GEOMETRICAL AND POSITIONAL ORIENTATION IN *anti*-E2 REACTIONS: THE EFFECT OF BASE ASSOCIATION IN A WIDER SCALE OF TRANSITION STATES*

M.PÁNKOVÁ and J.ZÁVADA

Institute of Organic Chemistry and Biochemistry,
*Czechoslovak Academy of Sciences, 166 10 Prague 6*

Olefin isomer composition from elimination of five 2-decyl derivatives (*I*; X = F, Cl, Br, I and OTs) with potassium tert-butoxide in benzene, tert-butanol and dimethyl sulphoxide was determined in the absence and in the presence of the crown ether *IV*. The effect of leaving group, base association and solvent on orientation was separately inspected on basis of these data and confronted with the variable E2 transition state theory. Applicability of several models proposed previously for the base-association effect was examined on these grounds. It is concluded that steric shielding and also lowering of base strength due to association have to be taken into account in interpretation of orientational changes induced by ionic association of the participating base.

Vast evidence accumulated already in literature[1−5] concerning the effect of base, solvent and leaving group on orientation in *anti*-E2 reactions. Majority of these effects could be interpreted in simple terms of the variable E2 transition state theory[2,3,6]. However, there remain some effects that cannot be explained satisfactorily by the theory and necessitate additional assumptions. Among them, the effects resulting from ionic association of participating alkoxide base deserve particular attention. A strong decrease in values of *trans/cis* ratios[1,7−9] and also, in some instances, an increase in values of Hofmann/Saytzeff ratios[9] was found to be induced by ionic base association in the reaction of non-activated substrates. On the other hand, an increase of the value of *trans/cis* ratio was found to result from the base association in elimination of the β-phenyl-activated analogues[10].

In order to get a further insight into the complex nature of the base-association effect, we have now examined its operation in a wider scale of transition states generated by variation of leaving group (X = F, Cl, Br, I, OTs) and solvent (benzene, tert-butanol and dimethyl sulphoxide) in the reaction of derivatives *I* with potassium tert-butoxide (Scheme 1). Similarly as in our previous studies[1], we employed dicyclohexyl-18-crown-6-ether (*IV*) as a diagnostic tool for the associated base and assessed,

accordingly, the effect of potassium tert-butoxide association on orientation from a comparison of the isomer-olefin composition obtained respectively in the absence and in the presence of *IV*.
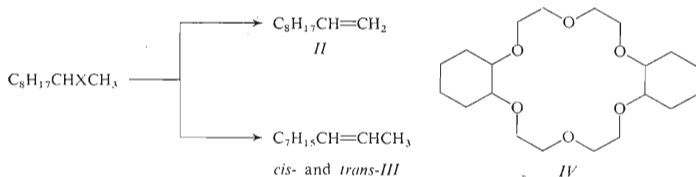
SCHEME 1

Relationship between the effect of base association and leaving group could be examined on these grounds. Validity of alternative models proposed previously[1,4,11,12] for explanation of the base-association effect could be considered.

EXPERIMENTAL

Starting substrates (*I*; X = F, Cl, Br, I, OTS) were prepared by the same procedures[1] as we described previously for the corresponding 5-decyl analogues in 40—70% yields. The crude fluoride (*I*; X = F) was found to contain about 10% of the corresponding chloro derivative (*I*; X = Cl); similar contamination was already noted in a few other instances[13]. The impurity was removed by selective elimination with an excess of 0·2M potassium tert-butoxide in dimethyl sulphoxide (20°C/20 min), followed by the recommended[1] isolation procedure. Purity of the

TABLE I

2-Decyl Halides: Boiling Points and Elemental Analyses

X	B.p., °C/Torr	Formula (m.w.)	Calculated/Found	
			% C	% H
F	80/10	$C_{10}H_{21}F$ (160·2)	74·94 75·20	13·21 13·05
Cl	98/12	$C_{10}H_{21}Cl$ (176·7)	67·95 67·81	11·97 11·82
Br	110/30	$C_{10}H_{21}Br$ (221·2)	54·30 54·21	9·57 9·32
I	120/12	$C_{10}H_{21}I$ (268·2)	44·78 45·02	7·89 7·95

substrates was checked by vapour-phase chromatography. Boiling points and elemental analyses are summarized in the Table I.

