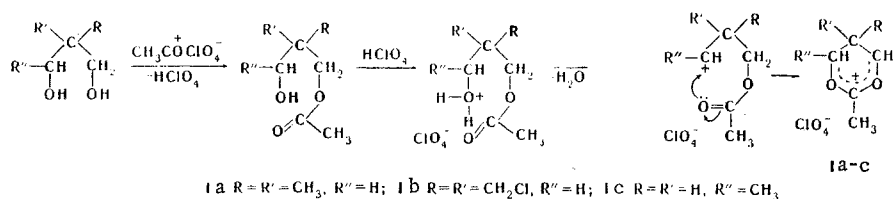


SYNTHESIS OF DIOXANIUM SALTS

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For the first time we have obtained dioxanium salts by the action of acetic anhydride on 1,3-diols in the presence of perchloric acid. The formation of these salts confirms the previously [1] proposed mechanism of the synthesis of heterocyclic systems with two oxygen atoms. The IR spectra of the salts (in mineral oil) contain an intense band at 1636 cm^{-1} and bands at $1502\text{--}1537\text{ cm}^{-1}$, which are not characteristic for dioxane derivatives but can be ascribed to the vibrations of the $\begin{matrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{matrix}$ fragment. An absorption band at $\lambda_{\text{max}} 284\text{ nm}$ is observed in the UV spectrum (acetic acid).



The acid hydrolysis of Ia gave 2,2-dimethyl-1,3-propanediol monoacetate, the IR spectrum of which contains an ester absorption at 1720 cm^{-1} and $\nu_{\text{OH}} 3500\text{ cm}^{-1}$.

EXPERIMENTAL

2,5,5-Trimethyl-1,3-dioxanium Perchlorate (Ia). A 2-ml (0.02 mole) sample of 70% HClO_4 was added to a cooled mixture of 2.08 g (0.02 mole) of 2,2-dimethyl-1,3-propanediol and 13 ml of acetic anhydride, and the mixture was heated at 60°C for 30 min. It was then diluted with ether, and the resulting oil was purified by repeated reprecipitation from acetone solution by the addition of ether. Cooling of an ether-acetic anhydride solution of the product precipitated 0.6 g (22%) of light-yellow crystals with mp $213\text{--}214^\circ$ (dec.). Found, %: C 37.7; H 5.5. $\text{C}_7\text{H}_{13}\text{ClO}_6$. Calculated, %: C 36.8; H 5.7.

A similar procedure was used to obtain 2-methyl-5,5-dichloromethyl-1,3-dioxanium perchlorate (Ib) [24% yield, mp above 200° (dec.)]. Found, %: C 28.6; H 3.7. $\text{C}_7\text{H}_{11}\text{Cl}_2\text{O}_6$. Calculated, %: C 28.5; H 3.7] and 2,4-dimethyl-1,3-dioxanium perchlorate (Ic) [25% yield, mp above 180° (dec.)]. Found, %: C 33.8; H 5.7. $\text{C}_6\text{H}_{11}\text{ClO}_6$. Calculated, %: C 33.6; H 5.1.]

LITERATURE CITED

1. L. V. Mezheritskaya and G. N. Dorofeenko, *Khim. Geterotsikl. Soedin.*, 1023 (1971).

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