

THE EFFECT OF BASE CONCENTRATION ON ORIENTATION
IN E2 REACTIONS: A COMMON FEATURE
IN METAL ALKOXIDE PROMOTED OLEFIN FORMATION
FROM ALKYL HALIDES AND TOSYLATES*

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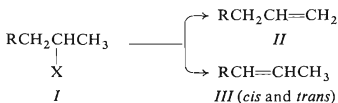
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The title effect has been investigated in the reactions of three 2-butyl (X = I, Br, OTs) and four 2-decyl (X = I, Br, Cl, OTs) derivatives with t-C₄H₉OK/t-C₄H₉OH, t-C₄H₉OK/tetrahydrofuran and t-C₄H₉ONa/t-C₄H₉OH as the base-solvent system. It has been found that a gradual increase of base concentration induces marked changes in positional as well as geometrical orientation by simultaneously increasing the 1-alkene/2-alkene and *cis*-2-alkene/*trans*-2-alkene ratios. The variations in orientation observed for the different substrates and/or base-solvent combinations are very similar. Concentration-dependent competition of dissociated and associated alkoxide species in the reaction or concentration-dependent solvation of leaving group by metal alkoxides are proposed to account for the changes in orientation.

According to the scattered evidence reported previously from the Lubbock and Prague Laboratories¹⁻³ and also by other authors⁴, geometrical and positional orientation sometimes vary significantly as the concentration of the participating base is changed. Now we have conducted a systematic investigation of this effect. In this paper we explore the occurrence of the base concentration effect in the reactions of 2-alkyl halides and tosylates with alkali metal tert-butoxides (Scheme 1).



R = CH₃, n-C₇H₁₅

X = I, Br, Cl, OTs

SCHEME 1

* Part XLIII in the series Elimination Reactions; Part XLII: This Journal 46, 833 (1981).

EXPERIMENTAL

Materials: 2-Halodecanes were prepared as described previously^{5,6}. 2-Butyl and 2-decyl *p*-toluenesulphonates were prepared from the corresponding alcohols by standard procedures.

Solvents: Tert-butanol was refluxed over calcium hydride. After distillation the alcohol contained less than 0.003% of water (K. Fischer). Tetrahydrofuran (Fluka; puriss.) was freshly distilled with clean sodium metal before use.

Base-solvent solutions: Stock solutions of potassium and sodium tert-butoxide in tert-butanol (1.0M and 0.6M, respectively) were prepared by reaction of the clean, freshly cut metal with tert-butanol under reflux and kept in closed flasks under nitrogen. A stock solution of potassium tert-butoxide in tetrahydrofuran (1.0M) was prepared by reaction of clean potassium metal (20% excess) with known amounts of tert-butanol in tetrahydrofuran⁷ (procedure A). Practically identical elimination results were obtained using base solutions prepared by dissolving sublimed or unsublimed potassium tert-butoxide in tetrahydrofuran (procedures B and C, respectively). Solutions required for the concentration study were prepared from the stock solutions by appropriate dilution and the resulting concentrations were checked titrimetrically.

Elimination runs: Reactions of 2-decyl halides and tosylate were carried out in nitrogen-flushed ampoules. Reactions of the 2-butyl analogues were carried out using a nitrogen gas sweep method⁸. Elimination products were analyzed by vapour phase chromatography under conditions previously described^{5,8}.

Control experiments: Within limits of experimental error (0.3%) no isomerisation of the resulting alkenes was observed under the conditions of the elimination runs. Incursion of solvolysis was shown to be negligible in the base-solvent combinations employed in the concentration studies.

RESULTS

The effect of base concentration on orientation in the reaction of the derivatives *I* with potassium tert-butoxide in tert-butanol and in tetrahydrofuran is summarized in Table I. Both positional and geometrical orientation vary with changes in the concentration of the participating base. For any reaction in Table I, the percentage of the terminal alkene *II* gradually increases and the ratio of the internal alkenes *trans-III/cis-III* gradually decreases on increasing the base concentration from 0.1 to 1.0 mol l⁻¹.

Table II shows that the observed effect is almost insensitive to variation of substrate structure. Practically the same changes in the positional (1-alkene : 2-alkene ratios) as well as in the geometrical (*trans*-2-alkene : *cis*-2-alkene ratios) orientation are produced by a ten-fold change of base concentration in the reaction of any derivative *I*, irrespective of alkyl substitution and/or leaving group.

