

Reactions of 1,3-Dioxenium Perchlorates with Nucleophiles

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Obtained recently 1,3-dioxenium perchlorates have shown extremely high reactivity of adjacent to heterocycle alkyl substituents in condensation reactions with electrophiles of a various nature - aldehydes, amides, sulfoxides, orthoesters, diazonium salts [1, 2]. However, 1,3-dioxenium derivatives of more complex structure were considered to be more interesting to study in interaction with nucleophiles.

For example, trimethinecyanines of 1,3-dioxenium series **1** due to symmetry of a structure and delocalization have pairwise identical reactive carbon atoms of heterocycles plus central carbon atom of methine chain. Therefore, it was quite reasonable to expect wide variety of products of nucleophile addition and subsequent heterocycle ring destruction as a result of alcoholysis, hydrolysis, and aminolysis.

Experiment showed, however, that alcoholysis selectively gives rise to addition product **2**. Hydrolysis and aminolysis yielded in keto-enol **3** and enaminketone **4** respectively as a result of transformation of either of two dioxenium rings. The structure of **2** was confirmed by an X-ray study [3].

It should be noted, that (1) the terminal carbons of the whole methine chain are the most electrophilic, (2) the very first act of nucleophile addition reduces electron deficit in **1** and therefore de-activates the second dioxen ring. Formation of addition products of type **2** substantially distinguishes alcoholysis of trimethinecyanine **1** from aminolysis and hydrolysis processes.

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2. E.P. Olekhovich, V.G. Arseniev, L.P.Olekhovich, V.I. Minkin. *Khim. Geterotsikl. Soedin*, 1996, No.11/12, 1445.
3. V.G. Arseniev, E.P. Olekhovich, O.Ya. Borbulevich, O.V. Shishkin, Yu.A. Zhdanov, V.I. Minkin, L.P. Olekhovich. *Izv. Akad. Nauk Ser. Khim.*, 1998 (accepted).