THE EFFECT OF HYDROGEN BONDING ON ORIENTATION IN *anti*-E2 REACTIONS*

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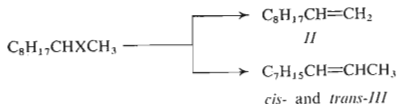
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The title effect induced by *p*-cresol was investigated in the reaction of four 2-decyl derivatives (*I*; X = OTs, Cl, Br, I) with potassium *p*-cresolate in dimethyl sulphoxide. A gradual decrease of the value of *trans*-2-decene/*cis*-2-decene ratio and in most instances also a gradual decrease in the proportion of 1-decene isomer was found to be induced by increasing the concentration of *p*-cresol. It is suggested that hydrogen bonding of the participating base as well as of leaving group may account for the trends observed.

Recent studies from this as well as from other laboratories demonstrated that the ability of alkali metal cations to coordinate (by ion-pairing) with the conjugate anions of the participating base and/or with leaving group may alter pronouncedly the orientational pattern[1-6] in bimolecular elimination. An obvious analogy which exists between the ability of metal cations and the ability of hydroxylic groups to coordinate by hydrogen bonding prompted us now to examine the effect of hydrogen bonding on the elimination course. Occasionally, hydrogen bonding has already been invoked for explanation of some specific features of the reaction in protic solvents[6]. However, to our knowledge, no unambiguous evidence has been obtained so far, at least as it concerns the effect on orientation in the reaction.

In this paper, we investigated the effect of *p*-cresol on geometrical and positional orientation in the elimination of four 2-decyl derivatives *I* (X = OTs, Cl, Br, I) with potassium *p*-cresolate (Scheme 1). Phenols are known[7,8] to be powerful hydrogen-bonding agents. The conjugate acid of the cresolate base may therefore provide

$$C_8H_{17}CHXCH_3 \longrightarrow \begin{cases} C_8H_{17}CH=CH_2 & \quad II \\ C_7H_{15}CH=CHCH_3 & \\ \textit{cis- and trans-III} & \end{cases}$$

SCHEME 1

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an efficient hydrogen bonding in the reaction. Accordingly, the effect of hydrogen bonding on orientation can be deduced simply from the changes observed in the olefin-isomer distribution induced by variation of the conjugate-acid concentration. In order to avoid complications which might arise from ion-pairing of the base, we performed the reaction in the ion-pairs dissociating solvent dimethyl sulphoxide.

Complementary informations on the nature of the examined effect were obtained from an analogous study of the reaction of the tosylate I (X = OTs) with potassium 2,4,6-tri-tert-butylphenoxide, where hydrogen bonding is sterically disfavoured[9,10].

EXPERIMENTAL

2-Decyl derivatives I were prepared by the procedures described earlier[5]. Phenols employed in this study were commercial products. Phenoxide solutions were prepared by dissolving known amounts of the conjugate acid in 0·28M potassium tert-butoxide in dimethyl sulphoxide.

Elimination runs: 2-Decyl derivative (0·15 mmol) was dissolved in an appropriate phenoxide solution (2-fold excess) and heated under nitrogen in sealed tubes at 80°C for 1—6 h. The contents were transferred into 50 ml volumetric flasks containing pentene (1 ml) and 2M sodium hydroxide (30 ml). The volumes were made up to mark with water, the contents shaken and a sample of the pentane layer injected into a gas-chromatograph. According to blank experiments (*cf.* ref.[5]) no isomerization took place under the employed conditions. The analyses were performed on the Carlo Erba Fractovap GT4 instrument equipped with digital integrator employing a 50 m capillary coated with di-n-butyl tetrachlorophthalate at 60°C. The reproducibility was about ±0·2%.

RESULTS AND DISCUSSION

Mechanistic assumptions: Duality of elimination pathways[1,4] (*anti-* and *syn-*) and also duality of base species[1-5] (associated and dissociated), encountered frequently in E2 reactions, necessitates separate analysis of individual contributing processes. As we already pointed out[4], this may be attained by a proper selection of reactants and reaction conditions favouring a single (homogeneous) elimination process. In the preceding paper[5] we summarized evidence that unbranched 2-alkyl derivatives possess an extremely low propensity to utilize *syn*-pathway even under conditions which are supporting it (*e.g.* strong base, non-polar solvent). Accordingly, we may assume that the present reactions involving a weak base and very polar solvent proceed prevalently by *anti*-pathway. Dimethyl sulphoxide is renowned for its capacity to dissociate ion-pairs. Direct evidence is available[3-5] that ion-paired (associated) base species is only of a minor importance in E2 reactions in this solvent. Admittedly, it is also known that hydrogen bonding may support[4] the associated base in the reaction. However, a closer examination of the present results will show that the observed effects cannot originate from the support of the associated base.

Incursion of solvolysis in the examined reactions was ruled out by blank experiments performed in the absence of potassium *p*-cresolate.

The effect of p-*cresol:* Table I summarizes the effect of p-cresol on the olefin-isomer distribution in the reaction of the derivatives I (X = OTs, Cl, Br, I) with potassium p-cresolate in dimethyl sulphoxide. The first impression from these data is that the effect is not large. However, the ability of the dipolar solvent to compete for hydrogen bonding with the reactants cannot be ignored. Accordingly, in appreciating the actual significance of the effect we have to take into account that only a part of the reaction was influenced by hydrogen bonding under present conditions.

