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REACTIONS OF I-ARYL-THYONIA-CYCLO-ALCANE PERCHLORATES WITH NUCLEOPHYLIC AGENTS

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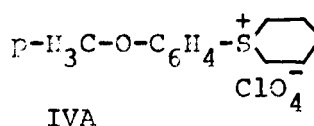
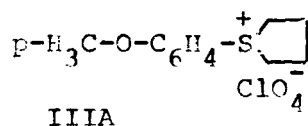
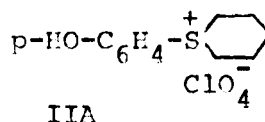
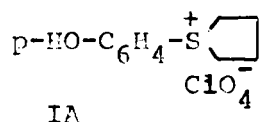
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REACTIONS OF I-ARYL-THYONIA-CYCLO-ALCANE PERCHLORATES WITH NUCLEOPHYLIC AGENTS

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For the characteristic of comparative >C-S^+ bond strength of heterocycles the interaction between four perchlorates of I-aryl-thyonia-cyclo-alcane (IA-IVA) and relative weak nucleophilic agents was investigated. The crystal structure of the initial salt (IIA) was established.



The perchlorates IA-IVA interacting in aqueous or alcoholic solution with potassium halogenides or caustic potassium undergo, according to the salt structure and nature of the nucleophilic agent, either change of the sulfonium salt anion or cyclic C-S bond cleavage forming substituted alkylarylsulfides $\text{Ar-S-(CH}_2)_n\text{X}$. Ease of the C-S bond cleavage decreases in sequence $\text{KOH} > \text{Cl} > \text{Br}$ in consequence of the nucleophilic agent nature.

The heterocycle C-S bond strength decreases in sequence $\text{II} > \text{I} > \text{IV} > \text{III}$.

All cations I-IV are stable by the action of picric acid and potassium iodide; and I-p-hydroxyphenylthioniacyclohexan

is stable by the action of other nucleophiles studied also. During the crystallisation of salt IIA from solutions the salt molecules interact forming hydrogen bonds. The crystal structure of IIA consists of two independent cations $p\text{-HO-C}_6\text{H}_4\text{-S}^+\text{C}_6\text{H}_5$ (II) and two anions ClO_4^- (A) forming the asymmetric part of cell. The cations are bonded with anions by two types of hydrogen bonds: the first type of bonds is formed by phenyl hydroxide of one of cation and oxygen atom of the anion, the second type of hydrogen bond is a bifurcated bond formed by phenyl hydroxide of another independent cation and two oxygen atoms of two another anions A. The first type of bonds forms isolated pairs of ions; the second type of bonds forms infinite chains united pairs of cations and anions.

The structure IIA is confirmed by X-ray analysis (M.Yu. Antypin, A.E. Kalinin, Yu.T. Struchkov - Institute of element organic compounds, Academy of Sciences, Moscow, USSR).