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THE ROLE OF BASE ION-PAIRING IN BIMOLECULAR ELIMINATION: THE EFFECT ON THE CIS- TO TRANS-OLEFIN RATIOS IN THE ANTI- AND THE SYN-PATHWAY[1]

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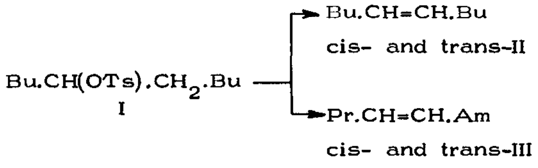
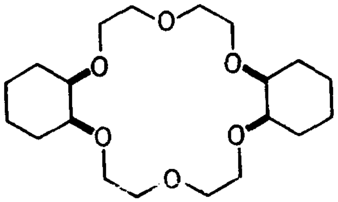
Macrocyclic polyethers[2] (crown ethers) are known to fill effectively the coordination sites of alkali metal cations and convert contact ion-pairs into separated ions[3-5]. It makes the crown ethers a very valuable tool for elucidation of ion-pairing effects: in bimolecular elimination, an evidence[6] on the operation of contact and separated ions of a participating base can be drawn from a comparison of the steric results obtained in the reaction performed with the "plain" and the ether-complexed base, respectively.

By this procedure, we demonstrated previously[6] that both the separated as well as the contact ions of potassium tert-butoxide take part in the reaction with medium-ring tosylates and exploit different mechanistic channels, the former preferring anti- but the latter syn-elimination. In this paper we wish to report an evidence that in the analogous reaction of a simple open-chain tosylate (I) the separated as well as the contact ions of the participating base utilise predominantly a single, anti-mechanistic pathway but, nonetheless, with strikingly different results, the former preferring trans- whereas the latter cis-olefin formation.

We have now investigated the effect of dicyclohexyl-18-crown-6-ether[2] (IV) on the trans- to cis-olefin ratio[7] (trans-II and trans-III/cis-II and cis-III) in the reaction of 5-decyl tosylate (I) with potassium tert-butoxide (Scheme 1) in three solvents of a very different ion-pairing capacity (benzene, tert-butanol and dimethylformamide) and the results summarised in TABLE 1.



Scheme 1



IV

It is immediately apparent from these data that the crown ether IV exerts a very substantial effect on the course of the reactions performed in the low polar solvents benzene and tert-butanol and leads to a complete reversal of the trans- to cis-olefin ratio. On the other hand, none effect at all was induced by addition of IV

TABLE 1 trans- to cis-Olefin Ratios (trans-4- and 5-Decene/cis-4- and 5-Decene) in Reaction of 5-Decyl Tosylate with the "Plain" and the Complexed Potassium tert-Butoxide in Different Solvents

Base	Benzene[a]	tert-Butanol[b]	Dimethylformamide[c]
t-BuOK	0.85	0.41	3.16
t-BuOK+IV (1:1)	2.12	2.54	3.16

[a] At 90°C; [b] at 100°C; [c] at 25°C. The reactions were carried out in sealed tubes under nitrogen using about threefold excess of the base (0.33 M). The olefin composition was determined by v.p.c.; the olefins were found to be stable under the conditions used.

in the reaction performed in dimethylformamide. These findings show that the nature of the participating base was changed by the crown ether IV only in the former two solvents; the identity of the steric results obtained in the highly polar solvent dimethylformamide using the "plain" as well as the complexed potassium tert-butoxide can be taken to indicate that an identical base operates[8] in the two reactions and the dissociated base accounts well for this result.

To make the present findings more meaningful, it is necessary to know the contributions of the individual mechanistic pathways participating in the reaction. Previously, we have shown[10,11] that both the anti- and the syn-pathway operate in the reaction of the tosylate I with the "plain" potassium tert-butoxide in benzene, tert-butanol and also in dimethylformamide, and determined, quantitatively, their contributions to the trans- and cis-5-decene formation. Using the same procedure[10,11], we have now accomplished an analogous mechanistic dissection in the corresponding reactions of I with potassium tert-butoxide complexed by IV (1:1) in the former two solvents. The results from the two parallel studies are compared in TABLE 2.

TABLE 2 Contributions (in %) of the syn- and the anti-Pathways to the cis- and trans-5-Decene Formation in Reaction of the Tosylate I with Potassium tert-Butoxide: The Effect of the Crown Ether IV

Conditions[a]	anti-Pathway[b]			syn-Pathway[b]		
	%trans	%cis	trans/cis	%trans	%cis	trans/cis
Benzene	33.6	50.4	0.67	12.4	3.6	3.4
Benzene+IV	63.9	29.2	2.19	4.1	2.8	1.5
t-BuOH	24.8	68.2	0.36	4.2	2.8	1.5
t-BuOH+IV	67.1	26.7	2.51	4.7	1.5	3.1
DMF	73.2	22.6	3.24	2.8	1.4	2.0

[a] cf. footnote a in Table 1; [b] %trans(anti) + %cis(anti) + %trans(syn) + %cis(syn) = 100.

The following facts emerge from the data of Table 2. The anti-elimination is the major process in all the reactions investigated, however, the trans- to cis-olefin ratios in the anti-component, $(\text{trans/cis})^{\text{anti}}$, differ greatly in the individual runs. The cis-olefin formation is pronouncedly favoured by the "plain" base in the solvents benzene and tert-butanol, the values of $(\text{trans/cis})^{\text{anti}}$ being in actual fact considerably lower than unity (0.67 and 0.36, respectively). In contrast, the trans-olefin formation is the more favoured process in the corresponding reactions with the complexed base and also in the reaction with the "plain" base in dimethylformamide, the values of the $(\text{trans/cis})^{\text{anti}}$ ratio here being considerably higher than unity (2.19 - 3.24).