Elimination Runs

Olefin isomer composition: Individual substrates (0·5 mmol) were dissolved in an appropriate alkoxide solution and heated under nitrogen in sealed tubes or stirred magnetically in stoppered flasks (reactions in dimethyl sulphoxide). The conditions are summarized in Table II. The con-

TABLE II

Conditions Employed in Elimination Runs

Solvent	Molar ratio base : IV	Concentration mol/l		Temperature °C	Time min
		base	substrate		
C_6H_6	1 : 0	0·13	0·084	130	120
C_6H_6	1 : 1	0·13	0·084	20	20
tert-C_4H_9OH	1 : 0	0·33	0·08	100	120
tert-C_4H_9OH	1 : 1	0·33	0·08	100	120
$(CH_3)_2SO$	1 : 0	0·5	0·25	20	5
$(CH_3)_2SO$	1 : 1	0·5	0·25	20	2

TABLE III

Olefin Formation and Isomerization with tert-C_4H_9OK in Dimethyl Sulphoxide

Substrate	Time min	Isomer composition		
		% 1-decene	% *trans*-2-decene	% *cis*-2-decene
1-Decene	5	98·0	0·2	1·8
	10	95·1	0·3	4·6
	50	82·9	0·9	16·2
	150	61·4	2·5	36·1
I; X = F	5	96·8	2·4	0·8
	10	96·0	2·4	1·6
	50	88·6	2·4	9·0
	150	77·2	4·3	18·5
I; X = Cl	5	59·4	33·9	6·7
	10	58·4	33·9	7·7
	50	54·3	34·4	11·3
	150	46·8	35·0	18·2

tents were transferred into 50 ml volumetric flasks containing pentane (2 ml), 1M hydrochloric acid (10 ml) and saturated solution of sodium chloride (25 ml). The volumes were made up to mark with water, the contents thoroughly shaken and a sample of pentane layer injected into the gas chromatograph.

Stability of products under reaction conditions: Olefin isomer composition resulting from the two most sluggish derivatives *I* (X = F and Cl) and also from the least stable olefin isomer (1-decene) was determined at several time intervals under conditions employed in elimination runs. No substantial isomerization was found in benzene and in tert-butanol, regardless of *IV*. However, a very pronounced isomerization occurred in dimethyl sulphoxide (Table III). As the data in Table III show, isomerization can be neglected, in absence of *IV*, only for the runs quenched after 5 min reaction at 20°C. Similarly, the elimination performed in dimethyl sulphoxide in the presence of *IV* necessitates quenching after 2 min reaction at 20°C in order to avoid substantial isomerization. Less than 2% conversion of the most sluggish derivative (*I*; X = F) could be attained under these conditions.

Vapour phase chromatography: The analyses were performed on the Carlo Erba Fractovap GT4 instrument with a digital integrator employing a 50 m capillary coated with di-n-butyl tetrachlorophthalate at 60°C.

RESULTS AND DISCUSSION

Stereochemical assumptions: According to the available[14−17] evidence, unbranched 2-alkyl derivatives possess extremely low propensity to utilize *syn*-pathway in bimolecular elimination. Even under conditions which are known to favour *syn*-pathway (strong base in low-polar solvent and/or a very poor leaving group), 2-alkyl derivatives were found to react nearly exclusively by *anti*-elimination pathway. It appears therefore justified to discuss the present reactions under assumption of a homogeneous *anti*-elimination course. The overall pattern of the obtained results lends additional support to this assumption.

