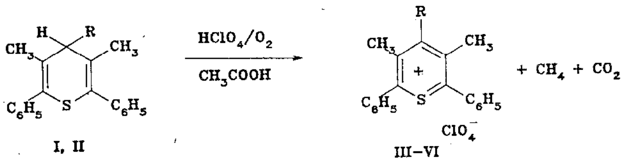
LETTERS TO THE EDITOR

PECULARITIES OF THE OXIDATIVE DEHYDROGENATION OF POLYSUBSTITUTED 4H-THIOPYRANS

V. G. Kharchenko and N. I. Kozhevnikova

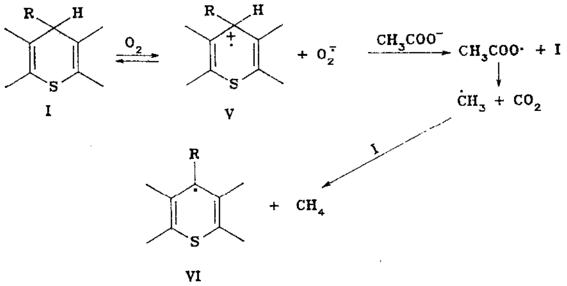
UDC 547.818.59

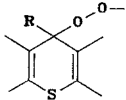
Polysubstituted 4H-thiopyrans I, II form thiopyrylium salts III and IV with perchloric acid in acetic acid only in the presence of oxygen [1].



I, III $R=C_6H_5$; II, IV $R=CH_3$

Methane and carbon dioxide were detected for the first time in the gaseous products of this reaction, which may be evidence of the formation of acetyloxy radicals in the reaction mixture. Methane and carbon dioxide were not detected in the gas phase above an acetic acid—perchloric acid mixture and above an acetic acid—perchloric acid—hydrogen peroxide mixture. Evidently the acetyloxy radicals, capable of fragmenting to carbon dioxide and the methyl radical, are formed in the reduction of the CH_3COO^- anion by the radical cation V.



One of the pathways of further conversion of the thiopyranyl radical VI is probably its interaction with oxygen, followed by disproportionation of the peroxide radical that thereby arises with a thiopyran molecule. In acid medium solvolysis of the 4H-thiopyran hydroperoxide thereby obtained  to the corresponding thiopyrylium cation (III, IV) and hydrogen peroxide is possible.

An analysis of the gas phase above the reaction mixture thiopyran (I, II)—perchloric acid—acetic acid, prepared by the method of [1] in a special setup, was performed after completion of the salt formation reaction on an LKhM-72 chromatograph.

LITERATURE CITED

1. V. G. Kharchenko, N. I. Kozhevnikova, and N. V. Voronin, Khim. Geterotsikl. Soedin., No. 4, 562 (1979).

N. G. Chernyshevskii Saratov State University, Saratov 410601. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1689-1690, December, 1983. Original article submitted March 4, 1983.

0009-3122/83/1912-1339$07.50