alcohol is known to cause a shift toward Hofmann-rule orientation in *E*2 reactions of alkyl halides[1,2] and tosylates.[3,4] Brown argues that the greater steric requirements of t-butoxide favour attack at a hydrogen on the less-substituted β-carbon. It has been pointed out, most recently by Froemsdorf,[5] that the base strength and the solvent are also changing. In order to decide whether a solvent effect on transition-state structure was a major factor, we decided to examine a leaving group of different charge type, where the solvent effect on ease of C–X bond breaking should be reversed.

We first tried pent-2-yltrimethylammonium ion. The results (Table 1) show a slight increase in pent-1-ene from ethanol–ethoxide to t-butyl alcohol–t-butoxide. The difference appears to be real, a conclusion supported by the results with other primary alcohol–alkoxide pairs, but is too small for complete confidence.

TABLE 1

Products in E2 *reactions of pent-2-yltrimethylammonium iodide*

RO$^-$–ROH	Pent-1-ene (%)	*trans-/cis-* Pent-2-ene	Olefin (%)
Et^{a,c}	96·0 ± 0·1	—	11–55
Et^{b}	94·0	—	63
Pr^{n} ^{b}	95·6 ± 0·2	0·32	57–65
Allyl^{b,e}	93·8	0·37	41
Bu^{n} ^{b,e}	94·6	0·32	66
Bu^{t} ^{a,d}	97·8 ± 0·2	0·41	76—85
Bu^{t} ^{b,e}	97·1	0·41	84

[a] Refluxing solvent.
[b] Sealed ampoules at 110°.
[c] Six runs.
[d] Two runs.
[e] One run.

TABLE 2

Products in E2 *reactions of 2-methylpent-3-yltrimethylammonium ion*[a]

R in RO$^-$–ROH	4-Methyl-pent-2-ene (%)	*trans-/cis-* 4-Methyl-pent-2-ene	Olefin (%)
Et^{b}	61 ± 1	5·2	42
Pr^{n} ^{b,d}	62	4·9	41
Allyl^{b}	58 ± 1	4·3	27—35
Bu^{n} ^{c}	64 ± 2	4·7	17—35
Pr^{i} ^{c}	72 ± 1	—	26
Bu^{s} ^{b}	76 ± 1	9·0	34—38
Bu^{t} ^{c}	84 ± 2	12·7	39—52

[a] Both the bromide and iodide were used and gave the same results under the same conditions.
[b] Sealed ampoules at 110°.
[c] Refluxing solvent, and sealed ampoules at 110°.
[d] Single run.

Consequently, we tried 2-methylpent-3-yltrimethylammonium ion. Here the competition is between elimination into branches bearing one and two β-methyl groups, and we expected less extreme Hofmann-rule orientation. The percentage of 4-methylpent-2-ene (Table 2) increases markedly along the series ethanol–ethoxide, isopropyl alcohol–isopropoxide, and t-butyl alcohol–t-butoxide. There is thus no doubt that quaternary ammonium salts, bromides,[1,2] and tosylates[3,4] show qualitatively the same changes in orientation with changes in the solvent and base.

These experiments tend to support Brown's[1] hypothesis of steric hindrance to proton abstraction with t-butoxide, or perhaps a steric effect operating through another mechanism. It is difficult to maintain that greater carbanion character in the t-butoxide eliminations is responsible for our results, because deuterium isotope effects and substituent effects with 2-arylethyltrimethylammonium bromides both indicate distinctly *less* carbanion character with t-butyl alcohol–t-butoxide than with ethanol–ethoxide.[6]

The *trans/cis* ratios deserve some comment. Those from pent-2-yltrimethylammonium ion show the same preference for *cis*-olefin previously noted for nonan-2-yl 'onium salts,[7] while those from 2-methylpent-3-yltrimethylammonium ion are in the "normal" direction. In both cases there is a trend toward more *trans*-olefin with the more branched alcohol–alkoxide pairs. Interpretation of this trend is difficult. It is by no means obvious whether reactant-like or product-like transition states leading to the *cis*-olefin would show greater nonbonded interactions, particularly in these systems with very bulky leaving groups.

Although various explanations have been advanced, the cause of preference for *cis*-olefin in some reactions of 'onium salts[7] and tosylates[3,4] remains unclear. A possibility that does not seem to have been mentioned is that solvation of the transition state should be easier when both α- and β-alkyl groups are on one side of the molecule. The effect, whatever its origin, is obviously small and easily overbalanced by relatively minor increases in eclipsing effects.

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