Variable E2 *transition state theory*: It is assumed in the theory[3,6,18] that the process of loosening the C_β—H and C_α—X bonds, although concerted in E2 reactions, need not exactly balance in transition state. By variation of polar (structural or en-
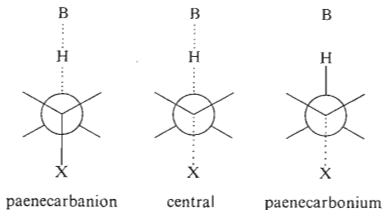

FIG. 1
Individual Transition States

paenecarbanion   central   paenecarbonium

vironmental) influences, either C_β—H or C_α—X bond loosening may progress more in transition state (Fig. 1) and decline thus the strictly synchronous central form towards the paenecarbanion (Elcb-like) form or towards the paenecarbonium (El-like) form. Such changes will become apparent in orientational pattern of the reaction. A gradual shift from Saytzeff orientation (preferential formation of the most alkyl-substituted olefin) to Hofmann orientation (preferential formation of the least substituted isomer) is assumed to be diagnostic for a gradual transition from the paene-carbonium to the paenecarbanion region of transition states. At the same time, a gradual increase of values of *trans/cis* isomer ratios is expected on passing from the paenecarbonium to the central region (where eclipsing alkyl–alkyl interactions due to a more advanced double bond development are more pronounced), followed again by a decrease of the value on going, further on, towards the paenecarbanion extreme.

In the following paragraphs, we shall examine to which extent the present results (Table IV) can be explained by the theory.

Effect of leaving group: As follows from Table IV, very similar trends, as regards the relationship between leaving group and orientation, are found in all the six base–solvent combinations examined. With a single exception (*I*; X = OTs in tert-butanol, in absence of *IV*), the proportion of 1-decene isomer increases always in order of leaving groups I < Br < Cl < OTs < F. The changes in positional orientation are accompanied by very regular changes in geometrical orientation: a gradual decrease of the value of *trans*-2-decene/*cis*-2-decene ratios occurs in most instances simultaneously with increasing the proportion of 1-decene isomer.

These general trends allow us to allocate the relative position of individual transition states in the variable scale (Fig. 1). The distribution of positional isomers in elimination of 2-decyl iodide balances (in presence of *IV*) between Hofmann and Saytzeff orientation, which suggests that the transition state lies in the central region. A gradual, and very pronounced, shift to the Hofmann orientation resulting from substitution the iodo group by other leaving groups may be taken to indicate a corresponding shift towards the paenecarbanion region; for the fluoro group, the transition state has to be already very close to the paenecarbanion extreme.

According to the variable transition state theory, increasing strength of C_α—X bond[2] (I < Br ≦ OTs < Cl < F) as well as increasing electron-withdrawing power[19] of the leaving group (I < Br < Cl < F < OTs) may be instrumental in shifting transition state towards the paenecarbanion side. The present results which show that the Hofmann orientation becomes always (in presence of *IV*) more pronounced in the order of leaving groups I < Br < Cl < OTs < F suggest that both these factors may be of comparable importance.

The accompanying effect of leaving groups on the value of *trans*-2-decene/*cis*--2-decene ratios is in full accord with the proposed location of transition states in the

variable scale. The regular decrease of the value which is found in all the base–solvent combinations examined, on going from the "softest" (iodo) to the "hardest" (fluoro) group, reflects obviously a decreasing importance of eclipsing interactions on passing from the central to the paenecarbanion-like transition state.

Effect of base association: Ionic association of potassium tert-butoxide occurs presumably in majority of solvents[1,4] according to Eq. (*A*), the equilibrium between dissociated and associated forms (*a* and *b*, respectively) being controlled mainly by ion-coordinating ability of the solvent employed. Irrespective of solvent, the ionic association can be suppressed efficiently by equimolar amounts of the crown-ether
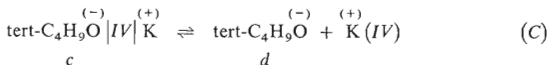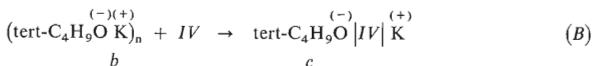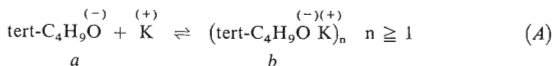
TABLE IV

Olefin Isomer Composition from Elimination of 2-Decyl Derivatives *I* (X = F, OTs, Cl, Br, I) Induced by Potassium tert-Butoxide in the Absence and in the Presence (figures in italics) of the Crown-Ether *IV*, Respectively, in Three Different Solvents

