Tetrahedron Letters No. 1, pp 23 - 26, 1972. Pergamon Press. Printed in Great Britain.

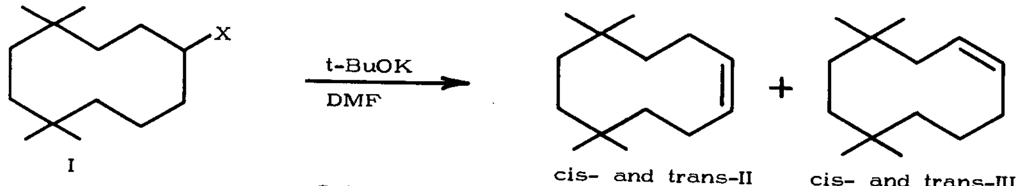
THE ROLE OF BASE ION-PAIRING IN BIMOLECULAR ELIMINATION : EFFECT OF BASE CONCENTRATION ON THE STERIC COURSE[1]

J. Závada and J. Svoboda

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

(Received in UK 22 November 1971; accepted for publication 1 December 1971)

Previously, we have shown that nature of solvent plays a very important role[2-6] in controlling the steric course of bimolecular elimination and suggested that ion-pairing of the participating base is a key factor. In this paper we wish to report further evidence in support of this view and to discuss an unprecedented observation indicating that steric course of bimolecular elimination can be altered pronouncedly by simple variation in concentration of the participating base. The pertinent results were obtained by determination of the isomer olefin composition in reaction of 1,1,4,4-tetramethyl-7-cyclodecyl derivatives with 0.1-1.0M solution of potassium tert-butoxide in anhydrous dimethylformamide (Scheme 1) and are exemplified[7] in TABLE 1 for the reaction of the corresponding tosylate I (X=OTs).



Scheme 1

From these data it is immediately apparent that the values of trans- to cis-olefin ratio (trans-II/cis-II and trans-III/cis-III) are not concentration-independent, but undergo a regular[8] and rather pronounced decrease with decreasing concentration of the base. About twofold decrease of these values is a net result of a tenfold lowering in the base concentration, both for isomer II and III.

An incursion of solvolytic elimination might be suspected to cause such changes; however, a comparison of the olefin composition data for the reactions performed in the presence of the base and those obtained in reaction with dimethylformamide alone[9] (last entry of Table 1) excludes this possibility.

TABLE 1

Effect of Base Concentration on the trans- to cis-Olefin Ratio in Reaction of the Tosylate I (X=OTs) with Potassium tert-Butoxide in Dimethylformamide

t-BuOK [a]	II %trans	 %cis	 trans/cis	III %trans	 %cis	 trans/cis
1.0M	47.7	36.5	1.31	3.8	12.0	0.32
0.8M	45.8	39.2	1.17	3.0	12.0	0.25
0.5M	42.1	41.8	1.01	3.0	13.1	0.23
0.2M	36.6	46.2	0.79	2.5	14.7	0.17
0.1M	34.3	47.2	0.73	2.4	16.1	0.15
0.0M[b]	73.6	1.3	56.6	15.3	9.8	1.56

[a] Concentration of the tosylate was kept approximately constant (about 0.02M). The reaction mixtures were heated under nitrogen at 25°C/20 h. The product composition was determined by vapour phase chromatography[6]. [b] Solvolysis[9] in dimethylformamide.

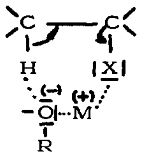
Hence, it has to be indeed the bimolecular elimination which accounts for these changes and an element of heterogeneity involved in this process has to be the responsible factor. We gave an ample evidence previously indicating that bimolecular elimination is frequently a heterogenous process being a blend of syn- and anti-processes[2-6,10,11] and pointed out that the two distinct mechanisms operate in the present system I in an exceptionally clear-cut manner[6,10], the syn-mechanism leading, exclusively, to the trans-olefin formation (trans-II and trans-III) but the anti-mechanism to the cis-olefin formation (cis-II and cis-III), again predominantly or perhaps exclusively. However, such a mechanistic duality does not suffice[12] to account for the observed changes, for, as a simple consideration immediately shows, contributions of the two bimolecular processes should be - other things being equal - concentration-independent. It follows, therefore, that the base has to be responsible and to be altered, gradually, by the concentration changes.

