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# MECHANISMS OF ELIMINATION REACTIONS—XXVI

## THE $\alpha'$-$\beta$ MECHANISM IN ELIMINATION REACTIONS OF SULFORIUM SALTS[1]

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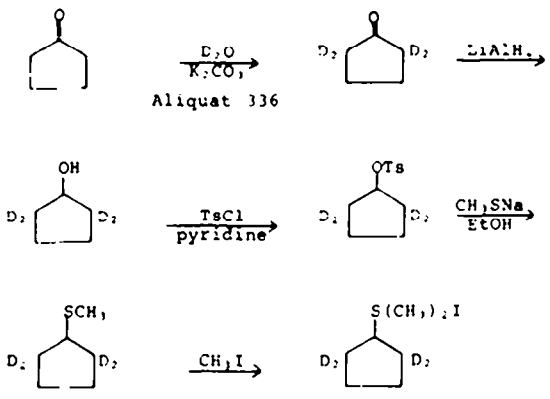
**Abstract**—Tracer studies with $\beta$-deuterated sulfonium salts have shown that the $\alpha'$-$\beta$, or ylid mechanism can be the major path of elimination in the reaction of sulfonium salts with *t*-butoxide in *t*-butyl alcohol, while the E2 reaction is dominant with hydroxide in water or *n*-butoxide in *n*-butyl alcohol. The structure of the sulfonium salt also affects the propensity toward $\alpha'$-$\beta$ elimination, with 3-pentyl > 3-propyl and cyclopentyl > 3-pentyl > cyclohexyl. The *S*-methyl protons of the sulfonium salt exchange at a rate much faster than that of the elimination reaction. A strongly basic medium and a *syn*-periplanar arrangement of the $\alpha$-C–S and $\beta$-C–H bonds seem to be the two most important factors favoring the $\alpha'$-$\beta$ mechanism.

The $\alpha'$-$\beta$, or ylid mechanism for base-promoted elimination was first suggested by Wittig and Polster.[2] Its applicability to elimination reactions of ammonium and sulfonium salts has been rather extensively investigated.[3] While the $\alpha'$-$\beta$ mechanism can be observed with very hindered substrates[4] or with organometallic bases,[5] it is seldom detectable and never predominant for the reactions of simple onium salts with hydroxide ion in aqueous medium,[6-9] even when the elimination is of *syn* stereochemistry.[9] More recent tracer work has confirmed that organometallic bases react with quaternary ammonium salts by the $\alpha'$-$\beta$ mechanism, and that potassium amide in liquid ammonia can promote the $\alpha'$-$\beta$ mechanism with some substrates.[10-12]

Our suspicion that at least some elimination reactions of sulfonium salts might involve either an $\alpha'$-$\beta$ or a *syn*-E2 mechanism was aroused by the observation that the *trans*/*cis* ratio of the 2-pentene from 2- and 3-pentyldimethylsulfonium salts is much higher with potassium *t*-butoxide in *t*-butyl alcohol than with other base-solvent combinations.[13] Subsequent tracer experiments confirmed that the high *trans*/*cis* ratios are associated with a substantial proportion of reaction via the $\alpha'$-$\beta$ pathway.[14] The present paper reports investigations of the effect of substrate structure and reaction conditions on the competition between the E2 and $\alpha'$-$\beta$ mechanisms in eliminations from sulfonium salts.

The synthetic sequence which was used in all cases is illustrated in Scheme 1 with cyclopentanone as the starting material. The exchange with deuterium oxide was markedly facilitated by the phase-transfer catalyst "Aliquat 336" (a quaternary ammonium chloride, see Experimental for further details), such that much milder conditions than those originally described by Starks[15] could be used. Room temperature and the weak base potassium carbonate sufficed for cyclopentanone, and our general experience has been that mild warming accomplishes equilibration within a few hours with most ketones. The remainder of the synthesis used standard procedures that require no special comment.

