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BASE-SOLVENT SYSTEMS FOR INDUCING CLEAN BIMOLECULAR 1,2-ELIMINATIONS

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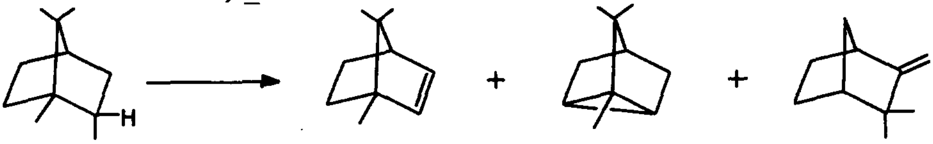
Base-promoted 1,2-dehydrohalogenations and dehydrotosylations of sensitive compounds are often accompanied by concomitant solvolytic elimination processes. In order to surpress these complicating E1 reactions, solvents of low polarity are often chosen. However, the rate of bimolecular elimination by metal alkoxide bases is also markedly retarded in such solvents due to base association.[1] We now report that control of this base association by use of crown ethers or "self-solvating"[2] bases provides effective reagents for promoting clean bimolecular 1,2-eliminations from a sensitive substrate.

Elimination from ℓ-bornyl tosylate, 1,[3,4] was selected as an appropriate model system. According to the literature,[3] 1 is prone to undergo solvolytic elimination producing the rearranged hydrocarbons tricyclene, 3, and camphene, 4, instead of the anticipated product of base-promoted elimination, 2.



1 2 3 4

Hydrocarbon products derived from small scale[5] reactions of 1 with a variety of base-solvent combinations are presented in the Table. With MeONa-MeOH (Entry 1), only solvolysis products 3 and 4 are observed. Changing to t-BuOK-t-BuOH or t-BuOK-C_6H_6 (Entries 2 and 3), systems which employ solvents of low polarity, increases the proportion of 2 somewhat. In the strongly basic t-BuOK-DMSO system (Entry 4), the bimolecular elimination product 2 is notably enhanced. However, 3 and 4 still represent nearly one fifth of the hydrocarbon products.

In sharp contrast with the results recorded in Entries 1-4, the base-solvent combinations in Entries 5-11 produce a minimal 95% relative proportion of the bimolecular elimination product 2. For the system t-BuOK and 18-crown-6 in benzene, Entries 5-8 reveal only very slight change in relative percentages of hydrocarbon or total hydrocarbon yields when the concentration of t-BuOK is increased while holding the concentration of 18-crown-6 constant at 0.50 M. Entries 9 and 10 demonstrate that the strong preference for bimolecular elimination is maintained even with "catalytic" ratios (0.05-0.10) ratios of 18-crown-6 to t-BuOK. With t-BuOK as the base and benzene or DMSO as the solvent, considerable (20-65%) borneol was detected in the reaction products. Since this was determined to be ℓ-borneol, its origin is most likely

Table. Hydrocarbon Products Formed in Base-Promoted Eliminations from Bornyl Tosylate[a] at 80°C.

Entry	Base-Solvent	[Base]	[18-Crown-6]	Time,(hr)	Percentage of Total Hydrocarbons[b]			Total Hydrocarbon Yield[c],(%)
					%2	%3	%4	
1	MeONa-MeOH	0.50	-	10	0	4	96	80
2[d]	t-BuOK-t-BuOH	0.50	-	24	10	9	81	29-33
3[e]	t-BuOK-C_6H_6	0.21	-	17	13	8	79	49[f]
4	t-BuOK-DMSO	0.45	-	1	82	0	18	22[f]
5[g]	t-BuOK-C_6H_6	0.50	0.50	3-13[h]	95	1	4	18-29[f]
6[d]	t-BuOK-C_6H_6	1.0	0.50	3	96	0	4	28[f]
7[d]	t-BuOK-C_6H_6	1.5	0.50	3	99	1	0	24-26[f]
8[d]	t-BuOK-C_6H_6	2.0	0.50	3	100	0	0	21-22[f]
9	t-BuOK-C_6H_6	0.50	0.05	13	96	0	4	11[f]
10[g]	t-BuOK-C_6H_6	1.0	0.05	3-13[h]	95	1	4	12-22[f]
11	$CH_3(OCH_2CH_2)_{7-8}OK$-C_6H_6	0.50	-	24	96	0	4	8

[a] [ROTs] = 0.25 M. [b] Determined by GLPC. Estimated uncertainty ± 1%. [c] Determined by GLPC with p-xylene as internal standard. [d] Duplicate runs. [e] [ROTs] = 0.15 M. [f] Considerable borneol detected. [g] Triplicate runs. [h] No consistent yield variations within this range of reaction times.

nucleophilic attack of the base at sulfur in 1.

Similar selectivity for formation of 2 is also exhibited by the self-solvating base $CH_3(OCH_2CH_2)_{7-8}OK$[6] utilized in Entry 11. However, in this instance, the total hydrocarbon yield appears to be distinctly lower than observed with t-BuOK and 18-crown-6.

In summary, we have demonstrated that base-solvent systems of t-BuOK and 18-crown-6 or of $CH_3(OCH_2CH_2)_{7-8}OK$ in benzene are effective reagents for inducing clean bimolecular eliminations.[8]

References and Notes

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

2) R. A. Bartsch and D. K. Roberts, Tetrahedron Lett., (in press).

3) W. H. Huckel, Chem. Ber., 77B, 805 (1944).

4) Our ℓ-bornyl tosylate was prepared from ℓ-borneol (Aldrich) and had a mp of 69-70°, $[\alpha]_D^{25}$ = -17.0 ± 0.5°, and gave correct carbon and hydrogen analysis. Since the ℓ-bornyl tosylate reported in Reference 3 had $[\alpha]_D^{20}$ = -16.7°, it appears that the reported mp of 55° is in error.

5) Conducted in stoppered glass vessels. The total volume of the reaction solutions or mixtures was 5.0 ml.

6) We thank Union Carbide Corporation for the sample of Carbowax 350, $CH_3(OCH_2CH_2)_{7-8}OH$.

7) The reaction of 1 with t-BuOK-DMSO also produced large amounts of isobutylene. This product is consistent with an initial displacement by t-butoxide at the sulfur atom of 1 forming t-butyl tosylate and the anion of ℓ-borneol. Under the strongly basic reaction conditions the former should readily eliminate to produce isobutylene.

8) Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.