OXIDATIVE FORMATION OF THIAPYRYLIUM SALTS BY POLYSUBSTITUTED THIOPYRANS

V. G. Kharchenko, N. I. Kozhevnikova, and N. V. Voronina

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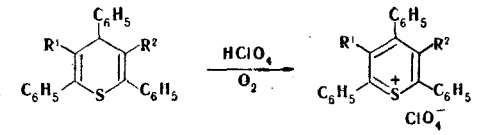
We have found that polysubstituted thiopyrans (I, II) do not react with perchloric acid in a helium atmosphere, whereas in air they form thiapyrylium perchlorates (III, IV). The rate of the process increases when oxygen is bubbled into the mixture.



I, II III, IV

I, III $R^1 = CH_3$, $R^2 = H$; II, IV $R^1 = R^2 = CH_3$

Thus 1.3 ml of 70% $HClO_4$ was added dropwise to a suspension of 1 g of thiopyran II in 30 ml of glacial acetic acid, and perchlorate IV was separated after 40 h [with monitoring by thin-layer chromatography (TLC) on Silufol]. The product was obtained in 89% yield and had mp 304-306°C (from acetic acid). Similarly, perchlorate III, with mp 191-193°C (from acetic acid), was obtianed in 86% yield from thiopyran I. No melting-point depression was noted for mixtures of these products with authentic samples of the corresponding thiapyrylium perchlorates; the IR spectra of thiapyrylium salts III and IV confirmed their structures.

If the reaction of thiopyrans I and II is carried out under oxygen-free conditions (three freezings and thawings in vacuo), 95% of starting thiopyran II (or 87% of thiopyran I) is isolated from the reaction mixture after 20 days.

The disproportionation observed for the previously investigated thiopyrans [1] does not occur in this case.

LITERATURE CITED

1. V. G. Kharchenko, M. E. Stankevich, N. M. Kupranets, A. R. Yakoreva, V. I. Kleimenova, and S. K. Klimenko, Zh. Org. Khim., 8, 193 (1972).

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