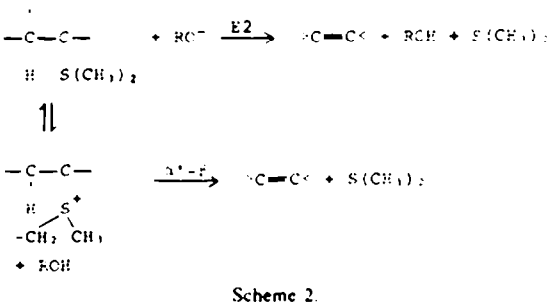
Each sulfonium salt was treated with base to effect




Scheme 1.

elimination, and the resulting methyl sulfide isolated by GLPC and examined for deuterium content in the mass spectrometer. The results are recorded in Table 1, where the column headed "percent $\alpha'$-$\beta$" gives simply the percentage of deuterated methyl sulfide uncorrected for isotope effects. Scheme 2 depicts the mechanistic pathways apparently involved in these reactions.

Considering first the effect of base and solvent, we see that the importance of the $\alpha'$-$\beta$ mechanism increases in the order $OH^- < n$-BuO $< t$-BuO . In agreement with earlier results on 2-phenylethyldimethylsulfonium ion,[8]




Scheme 2.

Table 1. The $\alpha'$-$\beta$ mechanism in eliminations from $\beta$-perdeuterated sulfonium iodides

| R in $RSMe_2I$ | Base/Solvent* | Temp., °C | Percent $\alpha'$-$\beta$ |
|---|---|---|---|
| 2-propyl | *n*-BuOK/*n*-BuOH | 35 | 0.9 ± 0.2 |
| 2-propyl | *t*-BuOK/*t*-BuOH | 35 | 22.2 ± 2.0 |
| 3-pentyl | *n*-BuOK/*n*-BuOH | 35 | 1.7 ± 0.3 |
| 3-pentyl | *t*-BuOK/*t*-BuOH | 35 | 65.2 ± 0.6 |
| 3-pentyl | *t*-BuONa/*t*-BuOH | 35 | 60.0 ± 2.0 |
| 3-pentyl | *t*-BuOK/5% *t*-BuOH-95% DMSO | 35 | 73.0 ± 0.2 |
| cyclopentyl | NaOH/$H_2O$ | 90 | 0.0 ± 0.1[b] |
| cyclopentyl | *n*-BuOK/*n*-BuOH | 35 | 2.6 ± 1.0 |
| cyclopentyl | *t*-BuOK/*t*-BuOH | 35 | 82.4 ± 0.4 |
| cyclohexyl | *n*-BuOK/*n*-BuOH | 96 | 0.0 ± 0.1[c] |
| cyclohexyl | *t*-BuOK/*t*-BuOH | 40 | 4.3 ± 0.2 |
| 2-phenylethyl | NaOH/$H_2O$ | 96 | 0.0[d] |
| 2-phenylethyl | NaOH/39% $H_2O$-61% DMSO | 30 | 1.0 ± 0.0 |
| 2-phenylethyl | NaOH/16% $H_2O$-84% DMSO | 30 | 12.2 ± 0.6 |
| 2-phenylethyl | NaOH/16% $H_2O$-84% DMSO | 60 | 9.2 ± 0.8 |

*Most reactions were carried out for 12–50 h under the indicated conditions, except for the cyclopentyl salt in water (100 hr). [b]Actual value—0.04%. [c]Actual value—0.3%. [d]W. H. Saunders, Jr. and D. Pavlović, *Chem. Ind.* (London), 180 (1962).

the reaction of cyclopentyldimethylsulfonium ion with hydroxide ion is entirely E2. Even *n*-butoxide gives 97+% E2 reaction, but the $\alpha'$-$\beta$ mechanism accounts for well over half of the total reaction between *t*-butoxide and two of the four substrates studied. That ion pairs are involved in *t*-butyl alcohol is suggested by the significantly greater proportion of $\alpha'$-$\beta$ elimination with potassium than with sodium *t*-butoxide. The addition of dimethyl sulfoxide to either *t*-butyl alcohol or water increases the proportion of the $\alpha'$-$\beta$ pathway. The effects of the cation and of DMSO indicate that a decrease in ion pairing of the base increases the importance of the $\alpha'$-$\beta$ mechanism.

