

TRANS/CIS OLEFIN RATIOS AS A FUNCTION OF THE LEAVING GROUP
IN THE REACTIONS OF 1-PHENYL-2-PROPYL HALIDES WITH SODIUM
ETHOXIDE IN ETHANOL

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In E2 β -elimination eclipsing effects have been invoked to explain the difference in reactivity of diastereomeric compounds and in the proportions of cis- and trans-olefins formed from a common substrate¹, and are frequently considered to be a measure of the extent of double bond formation in the transition state¹⁻³.

In the reaction of 2-alkyl halides in alcoholic solvents, it has been found that the 2-olefin trans/cis ratio decreases regularly in the order I > Br > Cl > F^{1b, 3}. This result is in agreement with the theory of the variable E2 transition state which predicts an increase of the carbanion character of the transition state, with consequent decrease of the extent of double bond formation, as the bond between the α -carbon and the leaving group becomes stronger.

In the present note we now report that when the substrate is activated by a phenyl group a different trend of the trans/cis olefin ratios as a function of the leaving group may be obtained. Our data refer to the reaction of 1-phenyl-2-propyl halides with EtO⁻ in EtOH and are reported in the table. In this system the order of trans/cis olefin ratios, I \geq Br \approx Cl < F, is quite different from that observed for the corresponding series of non-activated alkyl halides, the maximum value being observed in the substrate exhibiting the transition state with the largest carbanion character. Thus, the present data, in agreement with previous results for the 1,2-dibromo-1,2-diphenylethane system⁴, indicate that in a phenyl activated system a shift of the transition state structure toward Elcb extreme may be accompanied by an increase in the entity of the eclipsing effects.

Two explanations appear possible for this result. In the first place it could be suggested that the theory of the variable E2 transition state should be modified, for phenyl activated systems, in the sense indicated by Steffa and Thornton⁵. According to their model of variable transition state an increase in

Table
 Trans/Cis Olefin Ratios in the E2 Reactions of 1-Phenyl-2-X-propanes
 with EtO⁻ in Ethanol, at 60°. ^a

X	<u>trans/cis</u> β-methylstyrene
I	28.3 ± 1.7
Br	24.7 ± 1.3
Cl	25.0 ± 0.1
F	112.4 ± 4.5

a) The olefin proportions were measured by g.l.c. and were shown to be practically unaffected by both the isomerization of cis- into trans-β-methylstyrene and of allylbenzene into β-methylstyrene. The trans/cis ratios are the average of three determinations.

the carbanion character is coupled with an increase in the C=C double bond character.

The second explanation is related to the fact that in a phenyl activated system the eclipsing effects may derive from differences in the extent of conjugation of the phenyl group with the developing negative charge at the β-carbon, in addition to differences in the non-bonded interactions of substituents at C_α and C_β, as it occurs in the resulting olefins. Thus, in systems where the transition state possesses a high degree of carbanion character, as in the case of the fluoro derivative, differences in the conjugation of the phenyl group may play the largest role in determining the entity of the eclipsing effects. As a consequence, it is possible to have large values of the eclipsing effects even if the extent of double bond formation in the transition state is small.

Work is in progress to acquire further information on this problem.

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