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# AMINOSULFONIUM SALTS BY METATHESIS REACTIONS OF SULFINYL COMPOUNDS - STEREOCHEMISTRY FOR CYCLIC DERIVATIVES (1)

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The reaction of diastereomeric thiane-1-oxides with the cationic N-sulfinyl compound 2 leads to the same amino sulfonium salts 5 or 6.

Recently (1a,2) we reported the conversion of sulfinyl compounds into amino sulfonium salts 1 by their reaction with N-alkyl-N-sulfinylalkanaminium salts 2 (3,4)

$$[R_2NSO]^{(+)}\ BF_4^{(-)} + R'_2SO \longrightarrow [R_2NSR'_2]^{(+)}\ BF_4^{(-)} + SO_2$$

2 1

a : R = Me b : R = Et

By $^1$H-NMR-spectroscopy an intermediate could be detected (2) to which we assigned a cyclic sulfurane structure.

Mikolajczyk recently reported that the reaction of open-chain optically active sulfoxides with the ethyl derivative 2b proceeds with retention of configuration (5). In the case of the related metathesis reaction of sulfoxides with 4-methyl-N-sulfinyl-benzenesulfonamide to yield sulfimines (6-9) the stereochemical outcome depends on the reaction conditions used (10). We investigated, now, the stereochemistry of the reaction of 2a with two pairs of stereoisomeric cyclic sulfoxides, 3a/3b and 4a/4b. (Figure 1)

Figure 1

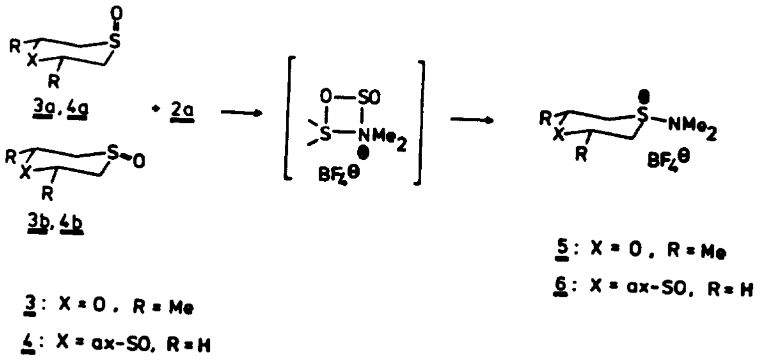


Figure 2

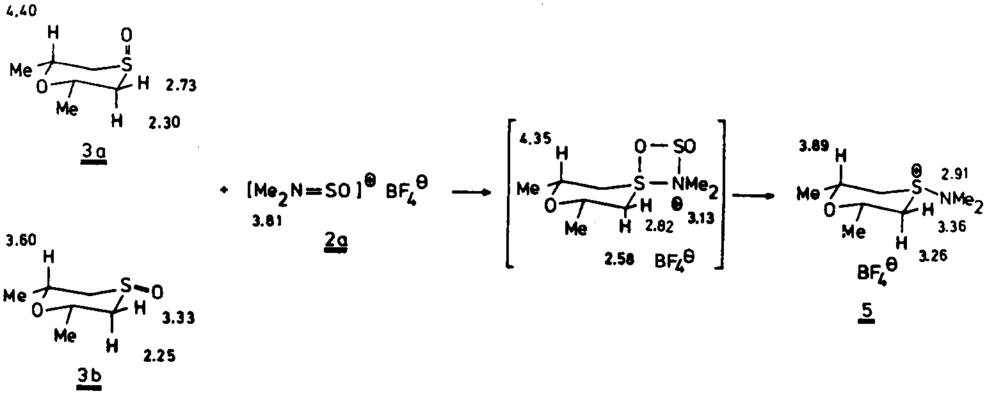
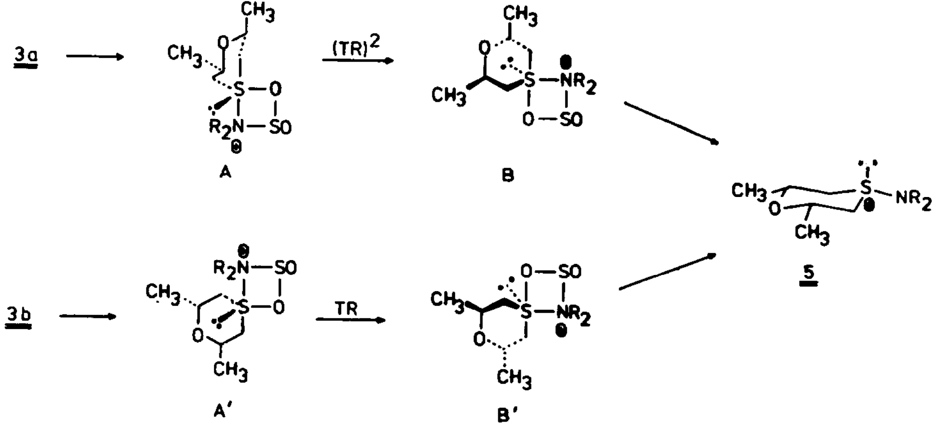