These results clearly show that an increase in base strength favors the $\alpha'$-$\beta$ more than the E2 mechanism. In order to determine whether this was caused by increased rate of ylid formation or increased ylid concentration, we carried out experiments in which 3-pentyldimethylsulfonium iodide was treated with sodium deuteroxide in deuterium oxide (Table 2). Even under these rather mildly basic conditions, the methyl hydrogens were *ca.* 98% exchanged within one half life of the elimination reaction, so the ylid must be formed rapidly and reversibly under all conditions. Change of solvent might also affect the rate of elimination from the ylid, but this is probably a minor factor compared to change in the equilibrium concentration of the ylid.

Table 2. Deuterium exchange of 3-pentyldimethylsulfonium iodide with sodium deuteroxide in deuterium oxide

| Run No. | Percent elimination* | Percent exchange of methyl | Percent exchange of methinyl |
|---|---|---|---|
| 1 | 52.3 | 97.8 | 60.0 |
| 2 | 45.8 | 97.8 | 62.0 |
| 3 | 44.7 | 97.8 | 45.0 |

*Reaction was allowed to run for *ca.* one half life of the elimination reaction. Sulfonium salt was isolated and deuterium content determined by NMR in $D_2O$.

The effects of substrate structure are particularly interesting. The considerably greater propensity for reaction via the $\alpha'$-$\beta$ mechanism shown by 3-pentyl relative to 2-propyl-dimethylsulfonium ion is probably primarily caused by the slower E2 reaction of the 3-pentyl derivative. One would not expect major differences in the equilibrium concentrations of ylid (if anything, the ylid should be more stable in the 2-propyl system). In addition, the ylid, once formed, should eliminate faster in the 2-propyl system, for the Hofmann-rule product from 2-pentyldimethylsulfonium ion is still predominant under conditions favoring $\alpha'$-$\beta$ elimination.[13]

The effect of conformation on the $\alpha'$-$\beta$ mechanism is shown by the comparison cyclopentyl > 3-pentyl > cyclohexyl. It is unlikely that this order arises from changes in the E2 rates, for the E2 reaction is normally more facile with cyclopentyl than with cyclohexyl derivatives.[16] The equilibrium concentration of the ylid does not seem likely to vary markedly over this series. The rate of elimination from the ylid remains as the most probable cause of the observed variation. One thus reaches the reasonable conclusion that the 5-member cyclic transition state is most easily formed when the $\alpha$–C–S and $\beta$–C–H bonds are most nearly eclipsed (cyclopentyl), and least easily formed when they are most nearly staggered (cyclohexyl). The 3-pentyl derivative, with relatively free rotation about the $C_\alpha$–$C_\beta$ bond, is intermediate in behavior, but much closer to the cyclopentyl than to the cyclohexyl derivative.

The results on 2-phenylethyldimethylsulfonium ion deserve brief comment. The deuterium isotope effect for elimination in this system goes through a maximum at about 40% dimethyl sulfoxide.[17] When we observed other cases of $\alpha'$-$\beta$ elimination in the present work, we considered it necessary to check on whether this maximum could be caused by a change from the E2 to the $\alpha'$-$\beta$ mechanism. The data in Table 1 show, however, that the $\alpha'$-$\beta$ mechanism remains insignificant until far past the $k_H/k_D$ maximum. Consequently, our work reinforces the conclusion that the maximum represents an E2 transition state in which the proton is half transferred.[17]

