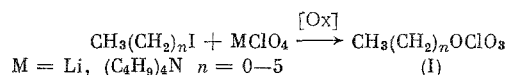


# COMPETING BINDING OF PERCHLORATE ANION IN OXIDATIVE ELIMINATION OF IODINE REACTIONS

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As already reported by us [1], the perchlorate anion, which is considered to be a superweak nucleophile, can combine with carbonium ion intermediates in  $Ad_E$  reactions in the presence of other stronger nucleophiles. This phenomenon induced us to study the possibility of formation of covalent perchlorates in other carbonium ion processes, in particular, during the oxidative decomposition of alkyl iodides [2]. The reaction was carried out by adding the oxidizing agent [Ox], for example  $Cl_2$  ( $-78^\circ C$ ),  $m-ClC_6H_4CO_3H$  ( $25^\circ C$ ), or  $H_5IO_6$  ( $50^\circ C$ ) to a solution of  $n$ -alkyl iodide in an aprotic solvent ( $Et_2O$ ,  $AcOEt$ , or  $CHCl_3$ ) in the presence of 1-5 equiv.  $LiClO_4$  or  $(C_4H_9)_4NClO_4$ . After distillation or chromatography on a  $SiO_2$  column, in all cases  $n$ -alkyl perchlorates (I) were isolated as the main products



The structure of (I) was confirmed by IR and PMR spectra (cf. [3]). The yields of the perchlorates depend on the nature of the oxidizing used and the salt added, reaching 50-70% in the reactions with chlorine.

The results obtained show a high nucleophilic reactivity of the  $ClO_4^-$  anion, which can take part in the concluding stage of the carbonium ion processes even in the presence of much more nucleophilic moieties, e.g.,  $Cl^-$ ,  $H_2O$ , etc., in the reaction mixture. The reaction can serve as a simple and convenient method for the synthesis of covalent organic perchlorates.

## LITERATURE CITED

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