The data contained in Table II also reveal a rather small influence of solvent. Although the olefinic isomer distributions for the reactions performed in tert-butanol and in tetrahydrofuran differ markedly, changes in the orientation due to base concentration in the two solvents are very similar.

Table III summarizes the effect of base concentration on orientation in the reaction of 2-decyl bromide promoted by sodium tert-butoxide in tert-butanol. A comparison with the results obtained in the corresponding reaction with potassium tert-butoxide (Table I) shows that base concentration effects for the two different counterions are almost identical.

DISCUSSION

Evidence from control experiments and from previous studies^{3,9,10} demonstrate that solvolysis is absent under the conditions of this study. Therefore, the observed influence of base concentration does not arise from an E1–E2 competition, but represents an intrinsic feature of the base promoted reaction.

TABLE I

Effect of Base Concentration on Orientation in $t\text{-C}_4\text{H}_9\text{OK}$ Promoted Elimination of Derivatives I in Two Different Solvents

$t\text{-C}_4\text{H}_9\text{OK}$ Molarity	X = I		X = Br		X = Cl		X = OTs	
	% II	$\frac{t\text{-III}}{c\text{-III}}$	% II	$\frac{t\text{-III}}{c\text{-III}}$	% II	$\frac{t\text{-III}}{c\text{-III}}$	% II	$\frac{t\text{-III}}{c\text{-III}}$
Tert-Butanol (R = CH_3) ^a								
0.10	24.4	2.36	37.7	1.86	<i>b</i>	<i>b</i>	52.9	0.70
0.25	28.6	2.14	41.6	1.78	<i>b</i>	<i>b</i>	60.4	0.37
0.50	29.9	2.09	44.1	1.66	<i>b</i>	<i>b</i>	62.9	0.35
1.00	33.3	1.95	50.6	1.47	<i>b</i>	<i>b</i>	63.5	0.39
Tert-Butanol (R = $n\text{-C}_7\text{H}_{15}$) ^c								
0.10	66.7	1.89	77.0	1.44	83.1	1.17	76.7	0.36
0.25	68.8	1.81	76.5	1.37	84.0	1.11	78.7	0.30
0.50	69.7	1.78	79.7	1.25	84.5	1.10	79.9	0.28
1.00	74.5	1.68	84.1	1.12	87.2	1.00	81.8	0.24
Tetrahydrofuran (R = $n\text{-C}_7\text{H}_{15}$) ^a								
0.10	36.3	5.51	52.5	4.86	66.2	4.04	83.2	1.47
0.25	37.5	5.44	54.0	4.61	69.5	3.48	84.1	1.30
0.50	39.5	5.30	55.6	4.09	70.5	3.15	84.5	1.18
1.00	42.2	4.90	58.8	3.72	72.8	2.36	85.7	1.10

^a At 50°C; ^b not determined; ^c at 120°C.

As we have suggested^{1,2}, such an effect can arise in E2 reactions from ionic association of the participating alkoxide base. Ample evidence has been presented^{2,3,5} that the dissociated and the associated species of potassium tert-butoxide follow very different patterns of orientation in reactions with the 2-butyl and also 2-decyl derivatives *I*. The former base species favour *trans*-2-alkene whereas the latter facilitates 1-alkene and *cis*-2-alkene formation. A competition of the two base species* can therefore explain the observed effect of base concentration on orienta-

TABLE II

Influence of Substrate Structure and Solvent upon the Effect of Base Concentration in the Reaction of 2-Decyl and 2-Butyl (figures in parentheses) Derivatives *I* with Potassium Tert-Butoxide

X	(1-Alkene/2-Alkene) _{0.1M/1M}		<i>(trans</i> -2-Alkene/ <i>cis</i> -2-Alkene) _{0.1M/1M}	
	t-C ₄ H ₉ OH	Tetrahydrofuran	t-C ₄ H ₉ OH	Tetrahydrofuran
I	0.68 (0.64)	0.77	1.12 (1.21)	1.12
Br	0.63 (0.59)	0.77	1.28 (1.26)	1.30
Cl	0.72 (^a)	0.73	1.17 (^a)	1.71
OTs	0.73 (0.64)	0.83	1.50 (1.79)	1.18

^a Not determined.