X	% *II*		% *trans-III*		% *cis-III*		*trans-III*/*cis-III*	
				Benzene				
F	94·0	*95·0*	2·0	*2·9*	4·0	*2·1*	0·5	*1·4*
OTs	88·2	*81·8*	4·9	*11·4*	6·9	*6·8*	0·7	*1·7*
Cl	86·0	*70·5*	5·6	*21·8*	8·4	*7·7*	0·7	*2·8*
Br	79·9	*62·2*	8·9	*27·7*	11·2	*10·1*	0·8	*2·7*
I	66·1	*46·5*	20·2	*40·7*	13·7	*12·8*	1·5	*3·2*
				tert-Butanol				
F	92·4	*91·4*	3·5	*6·4*	4·1	*2·2*	0·8	*2·9*
OTs	76·6	*75·4*	7·0	*17·0*	16·4	*7·7*	0·4	*2·2*
Cl	84·5	*64·6*	7·9	*27·8*	7·6	*7·6*	1·1	*3·6*
Br	79·4	*53·3*	11·8	*39·0*	8·8	*7·7*	1·3	*5·1*
I	68·2	*41·6*	20·5	*49·2*	11·3	*9·2*	1·8	*5·4*
				Dimethyl Sulphoxide				
F[a]	96·8	*97·0*	2·4	*2·3*	0·8	*0·7*	3·0	*3·0*
OTs	75·4	*79·1*	18·7	*17·9*	5·9	*3·0*	3·2	*6·0*
Cl	59·4	*58·9*	33·9	*34·8*	6·7	*6·3*	5·1	*5·3*
Br	48·0	*46·9*	43·8	*45·1*	8·2	*8·0*	5·3	*5·7*
I	32·1	*31·0*	57·8	*58·4*	10·1	*10·6*	5·7	*5·5*

[a] Less accurate figures (*cf.* Experimental).

IV, converting (Eqs (*B*) and (*C*)) the ion-associated form *b* into the ion-separated species *c* and/or *d*.

$$\overset{(-)}{\text{tert-C}_4\text{H}_9\text{O}} + \overset{(+)}{\text{K}} \;\rightleftharpoons\; \overset{(-)(+)}{(\text{tert-C}_4\text{H}_9\text{O K})_n} \quad n \geqq 1 \qquad (A)$$
$$\quad\;\; a \qquad\qquad\qquad\qquad b$$

$$\overset{(-)(+)}{(\text{tert-C}_4\text{H}_9\text{O K})_n} + IV \;\rightarrow\; \overset{(-)}{\text{tert-C}_4\text{H}_9\text{O}} \big|IV\big| \overset{(+)}{\text{K}} \qquad (B)$$
$$\qquad b \qquad\qquad\qquad\qquad\qquad c$$

$$\overset{(-)}{\text{tert-C}_4\text{H}_9\text{O}} \big|IV\big| \overset{(+)}{\text{K}} \;\rightleftharpoons\; \overset{(-)}{\text{tert-C}_4\text{H}_9\text{O}} + \overset{(+)}{\text{K}}\,(IV) \qquad (C)$$
$$\qquad\quad c \qquad\qquad\qquad\qquad\qquad d$$

Accordingly, the effect of potassium tert-butoxide association on the geometrical as well as positional orientation in the present reactions can be deduced simply from comparison of the olefin isomer composition data obtained respectively in the absence and in the presence of *IV*.

From Table IV it may be seen that in the majority of compared reactions the proportions of 1-decene are higher and the values of *trans*-2-decene/*cis*-2-decene ratios are lower in the absence of *IV*. The differences are very pronounced only in the low-polar solvents — benzene and tert-butanol. In dimethyl sulphoxide the differences are much smaller, which suggests in accord with previous experience[1,4] that the ion-separated base prevails in the very polar solvent already in absence of *IV*.

