Factors Affecting *trans/cis* Olefin Ratios in Elimination Reactions of Alkyl Bromides

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Summary Hindrance to free rotation of the alkyl group on C_α is used to explain abnormally high *trans/cis* olefin ratios and different *trans/cis* ratios of the same olefin formed from isomeric substrates in $E2$ reactions of alkyl bromides.

The factors affecting *trans/cis* olefin ratios in elimination reactions have been extensively studied. Eclipsing effects,[1] steric effects of unsymmetrical leaving groups and bases,[2] and the incursion of *syn* elimination[2d,3] have been found to have important consequences. We have investigated *trans/cis* ratios in *anti*, $E2$ reactions of substrates with symmetrical leaving groups. The olefin proportions formed upon treatment of 2-pentyl, 3-pentyl, 4-methyl-2-pentyl, and 2-methyl-3-pentyl bromides with KOEt in EtOH and with $KOBu^t$ in Bu^tOH were measured by g.l.c. [see equation (1); $R_\alpha = R_\beta =$ Me, Et, or Pr^i]. The results along with equilibrium *trans/cis* ratios, are given in Tables 1 and 2.

$$R_\beta C_\beta H_2\text{–}C_\alpha H(R_\alpha)\text{–}Br \rightarrow R_\beta C_\beta H{=}C_\alpha HR_\alpha \qquad (1)$$

The increase in the proportion of the Hofmann rule olefin and the simultaneous decrease in the *trans/cis* ratio as the base-solvent system becomes more highly branched has been previously observed in $E2$ reactions of alkyl bromides.[1d,6] This pattern is typical of an exclusively *anti* mechanism.[3b]

Table 1

Olefin proportions from E2 *reactions of pentyl bromides at* 60°[a]

Source	Solvent[b]	Pent-1-ene (%)	Pent-2-ene (%)	*trans/cis* Pent-2-ene
2-Pentyl bromide	EtOH	23	77	3·9
2-Pentyl bromide	Bu^tOH	70	30	1·8
3-Pentyl bromide	EtOH	—	100	4·0
3-Pentyl bromide	Bu^tOH	—	100	1·9
Equilibration[c]	C_6H_6	3	97	3·2

[a] The reaction times were 20—40 h. The concentration of pentyl bromide was 0·1—0·2M and concentration of base was 0·3—1·0M. Each value is an average of values obtained at two different base concentrations. Varying the base concentration had no effect on product proportions at the different base concentrations. [b] The base is the corresponding alkoxide. [c] 20°; ref. 4.

The *trans/cis* ratios we observed often exceed the thermodynamic ratios. Since *trans/cis* ratios reflect the degree of double bond character in the transition state,[1] a ratio in excess of the thermodynamic ratio requires at least one interaction in the transition state that is not present in the product olefin. An interaction recently suggested by Feit and Saunders[2c] can explain this. The departing bromine atom may restrict the free rotation of the alkyl group (R_α) attached to C_α. The energy of those conformations that minimize eclipsing between R_α and R_β in the *cis* olefin will thereby be raised in the corresponding transition state. Conformational requirements are less stringent in the transition state leading to *trans* olefin.

TABLE 2

Olefin proportions from E2 *reactions of methylpentyl bromides at* 60°[a]

Source	Solvent[b]	4-Methylpent-1-ene (%)	4-Methylpent-2-ene (%)	2-Methylpent-2-ene (%)	*trans/cis* 4-Methylpent-2-ene
2-Methyl-3-pentyl	EtOH	—	16	84	25·4
2-Methyl-3-pentyl	Bu^tOH	—	44	56	16·6
4-Methyl-2-pentyl	EtOH	34	66	—	11·6
4-Methyl-2-pentyl	Bu^tOH	95	5	—	4·6
Equilibration[c]	Me_2SO				6·0

[a,b] See corresponding footnotes, Table 1. [c] 55°; ref. 5.

The same effect can also explain the different *trans/cis* 4-methylpent-2-ene ratios formed from isomeric methylpentyl bromides under the same reaction conditions (compare line 1 with 3 and line 2 with 4 in Table 2). Eclipsing in the transition state will be enhanced with larger groups at R_α. The higher *trans/cis* ratio from 2-methyl-3-pentyl bromide ($R_\alpha = Pr^i$, $R_\beta = Me$) than from 4-methyl-2-pentyl bromide ($R_\alpha = Me$, $R_\beta = Pr^i$) is in the expected direction.

Apparently, the difference in hindrance to rotation on changing R_α from methyl to ethyl is not great enough to be experimentally discernible in these reactions. The ratio of *trans/cis* pent-2-ene is the same whether the substrate is 2-pentyl bromide ($R_\alpha = Me$, $R_\beta = Et$) or 3-pentyl bromide ($R_\alpha = Et$, $R_\beta = Me$).

Recently, elimination reactions promoted by weak hydrogen but strong carbon nucleophiles in dipolar aprotic solvents (*E2C* reactions) have been found to give abnormally high *trans/cis* ratios.[7] These reactions have been postulated to occur through transition states in which there is some interaction between the nucleophile and C_α.[7c-9] A modification of the explanation for high *trans/cis* ratios in some of our *E*2 reactions can be used to explain the even higher *trans/cis* ratios observed in the *E2C* reactions. The additional bulk of the nucleophile at C_α will further hinder free rotation of R_α causing even greater enhancement of eclipsing strain in the transition state.

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