TABLE III

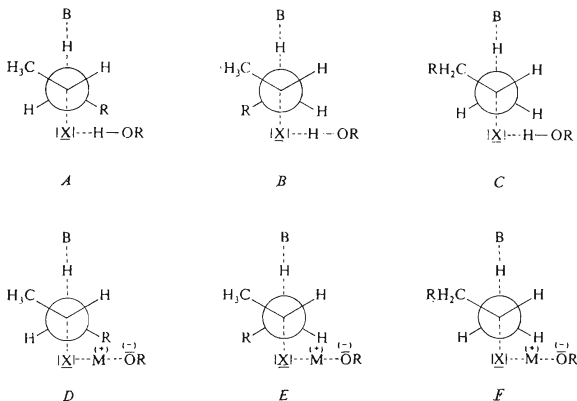
Effect of Base Concentration on Orientation in the Reaction of 2-Decyl Bromide with Sodium Tert-Butoxide in Tert-Butanol at 120°C

Base molarity	% 1-Decene	<i>trans</i> -2-Decene
		<i>cis</i> -2-Decene
0.05	71.4	1.42
0.14	73.1	1.30
0.27	74.1	1.30
0.53	76.2	1.07

* In accordance with the previous convention (ref.³, footnote 16) alkoxide anions, separated ion pairs and ion triplets are referred to as the dissociated base species, whereas contact ion pairs and their oligomers are considered to be the associated base species.

tion because it is anticipated¹ that the competition should be concentration dependent, with the contribution of the associated base in the reaction being enhanced by increases in the total base concentration.

However, since no direct evidence has been provided to date which supports such a base species competition* in reactions similar to those involved in the present study, another explanation for the changes in orientation must also be considered. It has been demonstrated^{9,10} that solvation of leaving groups by hydrogen bonding markedly lowers the *trans/cis* ratios in elimination from alkyl tosylates and halides performed in protic solvents or in the presence of protic additives. Steric interference between the protic solvate and the alkyl portion of the substrate is assumed¹⁰ to be the responsible factor which selectively disfavours the *trans*-alkene formation (Scheme 2; *A*). For the formation of *cis*-alkenes and of 1-alkene, the interference can be avoided by solvating the leaving group from that side where only hydrogen substituents are located (Scheme 2; *B* and *C*, respectively). Conceivably, a quite analogous situation may arise from solvation of the leaving group by a metal alkoxide (Scheme 2; *D–F*) since a pronounced propensity of alkali metal cations for coordination with electron donors is known¹². Such solvation could produce the observed changes in orientation since the coordination between leaving group



SCHEME 2

* Baciocchi and his colleagues suggest that a competition between ion pairs and ion-paired aggregates should be also taken into account; ref.¹¹.

and metal alkoxide should increase in importance with enhancement of the base concentration.

Viability of these two alternative proposals will be examined in the forthcoming paper¹³.

REFERENCES

1. Závada J., Svoboda M.: *Tetrahedron Lett.* 1972, 23.
2. Bartsch R. A., Pruss G. M., Buswell R. L., Bushaw B. A.: *Tetrahedron Lett.* 1972, 2624.
3. Bartsch R. A., Pruss G. M., Cook D. M., Buswell R. L., Bushaw B. A., Wiegers K. E.: *J. Amer. Chem. Soc.* 95, 6745 (1973).
4. Baciocchi E., Corsano S., Ruzziconi R.: *J. Chem. Soc., Perkin Trans. 2* 1977, 436.
5. Pánková M., Závada J.: *This Journal* 42, 1981 (1977).
6. Závada J., Pánková M., Svoboda M.: *This Journal* 41, 3778 (1976).
7. Lochman L., Čoupek J., Lím D.: *This Journal* 35, 733 (1970).
8. Bartsch R. A.: *J. Org. Chem.* 35, 1334 (1970).
9. Závada J., Pánková M.: *This Journal* 42, 3421 (1977).
10. Pánková M., Závada J.: *This Journal* 42, 2161 (1977).
11. Alunni S., Baciocchi E., Perucci P.: *J. Org. Chem.* 41, 2636 (1975).
12. Poonia N. S., Bajaj A. V.: *Chem. Rev.* 79, 389 (1979).
13. Závada J., Pánková M., Vitek A.: *This Journal*, in press.

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