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SULFONIUM SALTS II - SULFENYL PRODUCTS FROM A PUMMERER INTERMEDIATE

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We wish to report the first instance of β-elimination of a halosulfonium salt. By contrast to its normal relatives which decompose solely by way of the Pummerer Reaction (1-3), thiophane dibromide (I) suffers only elimination and rearrangement to 3-bromobut-3-ene sulfenyl bromide (V) (Fig. 1).

The dibromide (I) (4,5), a pale orange, crystalline solid, mp 81° (dec.), prepared by bromination of thiophane in carbon tetrachloride at -10°, dissolves slowly in carbon tetrachloride at 50° forming a red solution. Dissolution is accompanied by the rapid evolution of one equivalent of hydrogen bromide and a color change from deep red to pale clear yellow. In methylene chloride, solution may be achieved before hydrogen bromide evolution. Addition of slightly greater than one equivalent each of pyridine and methanol to the yellow solution after hydrogen bromide evolution leads to the precipitation of pyridinium hydrobromide, complete loss of color, and formation of a stable product mixture containing equimolar quantities of thiophane and methyl 3-bromobut-3-enesulfenate (VI) (96% yield) isolable by column chromatography on alumina. Only a trace of α-methoxythiophane, the methanolysis product of the Pummerer reaction, was observed in the final reaction mixture.

The assignment of the sulfenate structure VI requires that the unstable precursor be sulfenyl bromide V. In agreement with a sulfenyl bromide intermediate, a solution free of thiophane dibromide provided a positive starch-iodide test.

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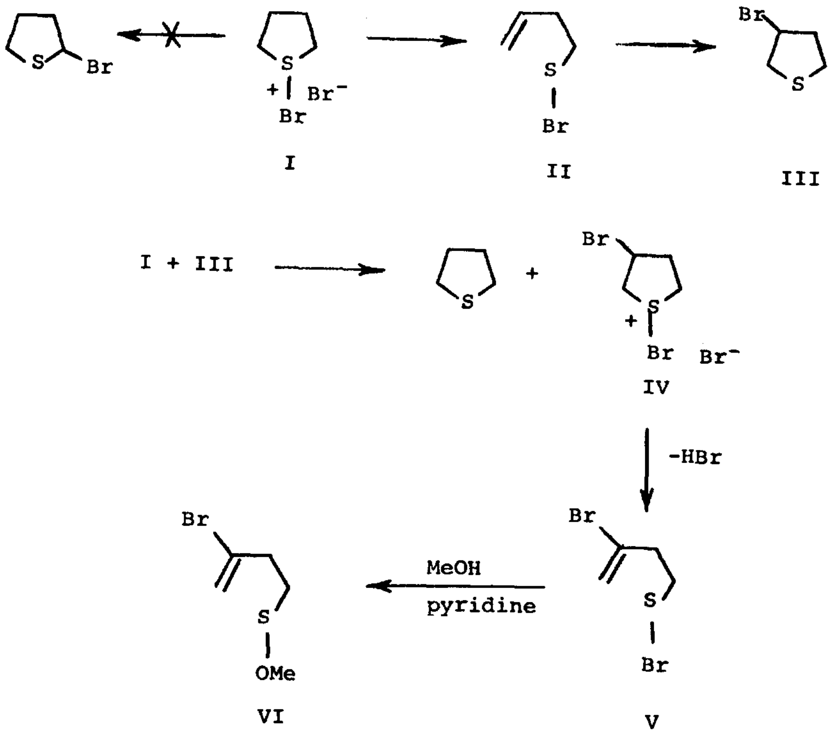

Fig. 1

The structural assignment of the sulfenate is based on the chemistry and on spectral data. The sulfenate gave a negative starch-iodide test but decolorized bromine in carbon tetrachloride. The infrared spectrum showed no peaks above 3000 cm^{-1} nor any peak in the 1600-1700 cm^{-1} region; absorption for a sulfoxide was also absent. A broad maximum was found in the ultraviolet at 210 mμ (ε730). The nmr spectrum showed a doublet with apparent coupling constant of about 1.5 Hz at 5.08 ppm (1H) and a structured single peak at 4.5 ppm (1H) broadened by coupling to the trans-methylene group. The methylene groups gave multiplets at 2.3 ppm (CH_2-S) and 3.0 ppm (CH_2-C=). A singlet methyl resonance at 3.24 ppm ruled out a sulfoxide structure. The mass spectrum confirmed the molecular weight (198) and the bromine content.

A possible mechanism for the reaction is shown in Figure 1. In the media used, the initial elimination must be concerted and product determining, and it is probably the slow step. Loss of the β-proton occurs preferentially with this halosulfonium salt probably because the bromide ion is too weak a base to remove the α-proton in this system. Subsequent intramolecular addition of the sulfenyl bromide to the proximately formed double bond (6) and intermolecular halogen transfer between sulfur atoms (1c,7) to form VI should be fast reactions. The rate constant for the last step (V → VI) should be greater than that for the initial hydrogen bromide elimination and selectivity should be high because of the presence of the bromine atom on the β-carbon of the thiophane ring.

In support of this mechanism sulfenyl bromide II has been shown to cyclize to III, and 3-bromothiophane reacts with bromine in the presence of lithium bromide to produce V.

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3. We propose that the name "Pummerer Reaction" to be broadened to include all those mechanistically similar transformations, including α-halogenations, which take place by way of sulfonium salts and which result in the formation of an α-substituted sulfide.

4. Thiophane dibromide is here represented as the sulfonium salt for simplicity only. The question of the structure of halosulfonium salts has not yet been completely resolved.

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