The ion-pairing capacity of the base-solvent combinations investigated can be invoked to account for the observations. In the low polar solvents benzene and tert-butanol the "plain" potassium tert-butoxide is assumed to exist predominantly in form of the contact ion-pairs[5,6,12] On the other hand, the contact ions are known to be greatly disfavoured[6,9,12] in the dipolar aprotic solvent dimethylformamide. More importantly, the contact ions are known to be suppressed[3,5] completely by complexing with an equimolar amount of the crown ether IV and converted into the separated ions. Clearly, then, only the separated ions of potassium tert-butoxide can account for the preferential trans-olefin formation in the reactions with the complexed base in all the solvents investigated and also in the reaction with the "plain" base in the ion-pairs dissociating solvent dimethylformamide[8]. On the other hand, a different species of the base has to be responsible for the opposite results obtained in reactions with the "plain" base in the low-polar solvents benzene and tert-butanol; it follows, therefore, that the contact ions of potassium tert-butoxide should account for the preferential cis-olefin formation.

In contrast to the anti-elimination, both the separated as well as the contact ions of the base prefer the trans-olefin formation in the alternative (minor) syn-pathway, the $(\text{trans/cis})^{\text{syn}}$ ratios being invariantly higher than unity (1.5 - 3.4) in the reaction with the "plain" as well as the complexed base. Concerning the relation between the proportion of syn-elimination and the base-solvent combination used, similar trends may be found in reaction of I as we observed previously in the reaction of the corresponding medium-ring derivative[6]. The proportion of syn-elimination is the greatest in reaction with the "plain" base in the non-polar solvent benzene (16%) and decreases significantly on complexing with the crown ether and/or on going to the more polar solvents. This lends further support to our recent proposal[9,10,13] that the ability of the contact ion-paired cation to coordinate simultaneously with the anion of the base and also with the leaving group affords some support for promoting of syn-elimination.

Summing up, the present results indicate that the contact ions of the participating base operate also in reactions of simple open-chain tosylates and exploit here prevalently anti-pathway. It contrasts sharply with our recent observation[6] that in analogous reactions of a cyclodecyl tosylate the contact ions of the same base exploit almost exclusively the alternative syn-mechanistic pathway. There is an ample evidence available[13,14] that for steric reasons syn-elimination is energetically favoured, but anti-elimination greatly disfavoured in medium-ring derivatives. On the other hand, anti-elimination is more favoured[13,14] than syn-elimination in the corresponding open-chain derivatives. Hence, the different behaviour of the contact ion-paired base in the reaction with the cyclic and the open-chain tosylate can be taken to be a consequence of a very different propensity of the two systems to take part in the alternative syn- and anti-pathway.

The important discovery that in anti-elimination of 5-decyl tosylate the contact ions favour the cis- but the separated ions the trans-olefin formation appears closely relevant to the long-standing problem[11,15-17] concerning the anomalous cis- to trans-olefin ratios in bimolecular elimination. We propose to re-examine the intriguing problem in the subsequent papers.

REFERENCES AND NOTES

1. This is the twenty sixth of a series of papers dealing with mechanism of elimination reactions; for previous paper see ref. 6.
2. C.J. Pederson: J. Am. Chem. Soc. **89**, 7017 (1967).
3. K.H. Wong, G. Konitzer and J. Smid: J. Am. Chem. Soc. **92**, 666 (1970).
4. Both free ions and separated (by the crown ether) ion-pairs can result from such a conversion. For reasons given elsewhere (note 9 in ref. 6) we do not distinguish between the two species and denote both of them as "separated ions".
5. J.N. Roitmann and D.J. Cram: J. Am. Chem. Soc. **93**, 2231 (1971).
6. M. Svoboda, J. Hapala and J. Závada: preceding paper in This Journal.
7. According to v.p.c. analysis the trans- to cis-olefin ratios are practically identical for the position isomers II and III.
8. By contrast, we found previously (ref. 6 and 9) that in the corresponding reaction of a cyclodecyl tosylate with the "plain" potassium tert-butoxide in dimethylformamide operate both the dissociated as well as the contact ions of the base. Presumably, a much greater ability of the cyclic derivative to utilise the contact ion-paired base accounts for the discrepancy.
9. J. Závada and M. Svoboda: This Journal, in press.
10. J. Závada, M. Pánková and J. Sicher: Chem. Comm. 1968, 1145.
11. J. Sicher, J. Závada and M. Pánková: Collection Czechoslov. Chem. Commun. **36**, 3140 (1971).
12. D.J. Cram: "Fundamentals of Carbanion Chemistry", Academic Press, New York 1965.
13. J. Závada, J. Krupička and J. Sicher: Collection Czechoslov. Chem. Commun. **33**, 1393 (1968).
14. J. Sicher and J. Závada: Collection Czechoslov. Chem. Commun. **33**, 1278 (1968).
15. H.C. Brown and R.L. Klimisch: J. Am. Chem. Soc. **87**, 5517 (1965).
16. D.H. Froemsdorf, W. Dowd and K.E. Leimer: J. Am. Chem. Soc. **88**, 2345 (1966).
17. I.N. Feit and W.H. Saunders: J. Am. Chem. Soc. **92**, 1630 (1970).