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REACTION OF 2-BUTYL HALIDES WITH SODIUM ETHOXIDE AND 2,2,2-TRIFLUOROETHOXIDE. EVIDENCE THAT ORIENTATION IS NOT DETERMINED BY THE STERIC REQUIREMENTS OF ALKOXIDE BASES.

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Interpretation of the effect of base upon orientation in eliminations from 2-alkyl halides induced by alkoxide ions has been complicated by concomitant variation of base strength and size. For example, in a change from ethoxide to t-butoxide, both the basicity and the bulk of the alkoxide ion increase. Thus, in eliminations from 2-butyl bromide, the enhancement in 1-butene/2-butenes ratio as the base-solvent combination is varied from EtOK-EtOH to t-BuOK-t-BuOH or from EtOK-DMSO to t-BuOK-DMSO[2] may be rationalized in terms of either steric[3] or non-steric[2,4] arguments.

A divergence from such parallelism between basicity and size of alkoxide ions is found in ethoxide and 2,2,2-trifluoroethoxide. Whereas 2,2,2-trifluoroethoxide should be slightly larger than ethoxide, ethoxide is a stronger base[5]. Possible complication due to differing solvation of these alkoxides may be removed by use of dipolar aprotic solvents in which anions are only poorly solvated[6].

The olefinic products observed in reactions of sodium ethoxide and 2,2,2-trifluoroethoxide with 2-butyl iodide, bromide, and chloride in DMF and DMSO are recorded in the Table. In all cases, the change from ethoxide to 2,2,2-trifluoroethoxide results in a decrease in the per cent 1-butene. This demonstrates that for alkoxide ions of modest proportions, base strength, not size, is of prime importance in determining orientation. The present study does not rule out steric effects with outsized alkoxide ions[7], but suggests that steric control of orientation[3] is the exception rather than the rule.

TABLE

Olefinic Products from Reactions of 2-Butyl Halides with Sodium Ethoxide and 2,2,2-Trifluoroethoxide in DMF and DMSO at 25°[a]

		Iodide		Bromide		Chloride	
Base	Solvent	% 1-Butene	t-2-Butene / c-2-Butene	% 1-Butene	t-2-Butene / c-2-Butene	% 1-Butene	t-2-Butene / c-2-Butene
CH_3CH_2ONa	DMF	16.2[b]	3.44[c]	26.0	3.66	36.3	4.18
CF_3CH_2ONa	DMF	12.6	3.66	21.8	3.88	29.0[d]	4.20
CH_3CH_2ONa	DMSO	17.1	3.22	27.2	3.54	38.4	3.87
CF_3CH_2ONa	DMSO	14.3	3.32	22.9	3.51	30.9[d]	3.84

[a] [2-BuX] = 0.2 - 0.3 M; [base] = 1.0 M; reaction time, 10 min.
[b] Standard deviation ± 0.5%
[c] Standard deviation ± 0.10
[d] Reaction time, 30 min.

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