The variable transition state theory explains effect of base on orientation solely in terms of base strength[2,3]. It is known that ion-associated tert-butoxide base is much weaker[20] than the ion-separated (dissociated) form. A shift from the paene-carbanion side towards the central region of transition states is predicted[2,3,21] to results from a decrease of strength of participating base. Accordingly, a decrease of the 1-decene proportion and, at the same time, an increase of the value of *trans*-2-decene/*cis*-2-decene ratio would be expected for operation of the associated base form, in exact opposite to the present observation. It appears therefore that another factor which operates in an opposite direction has to be also involved in these reactions and to be strong enough to overcome the effect of base strength.

Several recent proposals have to be taken into account in consideration of the elusive factor. Bartsch suggested[4] that steric hindrance resulting from very large steric bulk of the associated base may be responsible for such outcomes. According to Bartsch's model (Fig. 2, *A*–*C*), the steric hindrance will destabilize only the transition state for *trans*-2-alkene formation *A*; in the arrangement leading to *cis*-2-alkene *B* or to 1-alkene *C* formation, the hindrance can be avoided by tilting out the base to that side where only hydrogens are placed. Alternatively, coordination between

the associated base and leaving group in the transition state was proposed[1,5,11] by Schlosser and us. In a pseudo-cyclic arrangement[5] (Fig. 2, $D-F$) required for the
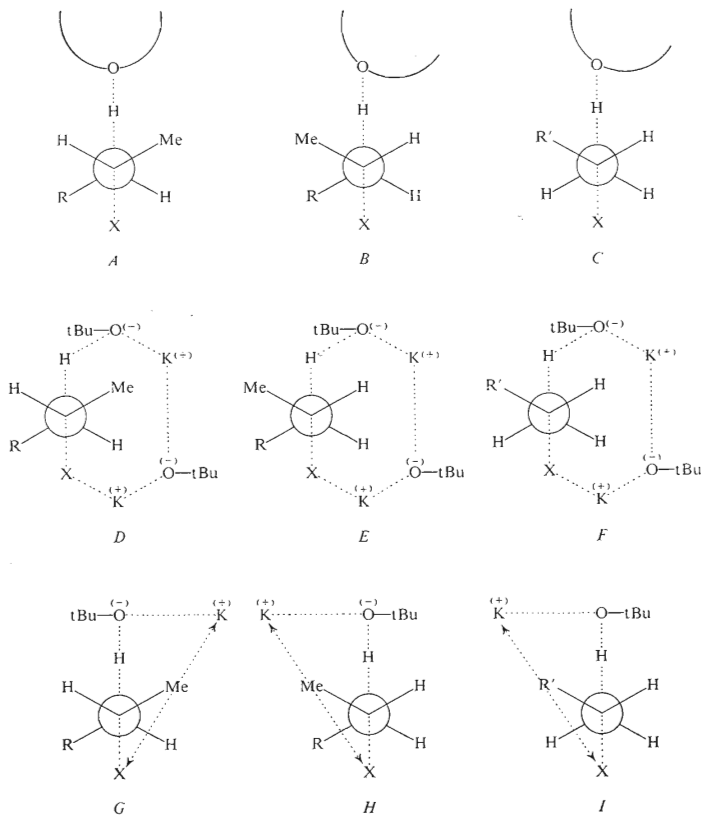

FIG. 2

Operation of $(\text{tert-}C_4H_9O\ K)_n$ in *anti*-Elimination
$n \geqq 2$; *cf.* ref.[23]; $R' = RCH_2$; Me = methyl; t-Bu = tert-butyl.

coordination, steric interactions between base and alkyl portions of substrate would be unavoidable only in the transition state leading to *trans*-2-alkene formation *D*, giving thus opportunity for the other isomers *E* and *F* to prevail. Finally, attractive ion-dipol interactions between cation of the associated base and leaving group operating "through" substrate were suggested by Saunders[12]. It was postulated by Saunders that the base does not avoid alkyl congestion in the substrate, but actually seeks it out as providing the most favourable medium of conduction for its interaction with leaving group. The attractive interactions may operate (Fig. 2, *G–I*) nearly entirely through substrate skeleton in *cis*-2-alkene formation *H* but they have to operate in part through solvent in *trans*-2-alkene *G* and in 1-alkene *I* formation. Accordingly, an increase in proportion of *cis*-2-decene and, simultaneously, a decrease in *trans*-2-decene as well as in 1-decene proportion should be induced by the associated base.

