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THE EFFECT OF BASE AND SOLVENT ON α'-β ELIMINATION FROM SULFONIUM SALTS

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Recently we reported high trans/cis ratios (3.5 and 5.0, respectively) for the 2-pentene obtained from the reaction of 2- and 3-pentyldimethylsulfonium ions with potassium t-butoxide in t-butyl alcohol, in contrast to the below-unity ratios observed with most other base/solvent combinations.[1] We suggested that the high ratios might result from incursion of syn-E2 or α'-β[2] pathways. The only prior examples of α'-β eliminations from sulfonium salts involved tritylsodium as base under aprotic conditions,[3,4] while hydroxide ion in water was reported to react with 2-phenylethyl-2,2-d_2-dimethylsulfonium ion entirely by the E2 mechanism.[5]

In order to test our explanation of the trans/cis ratios, we subjected 3-pentyl-2,2,4,4-d_4-dimethylsulfonium iodide to reaction with three different base/solvent systems, isolated the resulting methyl sulfide, purified it by glpc, and examined it for deuterium content in a mass spectrometer. After appropriate corrections, the abundance of methyl-d_1 sulfide represents the fraction of reaction occurring via the α'-β mechanism. The results are given in the Table.

Our speculation[1] is completely confirmed. There is little α'-β elimination with potassium n-butoxide in n-butyl alcohol, but it becomes the predominant mode of reaction with potassium t-butoxide in t-butyl alcohol or in 95% dimethyl

Table. The α'-β Mechanism in Eliminations from 3-Pentyl-2,2,4,4-d_4-dimethylsulfonium Iodide

Base/Solvent[a]	Percent α'-β[b]
n-BuOK/n-BuOH	1.7 ± 0.3
t-BuOK/t-BuOH	65.2 ± 0.6
t-BuOK/95 mole % DMSO, 5% t-BuOH	73.0 ± 0.2

[a]Reaction mixture heated in a sealed tube at 35° for 24 hr. Base concentration was 0.3-0.35 M. [b]Corrected for 3.75 deuterium atoms per molecule in starting material and for natural abundance of the P + 1 peak of methyl sulfide. Each figure is the average of two or three experiments. Measurements were carried out on an Atlas CH-4 mass spectrometer at 70 eV.

sulfoxide - 5% t-butyl alcohol. These more basic media doubtless increase both the rate of formation and the equilibrium concentration of the sulfonium ylid, and both of these effects should favor the α'-β mechanism. We intend to explore further the roles of steric and electronic factors in the α'-β mechanism for sulfonium-salt eliminations.

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