It would be of interest to know whether that portion of the elimination which is not $\alpha'$-$\beta$ is *anti*-E2 or *syn*-E2. Judging from experience with related quaternary ammonium salts,[18] it is not improbable that some of our E2 reactions are at least in part *syn* eliminations. Unfortunately, this information appears to be unattainable for systems used in this study. Table 2 shows that the methinyl hydrogen of 3-pentyldimethylsulfonium ion exchange at a rate comparable to the elimination rate, even with aqueous hydroxide.[19] Thus, it is likely that the stereochemical integrity of the $\alpha$-carbon would be lost rapidly enough to preclude determination of the stereochemistry of elimination except when the $\alpha$-carbon is tertiary.

As noted above, the values for "percent $\alpha'$-$\beta$" in Table 1 are uncorrected for isotope effects, so that we should consider briefly whether these figures reasonably approximate the values for the undeuterated systems. The rate-determining steps of both the E2 and $\alpha'$-$\beta$ mechanisms are subject to deuterium isotope effects, and the only question is whether these isotope effects differ.

The cyclic transition state of the $\alpha'$-$\beta$ mechanism can be expected to enforce a non-linear proton transfer. Model calculations predict smaller isotope effects for non-linear than for linear proton transfers.[20,21] The only direct evidence is based on a comparison of 1 - phenylethyl - 2 - $d_3$ - dimethylsulfonium ion with ethoxide in ethanol, and 1 - phenylethyl - 1 - $d_1$ - dimethyl - $d_6$ - sulfonium ion with ethoxide in ethanol-*O*-*d*.[22] Because the proportions of $\alpha'$-$\beta$ reaction are small, and because several assumptions are required, the derived $k_H/k_D$ values of 5.9 for the E2 and 3.5 for the $\alpha'$-$\beta$ reactions should not be assigned too much quantitative significance. Nonetheless, they are of a reasonable magnitude and in the expected order. They suggest that deuterium substitution should favor the $\alpha'$-$\beta$ mechanism, but the correction is not large. The 82.4% $\alpha'$-$\beta$ elimination from cyclopentyl-2,2,4,4-$d_4$-dimethylsulfonium ion would become about 74% for the undeuterated substrate. Such changes would clearly have no effect on the qualitative conclusions we have drawn.

## EXPERIMENTAL

M.ps and b.ps are uncorrected. NMR spectra were recorded on a JEOL C-60HL instrument, and analyses of methyl sulfide for deuterium were done on an Atlas CH-4 mass spectrometer. Purification of methyl sulfide by GLC utilized Varian-Aerograph A-90 or 920 instruments with thermal conductivity detectors.

*Deuterated ketones* were prepared by repeated exchanges with deuterium oxide, except for acetone -1,1,1,-3,3,3-$d_6$, which was purchased (Stohler Isotope Chemicals, 99.5%). Two exchange procedures were used. In the first, 0.4 mole of the ketone was mixed with 0.6 mole of deuterium oxide and 0.1 g anhydrous potassium carbonate and the mixture refluxed for 24 h.[23] The aqueous layer was removed, fresh deuterium oxide and potassium carbonate added, and the refluxing repeated. Six exchanges were followed by drying over magnesium sulfate and distillation to isolate pure product. The second procedure, used in most of the work, utilized a modification of the phase-transfer procedure of Starks.[24] A mixture of 0.4 mole of the ketone, 1.2 mole of deuterium oxide, 0.1 g of anhydrous potassium carbonate and 2 ml of "Aliquat 336" (methyltricaprylylammonium chloride, where "caprylyl" actually represents a mixture of $C_8$–$C_{10}$ alkyl groups, General Mills Chemicals, purchased from McKerson Corp., 3016 4th Avenue, Minneapolis, Minnesota 55408) was stirred at room temperature for 5 h, saturated with anhydrous potassium carbonate, and the layers separated. The process was repeated 5–8 times with fresh deuterium oxide and potassium carbonate (the phase transfer catalyst remains in the organic layer and need not be replenished). Isolation and purification of the product was carried out as above. Yields in both procedures ranged from 30 to 60%.

