NEW TRANSANNULAR REACTION OF SULFOXIDES

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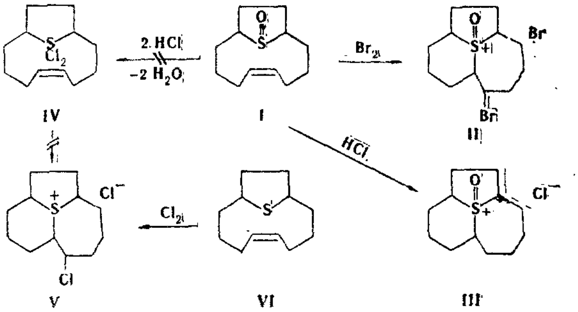
We have observed a new transannular reaction with the participation of sulfoxide sulfur and a double bond to give sulfonium salts.

The action of bromine in CCl_4 on 13-thiabicyclo[8.2.1]-cis-5-tridecene (I) gave a quantitative yield of 1-thionium-6-bromotricyclo[8.2.1.$0^{1,7}$]tridecane bromide S-oxide (II) with mp 213-214°. Found: C 38.7; H 4.9; Br 43.2; S 8.5%. $C_{12}H_{20}Br_2OS$. Calculated: C 38.7; H 5.2; Br 43.0; S 8.6%.

A similar transformation also occurs in the action of hydrochloric acid on I to give 1-thioniumtricyclo[8.2.1.$0^{1,7}$]tridecane chloride S-oxide (III) with mp 129-132° (in 90% yield).



The absence of a double bond in II and III, as proved by the IR and PMR spectra, the presence of ionically bonded chlorine and bromine, as confirmed by mercurometric titration, and the high solubility in water indicate the salt structure of these compounds.

The absence in the products of the reaction of I with HCl of a salt with structure V, the formation of which through intermediate IV [1] might be assumed, was proved by alternative synthesis. Salt V, obtained by the action of chlorine on 13-thiabicyclo[8.2.1]-5-tridecene (VI), differs from salt III with respect to melting point, spectral data, and elementary analysis.

The formation of structure III is also confirmed by alkaline hydrolysis, which gives a sulfoxide.

LITERATURE CITED

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