Figure 3



A solution of 2α,4β,6α-2,6-dimethyl-1,4-oxathiane-4-oxide, 3a, (slight excess) in dry acetonitrile was added dropwise at -2o$^{o}$C to a solution of 2a in the same solvent under stirring in an atmosphere of dry nitrogen. These conditions were maintained for 3 hours before warming to ambient temperature, after which stirring was continued for another 3 hours. Dichloromethane and ether were then added and the slightly muddy solution which resulted was cooled slowly to -3o$^{o}$C. The colorless needles which crystallized were filtered at -3o$^{o}$C under nitrogen and dried in vacuo, yielding 29% of 5, m.p. 135-136$^{o}$C. - $^{13}$C-NMR ($CD_3CN$): δ= 71.25 (-C-H); 42.72 ($-CH_2-$); 36.o3 ($N-CH_3$); 21.41 ($-CH_3$). $C_8H_{18}B_1F_4NOS$ (276.1) Calculated C: 35.97%; H: 6.74%; N: 5.24%. Found C: 35.47%; H: 7.33%; N: 4.92%. Compound 5 is the sole product also of the reaction of 2α,4α,6α-2,6-dimethyl-1,4-oxathiane-4-oxide (3b)(11) with 2a under the same conditions (yield: 27%). The stereochemistry of the 2α,4α,6α-aminosulfonium salt 5 was determined by hydrolysis with o,o1 M NaOH to the sulfoxide 3a. As the hydrolysis is known to proceed with inversion (12), 5 should have an equatorial dimethylamino group. We have to conclude, therefore, that the metathesis reaction proceeds with retention for the equatorial sulfoxide, but with inversion for the axial isomer.

In the same manner, both isomers of 1,4-dithiane-1,4-dioxide 4a and 4b (13) react with 2a to give the same aminosulfonium salt, namely the cis-isomer 6 (m.P. 178-18o$^{o}$C) the configuration of which was derived from its $^{1}$H- and $^{13}$C-NMR-spectra. 6 does not react further with 2a under our reaction conditions, even using an excess of the reagent.

The course of all the reactions mentioned was followed by $^{1}$H-NMR directly. Thereby it was ascertained that the metathesis occurs as the only observable reaction.

In the reactions of both isomeric sulfoxides 3, the $^{1}$H-NMR-spectrum of the reaction mixture shows the occurence of the same intermediate (observable after 1h until 28d at -2o$^{o}$C). A comparison of the shift values of educts, intermediate and product leads to the conclusion that in this example, too, the intermediate should have the four-membered ring sulfurane structure (Figure 2). In the case of the reaction of 4-methyl-N-sulfinyl-benzenesulfonamide with sulfoxides, entirely different mechanisms have been proposed for the retention or inversion process: a six-membered ring structure (ee), formed by 2 molecules of 4-methyl-N-sulfinyl-benzenesulfonamide and one of the sulfoxide or an 1:1 four membered sulfurane (ea) for the transition state, respectively. In our case, since both processes possess the same four-membered sulfurane as an intermediate, it seems unlikely that the transition states prior to this common intermediate should differ in their molecularities.

Notwithstanding this possibility, our stereochemical result, then, can be explained with the following assumptions:

- sulfurane - like structures A or A' are first formed, with the $NR_2$ group in an apical position for both isomers
- forms with the lone pair in an apical position show stereoelectronic strain
- in these sulfuranes, turnstile rotations (TR) are possible; turnstile rotations with the thiane ring functioning as the pair may lead to inversion or retention of configuration (14).

- $SO_2$ is split off only from forms with oxygen in an apical position.

The only forms favorable for $SO_2$ extrusion and without steric or stereoelectronic strain, then, are **B** or its mirror image **B**'. They are reached in the case of the equatorial sulfoxide after (TR), in the case of the axial sulfoxide after $(TR)^2$. **B** and **B**' lead to the amino sulfonium salt with the equatorial $NR_2$ group (Figure 3).

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