Elimination Reactions of 3-Pentyl Halides. Relative Deuterium Isotope Effects for *cis*- and *trans*-Pent-2-ene Formation

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THERE exist two apparently conflicting theories to explain the ratios of products accompanying reactions of bases with 2-halogenoalkanes, one based on steric requirements,[1] the other on the concept of a variable transition state.[2] Recently it has become apparent that both steric and electronic factors may, under appropriate conditions, exert important directive effects. For example, in t-butyl alcohol, triethylmethanol, and toluene, the steric requirements of the base have been found to exert an important directive effect,[3] while in tetrahydrofuran and dimethyl sulphoxide the effect of base size is of only minor importance.[3,4]

To assess the relationship between steric and electronic effects in controlling the products of elimination, we have studied the *cis*- and *trans*-pent-2-ene obtained from 3-pentyl and [2,2,4,4-$^{2}H_4$]-3-pentyl halides. These derivatives were selected in order to preclude complications arising from simultaneous Hofmann and Saytzeff elimination.

cis- *and* trans-*Pent-2-ene from elimination of* 3-*pentyl and* [2,2,4,4-$^{2}H_4$]-3-*pentyl halides*

		3-*Pentyl*			[$^{2}H_4$]-3-*pentyl*			
Base[a]	Halide	% *trans*	% *cis*	*trans*/*cis*	% *trans*	% *cis*	*trans*/*cis*	$\frac{(k_H/k_D)_{cis}}{(k_H/k_D)_{trans}}$
$KOCMe_3$	Chloride	61·4 ± 0·4[b]	38·6 ± 0·4	1·59 ± 0·02	67·0 ± 0·4	33·0 ± 0·4	2·03 ± 0·03	1·28 ± 0·04
$KOCMe_3$	Bromide	68·2 ± 0·3	31·8 ± 0·3	2·14 ± 0·02	70·6 ± 0·3	29·4 ± 0·3	2·40 ± 0·03	1·12 ± 0·03
$KOCMe_3$	Iodide	72·5 ± 0·3	27·5 ± 0·3	2·64 ± 0·03	73·5 ± 0·2	26·5 ± 0·2	2·75 ± 0·02	1·05 ± 0·03
KOEt	Chloride	78·0 ± 0·4	22·0 ± 0·4	3·55 ± 0·08	75·6 ± 0·3	24·4 ± 0·3	3·10 ± 0·04	0·87 ± 0·03
KOEt	Bromide	79·2 ± 0·2	20·9 ± 0·2	3·81 ± 0·04	78·2 ± 0·3	21·8 ± 0·3	3·60 ± 0·07	0·94 ± 0·03
KOEt	Iodide	81·1 ± 0·4	18·9 ± 0·4	4·31 ± 0·12	80·3 ± 0·3	19·7 ± 0·3	4·07 ± 0·08	0·95 ± 0·04

[a] The corresponding alcohols were used as solvent; [b] Errors reported as the standard deviation.

For each of the halides, elimination by potassium t-butoxide in t-butyl alcohol gave a higher *trans*-/*cis*-pent-2-ene ratio from the deuteriated halides than from the undeuteriated analogues. Clearly this indicates that in this base–solvent system the isotope effect for *cis*-product formation is greater than that for formation of *trans*-pent-2-ene. With potassium ethoxide in ethanol the opposite is true.

In addition to the dependence of the relative isotope effects on base and solvent, the magnitude of the isotope-effect difference is also much altered by changing the leaving group, Cl > Br > I.

Since for a single halide in a single base–solvent combination the isotope effects for *cis*- and *trans*-product formation differ, this difference cannot be only the result of changes in the β-alkyl groups, leaving group, base, or solvent; factors which could result in electronic differences in the transition states.[2] These differences may be a result of the differing steric environments of the transition states. Unfortunately, the stereochemical pathway for these eliminations is unknown. In fact it has been suggested[5] that elimination of cyclic bromides by potassium t-butoxide may proceed by a *syn*-mechanism to give *trans*-olefin and an *anti*-mechanism to give *cis*-olefin. These stereochemical ambiguities preclude a simple explanation at this time.

The relative electronic natures of the transition states for *cis*- and *trans*-product formation may be affected by a number of factors, including not only effects of the base, solvent, and leaving group, but also differences resulting from the steric environment or the stereochemical pathway. Similar effects may be observed in systems where both Hofmann and Saytzeff elimination are possible.

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