3-*Pentanone*-2,2,4,4,-$d_4$ contained 94% of the calculated amount of deuterium for complete exchange (MS analysis).

*Cyclopentanone*-2,2,5,5,-$d_4$ contained 94% of the calculated amount of deuterium (NMR analysis).

*Cyclohexanone*-2,2,6,6,-$d_4$ contained 95% of the calculated amount of deuterium (NMR analysis).

*Deuterated alcohols* were obtained by reduction of the corresponding ketones with lithium aluminium hydride. Workup was either by careful treatment with water followed by 10% sulfuric acid or (necessary for acceptable yields of 2-propanol) addition of just enough water and 15% sodium hydroxide to give the inorganic salts as a fine powder removable by filtration.[24]

2-*Propanol*-1,1,1,3,3,3,-$d_6$ was obtained in 44% yield, b.p. 80–82°C.

3-*Pentanol*-2,2,4,4,-$d_4$ ws obtained in 85% yield, b.p. 112–113°C.

*Cyclopentanol*-2,2,5,5,-$d_4$ was obtained in 55% yield.

*Cyclohexanol*-2,2,6,6,-$d_4$ was obtained in 74% yield, b.p. 155°C.

p-*Toluenesulfonates* were prepared by a standard procedure from the alcohol and *p*-toluenesulfonyl chloride in dry pyridine.[25]

2-*Propyl*-1,1,1,3,3,3,-$d_6$ p-*toluenesulfonate* was obtained in 98% crude yield after drying and removal of ether.

3-*Pentyl*-2,2,4,4,-$d_4$ p-*toluenesulfonate* was obtained in 67% yield, m.p. 43–44°.

*Cyclopentyl*-2,2,5,5,-$d_4$ p-*toluenesulfonate* was isolated by drying and removal of ether, and used directly without further purification.

*Cyclohexyl*-2,2,6,6,-$d_4$ p-*toluenesulfonate* was isolated in 90% crude yield by drying and removal of ether, and used directly without further purification.

*Alkyl and cycloalkyl methyl sulfides* were prepared by adding slowly an ether solution of the *p*-toluenesulfonate (0.14 mole) dropwise to a refluxing solution prepared by adding excess methanethiol to 0.21 mole of sodium ethoxide in 300 ml of absolute ethanol, using a Dry Ice-acetone condenser. The reaction mixture was refluxed and stirred for 5 h, and then treated with 300 ml of water and extracted four times with petroleum ether. The extracts were dried over magnesium sulfate and distilled.

2-*Propyl*-1,1,1,3,3,3,-$d_6$ *methyl sulfide* was obtained in 98% yield, b.p. 82–84°C.

3-*Pentyl*-2,2,4,4-$d_4$ *methyl sulfide* was obtained in 77% yield, b.p. 134–135°C.

*Cyclopentyl*-2,2,5,5,-$d_4$ *methyl sulfide* was obtained in 54% yield, b.p. 156°C.

*Cyclohexyl*-2,2,6,6,-$d_4$ *methyl sulfide* was obtained in 38% yield, b.p. 217–220°C.

2-*Phenylethyl*-2,2-$d_2$ *methyl sulfide* was prepared in 70% yield from a sample of 2-phentylethyl-2,2-$d_2$ *p*-toluenesulfonate prepared by Mr. E. D. Putnam according to the procedure of Saunders and Edison.[26] The sulfide had b.p. 90° (8 mm) (lit.[26] 121° (15 mm)).