Ion-pairing of the base affords the most plausible explanation for such a behaviour. Although no direct evidence is available concerning the ion-pair - free ions equilibrium for potassium tert-butoxide in dimethylformamide, it follows from general principles[13] that, in the present case, the equilibrium should be concentration-dependent, the proportion of the dissociated base being increased by gradual lowering of the total base concentration.

Clearly, then, the present results can be viewed as a consequence of the simultaneous operation of the dissociated and ion-paired species of potassium tert-butoxide differing in their propensity to take part in the alternative anti → cis and syn → trans processes: under such circumstances, the concentration-dependent ratio of the two reactive species accounts immediately for the observed variation in the trans- to cis-olefin ratios.

As data of Table 1 show, it is the anti → cis process which predominates considerably at lower concentrations (up to 0.8M) of the base and has to be, consequently, accounted for by the dissociated base. On the other hand, it is the syn → trans process which gains on importance by increasing the base concentration and becomes prevailing at 1.0M concentration; this has, by the same tenets, to be accounted for by the ion-paired base.

Thus, the present findings suggest strongly that both the dissociated and ion--paired potassium tert-butoxide take part in the reaction simultaneously, the former preferring strongly anti- and the latter syn-elimination. Moreover, as the anti → cis and syn → trans processes are rather equally represented in this reaction (Table 1), the present findings can be taken to imply that the contributions of the dissociated and ion-paired base are also comparable[14]. There is, however, an evidence available suggesting that the basicities of dissociated and ion-paired potassium tert-butoxide are very different[15], the former being at least by three powers of ten stronger base than the latter. Furthermore, the dissociated base can be assumed to prevail greatly[16] over the ion-paired base under present conditions. Hence, a question poses itself, namely, what makes the ion-paired base capable to compete so successfully in this reaction. We have suggested previously[3] that ion-pairing of the base cation might afford a substantial support for syn-elimination, the pairing of the cation with both the alkoxide anion as well as the leaving group being a driving force (Scheme 2). The present findings suggest that it is indeed so: therefore, it may well be the coordinating ability of the cation that promotes so effectively the reactivity of the ion-paired base.



X = e.g. OTs or halide

Scheme 2

REFERENCES and NOTES

1. This is the twenty third of a series of papers dealing with the mechanism of elimination reactions; for previous paper see ref.[2].

2. J. Závada, M. Pánková, J. Sicher: Collection Czechoslov. Chem. Commun. in press.

3. J. Závada, J. Krupička, J. Sicher: Collection Czechoslov. Chem. Commun. **33**, 1393 (1968).

4. J. Závada, M. Pánková, J. Sicher: Chem. Comm. 1968, 1145.

5. J. Sicher, J. Závada: Collection Czechoslov. Chem. Commun. **33**, 1278 (1968).

6. M. Svoboda, J. Závada, J. Sicher: Collection Czechoslov. Chem. Commun. **33**, 1415 (1968).

7. Very similar results were also obtained for the corresponding bromide (I, X=Br).

8. The decrease in the trans- to cis-olefin ratio becomes less regular and the results less reproducible on further lowering the base concentration (0.05-0.01M). This might be caused by incomplete exclusion of air and/or moisture from the reaction mixtures.

9. M. Svoboda, J. Závada, J. Sicher: Collection Czechoslov. Chem. Commun. **32**, 2104 (1967).

10. J. Závada, M. Svoboda, J. Sicher: Collection Czechoslov. Chem. Commun. **33**, 4027 (1968).

11. M. Pánková, J. Závada, J. Sicher: Chem. Comm. 1967, 394.

12. In actual fact, the mechanistic duality appears to be neither sufficient nor entirely necessary condition for such an effect. It will be pointed out in subsequent papers that analogous effects might, in principle, operate even within a homogeneous (anti- or syn-) process.

13. M. Szwarc: "Carbanions, Living Polymers and Electron Transfer Processes", p. 265; Interscience Publishers, New York, N.Y. 1968.

14. Obviously, the present findings do not exclude that the dissociated base contributes also to the syn-process and, on the other hand, the ion-paired base to the anti-process.

15. D. Bethell, A.F. Cockerill: J. Chem. Soc. B, 1966, 913.

16. A.J. Parker: "The Use of Dipolar Aprotic Solvents in Organic Chemistry" in the books "Advances in Organic Chemistry: Methods and Results", Vol. 5 (Eds. R.A. Raphael, E.C. Taylor, H. Wynberg), Interscience Publishers, New York, N.Y. 1965.