PERCHLORATE OF THE PHENOXAZINE CATION RADICAL

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We were able to develop a convenient method for the oxidation of phenoxazine (I) that makes it possible to isolate the perchlorate salt (II) of the phenoxazine cation radical, the existence of which in solutions has been demonstrated by EPR spectroscopy. For this, we carefully ground an equimolar mixture of phenoxazine with ferric perchlorate nonhydrate in a small amount of 57% perchloric acid. The dark-red precipitate of II was removed by filtration and washed with the minimum amounts of acetone and ether to give the product in 53% yield. The results of elementary analysis of the salt are in agreement with the empirical formula. Treatment of a solution of perchlorate II in acetonitrile with zinc dust gives phenoxazine. The EPR spectrum of a solution of II in acetonitrile (10^{-4} mole/liter) consists of a quartet of lines ($a_H^{NH} \sim a_N \sim 7.6$ Oe). The absorption spectrum in the visible region contains a band with λ_{max} 383, 409, and 530 nm.

The perchlorate of the phenothiazine cation radical was similarly obtained from phenothiazine (III). The IR spectra of the compound obtained and an authentic sample [1] coincided. The absorption spectrum, with λ_{max} at 438 and 515 nm (acetonitrile), was in agreement with the data [2] for the phenothiazine cation radical.

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