SYNTHESIS OF 11-OXOINDENO[1,2-c]-2-THIABENZOPYRYLIUM SALTS

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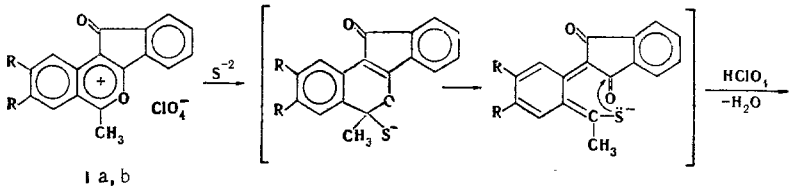
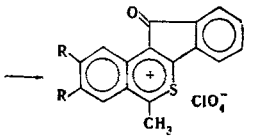
We have shown (despite the opinion expressed in [1] regarding the impossibility of replacement of the oxygen heteroatom by sulfur in 2-benzopyrylium salts) that 11-oxoindeno[1,2-c]-2-benzopyrylium salts (I) are readily converted to 2-thiabenzopyrylium salts (II) on treatment with sodium sulfide.



I a, b



II a, b I, II a R = OCH_3; b R + R = OCH_2O

Thus a suspension of 0.41 g (0.001 mole) of 1-methyl-8,9-dimethoxy-11-oxoindeno[1,2-c]-2-benzopyrylium perchlorate (Ia) in 15 ml of acetone was shaken for 10 min with 3 ml of 10% aqueous sodium sulfide solution, and the resulting clear bright-red solution was treated with 5 ml of 20% perchloric acid solution. The precipitated salt was removed by filtration and recrystallized from glacial acetic acid containing one drop of 70% perchloric acid to give brown crystals of 1-methyl-8,9-dimethoxy-11-oxoindeno[1,2-c]-2-thiabenzopyrylium perchlorate (IIa), with mp 250°, in 49% yield. PMR spectrum: singlets at 2.87 (3H), 3.7 (3H), and 3.9 (3H) and multiplet at 7.16-7.75 ppm (6H). The character of the spectrum is very close to that of starting Ia.

1-Methyl-8,9-methylenedioxy-11-oxoindeno[1,2-c]-2-thiabenzopyrylium perchlorate (IIb) was similarly obtained as dark-red crystals with mp 230° (glacial acetic acid) in 85% yield. The results of analysis for C, H, S, and Cl of both substances were in agreement with the calculated values. Absorption at 1730 and 1600 cm^{-1} is observed in the IR spectra of IIa, b.

LITERATURE CITED

1. V. Dimroth and H. Odenwälder, Ber., 104, 2984 (1971).

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