COVALENT BINDING OF THE PERCHLORATE ANION IN THE DESULFURIZATION OF β-CHLOROALKYL ARYL SULFIDES BY THE ACTION OF CHLORINE

N. S. Zefirov, V. V. Zhdankin,
V. D. Sorokin, and A. S. Koz'min

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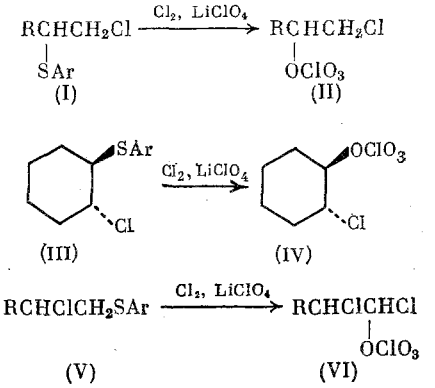
In a continuation of an investigation of the competitive binding of nucleophilic anions in reactions involving carbonium ions [1], we studied the chlorinolysis of alkyl aryl sulfides [2, 3] in the presence of lithium perchlorate.

The reactions of β-chloroalkyl aryl sulfides (I) and (III) which contain an ArS group at a secondary carbon atom with chlorine in the presence of lithium perchlorate in ether or ethyl acetate proceed at 0°C over 1-2 h to give β-chloroalkyl perchlorate (II) in 30-40% yield and perchlorate (IV) in 60-70% yield. These products were separated by column chromatography on silica gel and identified by the agreement of their spectral and physical indices with those reported in our previous work [4].



R = n-C_5H_{11}; Ar = 2-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$.

The chlorinolysis of alkyl aryl sulfides (V) containing a thioaryl group at a primary carbon atom proceeds much more slowly and is accompanied by the formation of a complex mixture. This mixture yielded 5-7% of a product assigned the structure of dihaloperchlorate (VI). This product is an explosive oil, R_f 0.45 (on silica gel with hexane eluent). IR spectrum (ν, cm^{-1}): 1275, 1250, 1235. PMR spectrum (δ, ppm): 5.8 d ($CHClOClO_3$), 4.05 m (CHCl), 2.1-0.9 m (C_5H_{11}).

Thus, these reactions revealed new directions for the chemical transformations of chlorosulfonium salts, which are intermediate species in desulfurization by the action of chlorine [2, 3], and obtain covalent perchlorates. The possibility of the formation of such perchlorates in these reactions was not considered previously [5]. These examples open new possibilities in both the preparative syntheses of perchlorates and in the study of the mechanism for desulfurization of sulfides by chlorine.

LITERATURE CITED

1. N. S. Zefirov, A. S. Koz'min, V. V. Zhdankin, V. N. Kirin, N. M. Yur'eva, and V. D. Sorokin, Chem. Sci., 21, 195 (1983).
2. G. E. Wilson, Tetrahedron, 38, 2597 (1982).
3. H. Kwart and R. K. Miller, J. Am. Chem. Soc., 78, 5008 (1956).
4. N. S. Zefirov, A. S. Koz'min, V. V. Zhdankin, A. V. Nikulin, and N. V. Zuk, J. Org. Chem., 47, 3679 (1982).
5. H. Kwart, R. W. Body, and D. M. Hoffman, Chem. Commun., 765 (1967).

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