Reaction of 2-Butyl Halides with Potassium t-Butoxide and t-Heptoxide. Evidence for a Steric Effect of the Attacking Base in influencing the Direction of Elimination in an *E*2 Reaction

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THE increasing ratio of 1-/2-alkenes accompanying the reaction of 2-halogenoalkanes with potassium ethoxide, t-butoxide, and t-heptoxide,[†] in the respective alcohols as solvents, was originally attributed to the increasing steric requirement of the attacking base, KOEt $<$ $KOCMe_3$ $<$ $KOCEt_3$, which favoured attack on a primary hydrogen rather than on a more hindered secondary or tertiary hydrogen.[1] This interpretation has recently been questioned.[2] It has been suggested that the observed effects are due primarily to the decreasing polar character of the solvents, EtOH $>$ Me_3COH $>$ Et_3COH.[3]

Both potassium t-butoxide and t-heptoxide are somewhat soluble in toluene, a common solvent with less polar characteristics than triethylcarbinol. The 2-butyl halides were subjected to elimination by these two bases, in the respective alcohols and in toluene as a common solvent.

For each of the halides, elimination by potassium t-heptoxide in triethylcarbinol gave a higher yield of but-1-ene than the corresponding elimination by potassium t-butoxide in t-butanol. Almost identical results were obtained with these two bases in toluene.

It follows that the consistent shift from Saytzeff toward Hofmann elimination previously observed with increasing steric requirement of the alkoxide base[1] cannot be primarily the result of changes in the solvent characteristics of the corresponding alcohols.

We also examined the corresponding eliminations in tetrahydrofuran (THF) and dimethylsulphoxide (DMSO) as solvents, which are very fast,[4] unlike the reactions in the alcohols and in toluene which require several hours at 50°. Accordingly, the temperature was lowered to 25° and special precautions adopted to avoid isomerization of the olefins formed.

In all cases we observe an increase in the amount of but-1-ene with potassium t-heptoxide, as compared with potassium t-butoxide. However, the differences are considerably smaller than those observed in the alcohols or in toluene.

The remarkably high reactivity of alkoxide bases in THF and DMSO is usually attributed to solvation of the cation, leaving an essentially unsolvated anion, in highly reactive form.[5] It may be that the tremendous reactivity of alkoxide bases in these solvents means they are less selective reagents, less sensitive to small steric influences of the environment. In addition, in the alcohols,

TABLE

Products of elimination from 2-butyl halides[a]

Base	Solvent	Chloride		Bromide		Iodide	
		But-1-ene[b]	*trans*-2[c] / *cis*-2	But-1-ene[b]	*trans*-2[c] / *cis*-2	But-1-ene[b]	*trans*-2[c] / *cis*-2
$KOCMe_3$	Me_3COH	67[d](%)	1·28	53·5%	1·47	34[d](%)	2·04
$KOCEt_3$	Et_3COH	80·1	1·14	71·3	1·26	49·3	1·50
$KOCMe_3$	Toluene	66·8	1·03	52·2	1·38	36·1	1·70
$KOCEt_3$	Toluene	77·0	1·29	65·8	1·37	46·8	1·75
$KOCMe_3$	THF	48·6	2·92	33·6	3·33	20·4	3·57
$KOCEt_3$	THF	49·1	2·72	34·1	3·09	25·1	4·06
$KOCMe_3$	DMSO	41·2	4·07	31·5	3·76	19·6	3·47
$KOCEt_3$	DMSO	43·6	4·22	32·7	3·91	21·4	3·79

[a] Reactions in DMSO and THF at 25°; Reactions in toluene and the alcohols at 50°; [b] Standard deviation ±1%; [c] Standard deviation ±0·20; [d] H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, 1966, **88**, 1425.

[†] For convenience, the abbreviated term potassium t-heptoxide will be used here to refer to the potassium salt of triethylcarbinol, $KOCEt_3$.

association of solvent with the anion may enhance its steric requirements, as may the formation of ionic clusters in poorly dissociating solvents.

The data also reveal interesting changes in the 1-/2- and *trans*-2/*cis*-2 ratios with solvent and with halide. These are under investigation and will be discussed later. The present study, however, was directed to the question of whether, in a common solvent, an increase in the steric requirement of the base enhances elimination according to the Hofmann rule. The data clearly support that conclusion. Moreover, since even more highly branched tertiary alcohols are now readily available,[6] it suggests that alkoxides derived from such alcohols may be highly effective in directing elimination along a preferred path. This is currently under investigation.

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[2] J. F. Bunnett, *Angew. Chem., Internat. Edn.*, 1962, **1**, 225.

[3] (a) D. H. Froemsdorf and M. E. McCain, *J. Amer. Chem. Soc.*, 1965, **87**, 3983; (b) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkinson, *ibid.*, 1965, **87**, 3984.

[4] For example, it is reported that the reaction of potassium t-butoxide in DMSO with 2-chlorobutane is 67% complete in 30 sec. at room temperature (J. E. Hofmann, T. J. Wallace, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1964, **86**, 1561).

[5] D. Martin, A. Weise, and H. J. Niclis, *Angew. Chem., Internat. Edn.*, 1967, **6**, 318.

[6] H. C. Brown and M. W. Rathke, *J. Amer. Chem. Soc.*, 1967, **89**, 2737.