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SELF-SOLVATING BASES FOR 1,2-ELIMINATION REACTIONS

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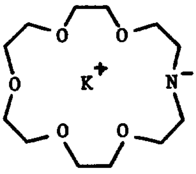
A pronounced effect of base association upon positional and geometrical orientation in base-promoted 1,2-eliminations from 2-alkyl halides and arenesulfonates has recently been recognized.[1,2] In solvents of low polarity, association of an anionic base with its alkali metal cation yields base species which produce an enhanced proportion of 1-alkene and a lower *trans*-2-alkene:*cis*-2-alkene ratio when compared with the same base in dissociating solvents. For example, in eliminations from 2-bromobutane promoted by 1.0 M *t*-BuOK, the relative proportion of 1-butene is elevated from 30% to 50% and the *trans*-2-butene:*cis*-2-butene ratio decreases from 2.99 to 1.47 as the solvent is changed from dimethyl sulfoxide (DMSO) to *t*-BuOH[1]. Such changes in orientation have been attributed to the large steric requirements of the associated base species.[1] For reactions with *t*-BuOK-*t*-BuOH, addition of an appropriate crown ether apparently converts the associated base to a dissociated one since the elimination orientation becomes very similar to that observed with *t*-BuOK-DMSO.[1]

Using orientation in base-promoted 1,2-eliminations as a probe, we have undertaken a search for anionic bases in which the basic atoms remain unassociated from their alkali metal counterions even in solvents of low polarity. We now report that bases 1[3] and 2, which are generated by treating Carbowax 350 methoxy polyethyene glycol[5] and monoaza-18-crown-6[6] with KH, function in this manner.

$CH_3(OCH_2CH_2)_{7-8}OK$

1



2

Table 1 records the relative proportions of olefinic products observed in reactions of 2-iodobutane with five anionic bases in DMSO and in toluene. Manifestation of base association in toluene is clearly evident for the first three entries. In marked contrast, positional orientation for bases 1 and 2 is constant in DMSO and toluene and the *trans*-2-butene:*cis*-2-butene ratios are high. These results demonstrate that the active bases in the reactions employing 1 and 2 are species in which the basic atoms are not ion-paired, even in toluene. Coordination of potassium ions by the ether oxygens of 1 and within the macrocyclic cavity of 2 seems most reasonable. Such coordination of these "self-solvating" bases also produces high solubility in solvents of

Table 1. Orientation in Reactions of 2-Iodobutane[a] with Bases at 50°.

	DMSO Solvent		Toluene Solvent	
Base	% 1-Butene	*Trans*-2-Butene: *cis*-2-Butene	% 1-Butene	*Trans*-2-Butene: *cis*-2-Butene
t-BuOK[b]	20[c]	3.5[d]	36[e]	1.7
Et_3COK[b]	21	3.8	47[e]	1.8
$CH_3(CH_2)_{17}OK$	18	3.1	29[e]	2.6
1	19	3.4	20	3.7
2	22	3.0	21	3.8

[a] [RI]=0.10 M., [Base]=0.25 M. [b] Reference 7. [c] Estimated uncertainty ± 1%. [d] Estimated uncertainty ± 0.15. [e] [Base]=saturated solution.

low polarity.[4] Concentrated (3.0 M) solutions of **1** in toluene and *o*-xylene may readily be prepared.

Such "self-solvating" bases in hydrocarbon solvents possess synthetic potential as reagents for inducing clean bimolecular eliminations.[8] For substrates prone to undergo competitive solvolytic and base-promoted eliminations, the solvent of low polarity supresses the tendency for E1 reaction while the basic site of the base remains in a highly reactive (not ion-paired) form.

References and Footnotes

1) R. A. Bartsch, G. M. Pruss, D. M. Cook, R. L. Buswell, B. A. Bushaw, and K. E. Wiegers, *J. Am. Chem. Soc.*, **95**, 6745 (1973).

2) R. A. Bartsch, *Accounts Chem. Res.*, **8**, 239 (1975).

3) Ugelstad and coworkers[4] have reported a high activity of **1** (compared with *t*-BuOK) as a hydrocarbon isomerization catalyst in Et_2O.

4) J. Ugelstad, P. C. Mork, and B. Jenson, *Acta Chem. Scand.*, **17**, 1455 (1963); O. A. Rokstad, J. Ugelstad, and H. Lid, *Acta Chem. Scand.*, **23**, 782, (1969).

5) A gift of Carbowax 350 methoxy polyethylene glycol was provided by the Union Carbide Corporation, South Charleston, West Virginia.

6) G. W. Gokel and B. J. Garcia, *Tetrahedron Lett.*, (preceeding communication). We thank these authors for a gift of monoaza-18-crown-6 and communication of their results prior to publication.

7) D. L. Griffith, D. L. Meges, and H. C. Brown, *Chem Commun.*, 90 (1968).

8) R. A. Bartsch, J. R. Allaway, and J. G. Lee, (unpublished results).

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