As Table I shows, increasing concentration of p-cresol leads, for all the derivatives I, to a gradual decrease of the value of *trans*-2-decene/*cis*-2-decene ratio and also

TABLE I

The Effect of p-Cresol on the Olefin-Isomer Distribution in the Reaction of Derivatives I (X = = OTs, Cl, Br, I) with Potassium p-Cresolate in Dimethyl Sulphoxide at 80°C

Base: p-cresol molar ratio	% II	trans-III/cis-III
	X = OTs	
1 : 0·1	41·3	3·02
1 : 1	38·5	2·51
1 : 2	36·3	2·19
1 : 3	35·7	2·10
	X = Cl	
1 : 0·1	31·0	4·18
1 : 1	30·5	4·11
1 : 2	29·6	4·00
1 : 3	28·6	4·00
	X = Br	
1 : 0·1	20·6	5·25
1 : 1	21·2	4·83
1 : 2	21·8	4·35
1 : 3	22·2	4·22
	X = I	
1 : 0·1	12·9	5·54
1 : 1	12·3	5·52
1 : 2	11·3	5·48
1 : 3	11·0	5·44

(with the exception of *I*; X = Br) to a gradual decrease in the proportion of 1-decene isomer. For explanation of these changes, the solvatation by hydrogen bonding of both the participating base as well as the leaving group has to be considered. Assumedly, hydrogen bonding of the *p*-cresolate anion leads to a decrease of the base strength, while hydrogen bonding of the leaving group assists in loosening the C_α—X bond in transition state. A convincing evidence is available that with decreasing base strength[11,12] as well as with increasing easiness of the leaving group departure[6-13] decreases usually the proportion of the least substituted olefin in the reaction. Table II provides an additional evidence that it holds also for the present systems. In this way, hydrogen bonding of the cresolate base and/or of leaving group may account equally well for the decrease in 1-decene proportion induced by *p*-cresol in the reaction of the three derivatives *I* (X = OTs, Cl, I).

However, a somewhat different situation holds, as it concerns the effect of *p*-cresol on the *trans*-2-decene/*cis*-2-decene ratios. As the data of Table II show, a decrease in base strength leads to a decrease in the value of this ratio. On the other hand, increasing easiness of the leaving group departure (Cl < Br < I; for a special behaviour of the tosyloxy group *cf*. ref.[5]) leads to an increase of this ratio. We could therefore conclude that hydrogen bonding of the cresolate base but not that of the leaving group is responsible for the trends observed in Table I.

Despite this, the possibility that hydrogen bonding of leaving group affects the *trans/cis* ratio cannot be ruled out, when steric interactions between the solvating molecules and alkyl portion of reactant are taken into account. In an analogy with the steric models proposed for metal-ion coordination in E2 reactions[3-5], the interactions should be more severe in the *trans*-isomer formation (Scheme 2*A* or *B*).
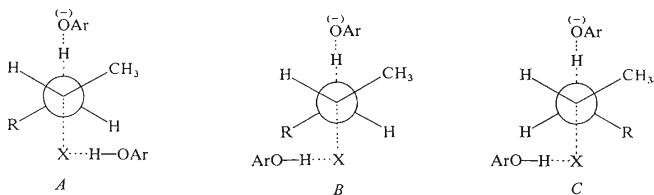
Scheme 2

In the *cis*-isomer formation, the interactions can be avoided by hydrogen bonding of leaving group from that side where only hydrogen atoms are placed (Scheme 2*C*). Obviously, this difference can provide some advantage for the latter isomer formation and thus cause a decrease in the value of the *trans/cis* ratio. The circumstance that the decrease is particularly pronounced for the tosyloxy group which is very suc-

ceptible to hydrogen bonding (owing to the presence of three oxygen atoms) lends a credence to this suggestion.

It might be argued that a mere change in dielectric constant of the solvent resulting from addition of *p*-cresol could change the olefin isomer composition. However, the observation that in the reaction of the tosylate *I* with potassium 2,4,6-tri-tert--butylphenoxide the product composition (Table III) is completely unaffected by addition of the overcrowded conjugate acid, in which hydrogen bonding is practically precluded[9,10], speaks strongly against such a possibility.

We pointed out previously[4] that hydrogen bonding supports operation of ion-paired forms of base in bimolecular elimination. We also showed that ion-paired base causes a substantial decrease in *trans/cis* ratios in the reaction[5]. Accordingly, ion--pairing of the cresolate base rather than hydrogen bonding could be actually respon-

TABLE II

The Effect of Base Strength and Leaving Group on the Olefin-Isomer Distribution in the Reaction of Derivatives *I* (X = OTs, Cl, Br, I) with Potassium Tert-Butoxide and with Potassium *p*-Cresolate, Respectively, in Dimethyl Sulphoxide

X	% II		*trans-III/cis-III*	
	tert-$C_4H_9OK^{a,b}$	*p*-$CH_3C_6H_4OK^c$	tert-$C_4H_9OK^{a,b}$	*p*-$CH_3C_6H_4OK^c$
OTs	75·4	41·3	3·20	3·02
Cl	59·4	31·0	5·10	4·18
Br	48·0	20·6	5·30	5·25
I	32·1	12·9	5·70	5·54

[a] Data from ref.[5]; pK value[12] of the conjugate acid in dimethyl sulphoxide: [b] 29; [c] 16·4.

TABLE III

Olefin-Isomer Composition in the Reaction of Tosylate *I* (X = OTs) with Potassium 2,4,6-Tri-tert-butylphenoxide in Dimethyl Sulphoxide

Base : Conjugate acid molar ratio	% II	*trans-III/cis-III*
1 : 0·1	58·6	1·7
1 : 1	58·8	1·7
1 : 2	58·9	1·7

sible for the changes in Table I. However, it is known that ion-pairing of base also leads almost invariantly to a significant increase[5,14] in the proportion of the least substituted isomer in the reaction, contrary to the prevailing evidence from the Table I. At least for three of the four derivatives I (X = OTs, Cl, I), operation of the ion--paired base in the elimination can be ruled out on these grounds.

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