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MECHANISM OF DECOMPOSITION OF SULFONIUM BETAINES TO EPOXIDES

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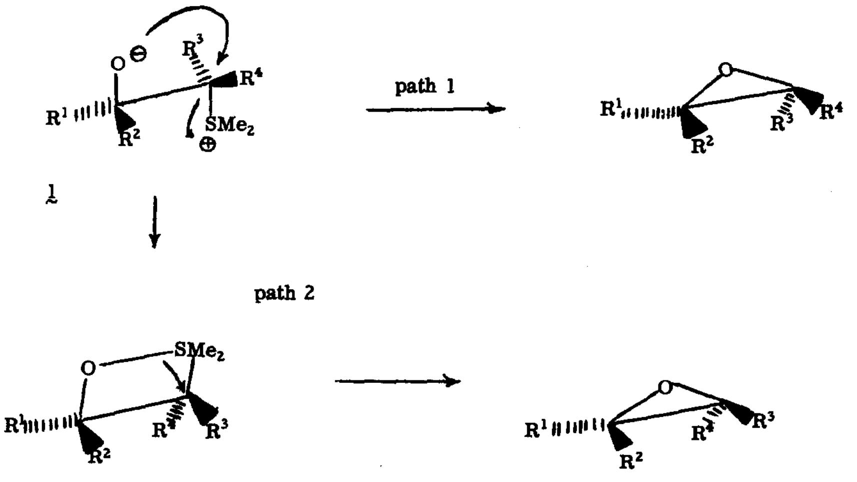
The addition of sulfur ylids to carbonyl compounds followed by decomposition of the resulting betaines constitutes an important synthesis of epoxides and cyclopropane derivatives.[1] The fragmentation of sulfonium betaines of type 1 to yield epoxides is commonly assumed[1-3] to occur via backside displacement of dimethyl sulfide by the oxido oxygen as shown in path 1 (Scheme I). The retention of configuration about the carbon bearing oxygen in 1 implied by this mechanism has been demonstrated in at least one case by Johnson and Schroeck,[4] who concluded that reversion to carbonyl compound and sulfonium ylid was slow relative to epoxide formation.[4] However, none of the examples described to date directly demonstrates the implied inversion about the carbon bearing sulfur in 1. Because of

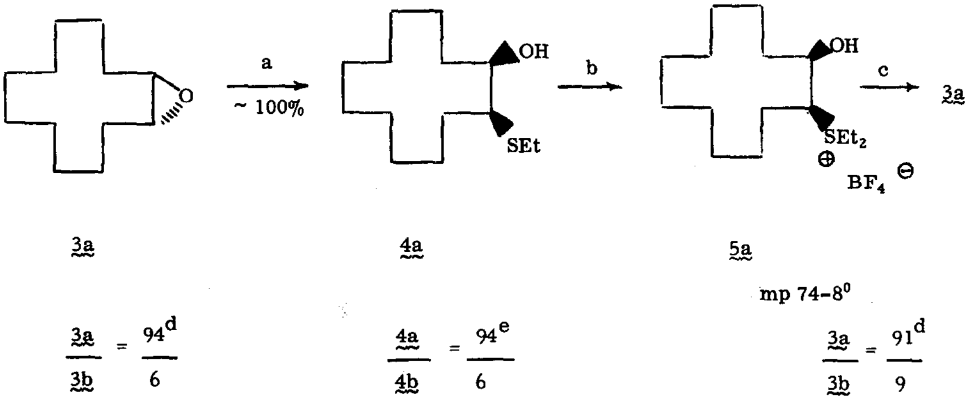
Scheme I

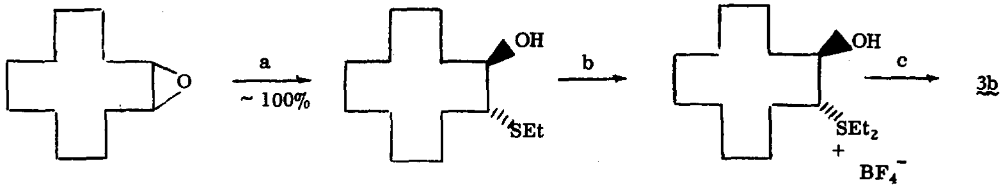


work in a related area,[5] we considered it important to rule out an alternative mechanistic possibility involving reductive elimination about sulfur[6] from the four-membered ring species 2 (path 2 in Scheme I); 2 is analogous to the accepted intermediate in the Wittig reaction. We report here an unambiguous verification of path 1.

Trans- and *cis*-cyclododecene epoxides were opened to the corresponding isomeric hydroxy sulfides 4a and 4b shown in Scheme II. Purification of 4a by preparative thin layer chromatography (tlc) and of 4b by recrystallization provided samples of the indicated isomeric purity.[7] The stereochemical assignments assume a normal S_N2 opening of the epoxide ring, which is supported by the relative reactivities of the two epoxides in this step. Examination of models reveals that backside attack will be more hindered in the *trans* isomer 3a, which does indeed react some ten times more slowly than 3b with the thiol anion. Alkylation of the hydroxy sulfides with Meerwein's reagent provided sulfonium salts 5a and 5b, isolated in 92% and 70% yield, respectively. Exposure of THF solutions of salts 5a and 5b to sodium hydride at 0° regenerated the respective starting epoxides in high yield, with only traces of two other products detectable by tlc. The isomeric composition of the product epoxides permits no more than 3% of the crossover required by path 2. Moreover, at least two other explanations are available for this very minor, but probably real, leakage. Reversion to ylid and carbonyl compound on this scale is not incompatible with the results of Johnson and Schroeck.[4] Alternatively, proton exchange[2] involving the oxido oxygen and the ring carbon adjacent to sulfur would render the betaines derived from 5a and 5b equivalent.

Scheme II





3b 4b 5b

mp 41-4° mp 65-70°

$\frac{3b}{3a} = \frac{98^d}{2}$ $\frac{4b}{4a} = \frac{> 99.5^e}{< 0.5}$ $\frac{3b}{3a} = \frac{97^d}{3}$

[a] 5 eq NaSEt, DMF, 80° for 15 hr (3a), or for 2 hr (3b).

[b] 1 eq $Et_3O^+BF_4^-$, CH_2Cl_2, 25°, < 5 min.

[c] NaH, THF, 0°.

[d] Determined by glpc analysis using 3% OV-17 on 100-120 mesh gas chrom Q (Applied Science Labs.) in a 4' x 1/8" glass column at 130°.

[e] Determined by glpc analysis using 3% HI-EFF 8BP on 60-80 mesh gas chrom Q (Applied Science Labs.) in a 6' x 1/8" glass column at 200°.

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2) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, 1966, pp 304-362.

3) T. Durst, R. Viau, R. VanDen Elzen, and C. H. Nguyen, Chem. Commun., 1334 (1971).

4) C. R. Johnson and C. W. Schroeck, J. Amer. Chem. Soc., **93**, 5303 (1971). In contrast, betaines derived from two less reactive sulfur ylids revert to ylid and electrophile more rapidly, leading to loss of stereochemistry about this center.

5) K. B. Sharpless and A. Y. Teranishi, manuscript in preparation.

6) For some interesting examples of reductive elimination about sulfur see B. M. Trost, W. L. Schinski, F. Chen, and I. B. Mantz, J. Amer. Chem. Soc., **93**, and references

cited therein.

7) Hydroxy sulfides 4a and 4b were completely characterized by ir and nmr spectra and by elemental analyses. The cis isomer 4a gave a 1-naphthyl urethane derivative of mp 130 - 1°