*Alkyldimethylsulfonium iodides* were prepared from the alkyl methyl sulfide and methyl iodide (50–100% molar excess). In most of the preparations, the reactants in nitromethane, ether or an ether-ethanol mixture were allowed to stand 2–10 days, the product precipitated where necessary by addition of ether, and recrystallized from methanol, ethanol or ethanol-ether. The best yield (83% from 3-pentyl methyl sulfide) was obtained simply by letting the neat reactants stand 24 h at room temperature, followed by recrystallization from ethanol.

2-*Propyl*-1,1,1,3,3,3,-$d_6$-*dimethylsulfonium iodide* was obtained in 4.4% yield (reaction in nitromethane).

3-*Pentyl*-2,2,4,4,-$d_4$-*dimethylsulfonium iodide* was obtained in 20% yield (reaction in ether), or 83% yield (neat reactants).

*Cyclopentyl*-2,2,5,5-$d_4$-*dimethylsulfonium iodide* was obtained in 70% yield (reaction in nitromethane).

*Cyclohexyl*-2,2,6,6-$d_4$-*dimethylsulfonium iodide* was obtained in 33% yield (reaction in nitromethane).

2-*Phenylethyl*-2,2-$d_2$-*dimethylsulfonium iodide* was prepared in ethanol-ether, m.p. 131–132°C (dec).

*Solvents and bases.* *n*-Butyl and *t*-butyl alcohols were treated with potassium metal and distilled. Dimethyl sulfoxide was dried over grade 5A Molecular Sieves (Linde), then over calcium hydride, and distilled. Mixtures of dimethyl sulfoxide and *t*-butyl alcohol were prepared by volume. Alkoxide solutions were prepared by scraping clean the appropriate metal under hexane and then dissolving it in the alcohol. Carbonate-free sodium hydroxide solution was used for the runs in aqueous solution. Base solutions were made up to *ca.* 0.3 M and standardized by titration with hydrochloric acid.

*Elimination reactions* were performed in a reinforced glass test tube or volumetric flask covered with a tight-fitting serum cap. The reaction vessel was immersed in a constant-temperature bath for 12–100 h. Two syringe needles were then inserted in the cap. Dry prepurified nitrogen was bubbled through one of them for 1 h, and the vapors from the other were carried through an ice-salt-water trap, a calcium chloride tube, and condensed in a liquid nitrogen trap. The sample was warmed and carried by a helium flow into the inlet of the gas chromatograph with a 10-ft × 0.25-in column of 20% Ucon 50HB 5100 on 60–80 mesh Chromosorb P. The methyl sulfide was collected in a liquid nitrogen trap. The trap was transferred to a vacuum line where the sample was degassed, dried over phosphorus pentoxide, and transferred to a mass spectrometer sample tube. The sample was transferred to the mass spectrometer and first scanned at 70 eV over the range *m/e* 12–98 to determine if any impurities were

present. The *m/e* 62 and 63 peaks were then scanned repeatedly at 13–14 eV. The observed ratio was corrected for the calculated 3.05% normal abundance of *m/e* 63 due to naturally-occurring heavy isotopes.

*Exchange experiments* were performed by heating *ca.* 6 mmole of 3-pentyldimethylsulfonium iodide in 20 ml of 0.5 N sodium deuteroxide in deuterium oxide for 39 h at 79.9°C. Preliminary rough kinetics had shown that the elimination proceeded to approximately one half life under these conditions. The reaction mixture was cooled and three 2.0-ml aliquots each added to 10 ml of 0.1 N hydrochloric acid. The solutions were back titrated with 0.1 N sodium hydroxide to determine the extent of reaction. The solutions were made acidic to litmus with hydrochloric acid and evaporated on a rotary evaporator. The residue was extracted three times with hot benzene and recrystallized from absolute ethanol. The crystals were dried in a vacuum desiccator and dissolved in deuterium oxide. The proton NMR spectra were then determined. Results of the integrations of the *S*-methyl and *S*-methinyl peaks relative to the terminal methyl peaks were used to determine the extents of exchange recorded in Table 2.

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