

STEREOCHEMICAL STUDIES. LXX.*

THE ROLE OF BASE ION-PAIRING IN BIMOLECULAR ELIMINATION:
THE EFFECT OF A BASE COUNTERION ON THE STERIC COURSE**

M.SVOBODA and J.ZÁVADA

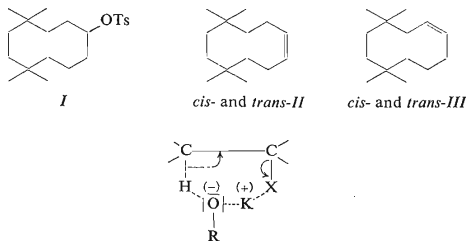
*Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, Prague 6*

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The effect of base counterion (Na^+ , K^+ , Rb^+ , $\text{N}^+(\text{CH}_3)_4$) on the steric course of bimolecular elimination has been investigated in the reaction of the medium-ring tosylate *I* with tert-butoxide in tert-butanol. A gradual decrease in the resulting *trans*- to *cis*-olefin ratios has been found on going from sodium to heavier alkali metal cations and, much more pronouncedly, on going to the tetramethylammonium cation. It is suggested that the different ion-pairing ability of the cations investigated is responsible for the observed differences.

In preceding paper¹ we have shown that a variation of the base concentration can exert a substantial effect on the steric course of bimolecular elimination and pointed out that ion-pairing of the base is the responsible factor. We now report closely related observation indicating that similar effect can be induced by changes of the base counterion.

We have investigated the effect of cation on the steric course of elimination in the reaction of 1,1,4,4-tetramethyl-7-cyclodecyl tosylate (*I*) with tert-butoxide in tert-



SCHEME 1

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** This is the twenty-fourth of a series of papers dealing with elimination reactions; for previous paper see ref.¹.

butanol, using sodium, potassium, rubidium and tetramethylammonium cation as a counterion of the base. As follows from the data of Table I, a considerable decrease of *trans*- to *cis*-olefin ratio has been found for olefin II on going from sodium cation to the heavier alkali metal ion; a much more pronounced decrease has been found with tetramethylammonium cation. Similar, but not so marked trend has been found for the corresponding ratios of the position isomers *trans*- and *cis*-III.

Bimolecular elimination of the tosylate I is known to proceed in a unique fashion^{2,3}, the *trans*-olefins (*trans*-II and *trans*-III) being formed mainly by *syn*-elimination, and the *cis*-olefins (*cis*-II and *cis*-III) by *anti*-elimination, regardless of the reaction conditions as well as the base counterion used. Hence, the observed *trans*- and *cis*-olefin proportions correspond directly to the proportions of the *syn*- and *anti*-processes, respectively, and the differentiating effect of the counterion on the two distinct mechanisms can be deduced immediately from the observed trends in the *trans/cis* ratios.

TABLE I
Effect of the Base Counterion on the *trans*- to *cis*-Olefin Ratio

Cation	II			III		
	% <i>trans</i>	% <i>cis</i>	<i>trans/cis</i>	% <i>trans</i>	% <i>cis</i>	<i>trans/cis</i>
+ Na	77.7	1.5	52	10.4	10.4	1.0
+ K	74.3	3.1	24	11.2	11.4	0.98
+ Rb	73.7	4.4	17	10.7	11.2	0.95
+ N(CH ₃) ₄ ^a	24.4	53.5	0.46	3.3	18.8	0.18

^a At 50°C/27 h.

Two interrelated factors can be invoked to account for the observed data. First, the organizing ability of the cation^{1,3-7} has to be considered. We suggested^{1,5} previously that the ion-pairing of potassium cation with tert-butoxide anion and, simultaneously, with the leaving group (Scheme 1) can afford a substantial support for promoting the *syn*-process in eliminations of halides⁵ and tosylates^{1,3}. In contrast, we gave some evidence indicating that the bulky tetramethylammonium cation⁵ is capable to afford only a meagre, if any, support to the *syn*-process in these reactions. Similar conclusions have been drawn recently by Hunter and Shearing⁷ from the study of the steric course of E1cB reactions suggesting that the organizing capacity of the counterion decreases in order Li⁺ > K⁺ > Cs⁺ > N⁺Me₄, in excellent agreement with the present results.

However, another factor may also be responsible for these observations. As follows from conductivity measurements, sodium tert-butoxide⁸ exists predominantly or almost exclusively in the ion-paired form in tert-butanol; a somewhat more pronounced dissociation has been found on going to the more bulky potassium⁹ counterion. In contrast, tetraalkylammonium tert-butoxide⁸ appears to be prevalently dissociated in the same solvent. Hence, it is in accord with this as well as previous evidence¹ to assume that both the ion-paired and the dissociated base can take part in the elimination reaction. Then, it has to be the ion-paired base that is responsible for the greater part of the reaction, if an alkali metal counterion is involved, and exploits preferentially (though not perhaps exclusively) the *syn*-mechanism leading to the *trans*-olefin formation. On the other hand, the dissociated base can be assumed to be of an overwhelming importance in reaction involving the tetramethylammonium counterion and to utilise preferentially the *anti*-mechanism leading to the *cis*-olefin formation.

EXPERIMENTAL

Alkoxide solutions: Clean alkali metals were dissolved under nitrogen in the dry tert-butanol. Tetramethylammonium tert-butoxide was prepared a) by dissolving the syrupous tetramethylammonium hydroxide in tert-butanol and subsequent careful drying over molecular sieves (3 Å), or b) by shaking the finely powdered tetramethylammonium chloride with potassium tert-butoxide in tert-butanol for 2 days. Identical results were obtained in the elimination runs using the base prepared by any of the two procedures.

Elimination runs: A solution of tosylate (50 mg) in 0.3M solution of the alkoxide (2.5 ml) was heated under nitrogen in sealed tubes at 100°C for 11 hours. After usual work-up the olefin composition (Table I) was determined by vapour phase chromatography².

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