Apparently, the circumstance that proportion of *trans*-2-decene isomer is always significantly lower in the reactions which were induced by the associated base (*i.e.*, in benzene and in tert-butanol in absence of *IV*) is in reasonable accordance with any of the proposals. However, that part of present evidence which shows that only a slight, if any, increase in proportion of *cis*-2-decene isomer results from the operation of the associated base and, moreover, that it is accompanied in most cases by a very pronounced increase in 1-decene formation, disagrees with the Saunders' prediction. Accordingly, the Saunders' model can probably be rejected on these grounds.

Relationship between the base-association effect and leaving group: As a more detailed inspection of the data obtained in benzene and in tert-butanol shows, the effect of base association depends to some extent on the nature of leaving group. A comparable decrease in the proportion of *trans*-2-decene (by a factor 2–3) is induced by the association of participating base for any of the examined leaving group. However, for the iodo, chloro and bromoderivative, this decrease is compensated almost exclusively by a corresponding increase in 1-decene proportion. In contrast, for the fluoride and also for the tosylate (in tert-butanol), the decrease in *trans*-2-decene leads prevalently to an increase in proportion of the corresponding *cis*-isomer.

A plausible explanation of these differences may be given in terms of the variable transition state theory. As we already suggested, lowering of base strength by ion--association should lead to orientational changes in opposite direction than those which would arise from steric shielding in the transition state (Fig. 2; *A–C* or *D–F*). Accordingly, it appears quite reasonable to assume that balance of the opposing effects on 1-decene formation is attained most easily for the substrates which react in the carbanion region (*I*; X = F, OTs). On the other hand, for the substrates which react more closely to the central region of transition states, increasing weight of eclipsing interactions will oppose an increase in *cis*-2-decene proportion.

Effect of solvent: As Table IV shows for any of the examined reactants, the differences in olefin isomer distribution due to solvent are always much greater in the absence of the base-association suppressing agent *IV* which indicates that a major part of the solvent effect on orientation may be attributed to base association. The minor differences which persist in the presence of *IV* may be explained satisfactorily by the variable transition state theory. A change from a polar (or protic) solvent to a non-polar (or aprotic) one is predicted[18] to cause a shift in the scale of transition states towards the carbanion side. Accordingly, the increase in 1-decene proportion and/or the decrease of the value of *trans*-2-decene/*cis*-2-decene ratio which is observed for the majority of the reactions on going from very polar aprotic dimethyl sulphoxide over low-polar and weakly protic tert-butanol to non-polar aprotic benzene appears to be in a reasonable agreement with the theoretical prediction. However, these differences may also be accounted by residual base association: while dissociated tert-butoxide is presumably the sole base species operating in presence of *IV* in dimethyl sulphoxide, ion-paired species separated by *IV* (*c* in Eq. (*B*)) may take part in the corresponding reactions performed in benzene and tert-butanol.

Comments on some related data in literature: Olefin-isomer composition data from elimination of the corresponding 2-hexyl derivatives with potassium tert-butoxide (in absence of *IV*) in tert-butanol and in dimethyl sulphoxide were reported by Bartsch and Bunnett[18,22]. In most instances, agreement with the present data is excellent, the individual difference being usually less than $2-3\%$. However, very different data obtained in dimethyl sulphoxide from 2-hexyl fluoride[22] (81.3% of 1-hexene, 5.3% of *trans*-2-hexene and 13.4% of *cis*-2-hexene) and from 2-decyl fluoride (96.4% of 1-decene, 2.4% of *trans*-2-decene and 0.8% of *cis*-2-decene) represent a striking exception. As we pointed out in the Experimental part, a subsequent isomerization of 1-alkene to *cis*-2-alkene isomer by potassium tert-butoxide in dimethyl sulphoxide is particularly dangerous in elimination of the sluggish fluorides. The data of Table III strongly suggest that the precautions taken by the American authors did not suffice to preclude a sizeable isomerization.

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