Tetrahedron Letters No. 26, pp 2621 - 2624, 1972. Pergamon Press. Printed in Great Britain.

THE ROLE OF BASE ASSOCIATION IN BASE-PROMOTED β-ELIMINATIONS FROM 2-ALKYL HALIDES AND ARENESULFONATES

Richard A. Bartsch*, Gerald M. Pruss, Richard L. Buswell, and Bruce A. Bushaw
Department of Chemistry, Washington State University, Pullman, Washington 99163

(Received in USA 1 May 1972; received in UK for publication 22 May 1972)

The factors which control positional and geometrical orientation[1] in base-promoted β-eliminations from 2-alkyl halides and arenesulfonates have been the subject of numerous investigations in recent years.[2] We wish to report a heretofore unexpected effect of base association.

Olefin products observed in reactions of 2-butyl bromide and p-toluenesulfonate with t-BuOK-t-BuOH and t-BuONnPr$_4$-t-BuOH are recorded in the Table. It is immediately evident from these results that positional and geometrical orientation are dependent upon base concentration for reactions of 2-bromobutane with t-BuOK-t-BuOH (Expt. 1-4). Increase in the base concentration affords a higher percent of 1-butene and lower trans-:cis-2-butene ratio.[5] In contrast, the relative proportions of isomeric butenes are unaffected by variation of the base concentration in reactions of 2-bromobutane with EtOK-EtOH and t-BuOK-DMSO.[6]

Under the reaction conditions which were employed for the reaction with t-BuOK-t-BuOH, formation of butenes by solvolysis of 2-butyl bromide in t-BuOH is negligible.[6] This precludes conceivable explanations for the effect of base concentration upon orientation which involve concomitant solvolytic and base-induced eliminations.

The most reasonable interpretation of these observations is an effect of base association upon orientation in solvents of low polarity. In a solvent of such low dielectric constant as t-BuOH (ϵ = 8.5 at 50°)[7] and at base concentrations of 0.1-1.0 M, t-BuOK undoubtedly exists to a very large extent as ion pairs and aggregates of ion pairs. Nevertheless, even a small concentration of free t-butoxide ions could compete effectively as the elimination-inducing species because of the much greater basicity of the dissociated base in t-BuOH.[8] The equilibrium between dissociated and associated t-BuOK should be concentration dependent with the proportion of associated base being enhanced by increases in the total base concentration.[9] It is proposed that the changes in orientation which attend increases in the base concentration for reactions of 2-bromobutane with t-BuOK-t-BuOH (Expt. 1-4) result from a greater proportion of the elimination being induced by the associated base when the total base concentration is increased.[10] If this hypothesis is correct, a lower percent of 1-butene and a higher trans-:cis-2-butene ratio should result from an increase in the proportion of the dissociated base. For reactions of 2-bromobutane with t-BuOK-t-BuOH in the presence of the crown ether[12] dicyclohexyl-18-crown-6 (Expt. 5) or with t-BuONnPr$_4$-t-BuOH[13] (Expt. 6), the proportion of dissociated base should be markedly increased over that for t-BuOK-t-BuOH. As can be seen from the data in the Table, the predicted changes in orientation occur.

The results presented in the Table (Expt. 7 and 8) also strongly implicate base association as the causative factor for the trans-:cis-2-alkene ratios of less than unity which have been reported for reactions of 2-alkyl arenesulfonates with t-BuOK-t-BuOH.[14,15]

Thus, dramatic differences in orientation are observed for reactions of 2-butyl bromide and p-toluenesulfonate with associated and dissociated t-BuOK in t-BuOH. These differences may be readily rationalized in terms of existing steric theories of orientation[14,16] when the large steric requirements of the associated base (aggregates of ion pairs) are considered.

TABLE

Olefinic Products in Eliminations from 2-Butyl Bromide and *p*-Toluenesulfonate at 50°.

Expt.	X of 2-BuX[a]	Base-Solvent	[Base]	% 1-Butene	*trans*-2-Butene / *cis*-2-Butene
1	Br	*t*-BuOK-*t*-BuOH	1.0	50.6	1.47
2	Br	*t*-BuOK-*t*-BuOH	0.5	44.1	1.66
3	Br	*t*-BuOK-*t*-BuOH	0.25	41.6	1.78
4	Br	*t*-BuOK-*t*-BuOH	0.1	37.7	1.86
5	Br	*t*-BuOK-*t*-BuOH[b]	0.5	32.5	2.92
6	Br	*t*-BuON*n*Pr$_4$-*t*-BuOH[c]	0.25	31.3	3.00
7	$OSO_2C_6H_4$*p*-CH_3	*t*-BuOK-*t*-BuOH	0.5	63.5	0.40
8	$OSO_2C_6H_4$*p*-CH_3	*t*-BuOK-*t*-BuOH[b]	0.5	53.6	1.88

[a] [2-BuX] = 0.1 M. [b] Dicyclohexyl-18-crown-6 (0.3 M) present. [c] Prepared by mixing 0.25 M *t*-BuOK-*t*-BuOH with an appropriate amount of *n*Pr$_4$NBr. Glpc analysis of the reaction products revealed the presence of a compound with greater volatility than butenes which was assumed to be 1-propene produced by a competitive base-induced elimination from the tetra-*n*-propyl ammonium ion. In view of the low basicity of *n*Pr$_3$N compared to *t*-BuOK, this side reaction should not seriously influence the butene-forming elimination.

REFERENCES AND FOOTNOTES

(1) Positional orientation refers to the relative proportions of 1- and 2-alkenes formed; whereas geometrical orientation compares the relative amounts of *trans*-2-alkene and *cis*-2-alkene produced.

(2) See references 3 and 4 and publications cited therein.

(3) R. A. Bartsch, C. F. Kelly, and G. M. Pruss, *J. Org. Chem.*, **36**, 662 (1971).

(4) I. N. Feit and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 1630 (1970).

(5) No change in orientation was noted for variation of the concentration of 2-bromobutane (0.1, 0.25, 0.5 M) in reactions with 1.0 M *t*-BuOK-*t*-BuOH.[6]

(6) R. A. Bartsch, G. M. Pruss, R. L. Buswell, and B. A. Bushaw, unpublished data.

(7) R. C. Weast, "Handbook of Chemistry and Physics", 48th ed., The Chemical Rubber Co., Cleveland, Ohio, 1967, p. E-57.

(8) D. Bethell and A. F. Cockerill, *J. Chem. Soc. B*, 913 (1966).

(9) J. Zavada and J. Svoboda, *Tetrahedron Lett.*, 23 (1972).

(10) An explanation involving competition between dissociated and ion-paired base species in *syn*- and *anti*-elimination pathways has recently been advanced by Zavada and Svoboda in order to interpret the base dependence of orientation in reactions of 1,1,4,4-tetramethyl-7-cyclodecyl *p*-toluenesulfonate with *t*-BuOK in DMF.[9] An important difference between the reactions studied by Zavada and Svoboda and those in the present investigation is the exclusive *anti*-elimination stereochemistry which is observed in base-promoted eliminations from 2-bromobutane.[11]

(11) R. A. Bartsch, *J. Amer. Chem. Soc.*, **93**, 3683 (1971).

(12) Crown ethers complex strongly with potassium ions. See C. J. Pederson, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(13) Benzyltrimethylammonium *t*-butoxide is dissociated to a much greater extent than is *t*-BuOK in *t*-BuOH.[8]

(14) H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, **87**, 5517 (1965).

(15) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 1376 (1969).

(16) H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, **88**, 1425 (1966).