SYNTHESIS OF 4-OXO-1,3-BENZOTHIAZINES AND THEIR SALTS

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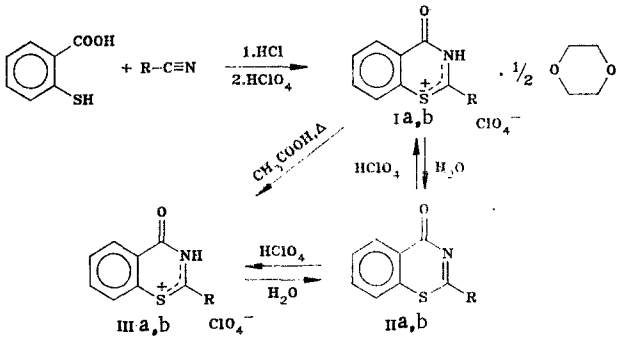
4-Oxo-1,3-benzoxazinium salts are convenient intermediates in the synthesis of o-hydroxyphenyl-substituted 1,3,5-triazines [1] and 1,2,4-triazoles and oxadiazoles [2]; however, their sulfur analogs, viz., 4-oxo-1,3-benzothiazinium salts (III), which are potential synthones of o-mercaptophenylazoles and azines, have been virtually inaccessible until now [3].

We have found that benzothiazinium perchlorates in the form of 2:1 complexes with dioxane (I) are formed in 60-70% yields by saturation with hydrogen chloride of equimolar amounts of thiosalicylic acid and benzonitrile and phenylacetonitrile in a 15-fold excess of dioxane at 0°C with subsequent treatment of the reaction mixture with 70% perchloric acid in acetic anhydride (1:3).



I–III a R=C_6H_5; b R=$CH_2C_6H_5$

Complexes I are stable during storage, but upon heating or recrystallization from glacial acetic acid they are desolvated and are converted quantitatively to stable perchlorates III, and, upon reaction with water or triethylamine in benzene, they are converted to the previously described [4] 4-oxo-1,3-benzothiazines IIa [mp 125°C (from alcohol)] and IIb [mp 155°C (from dioxane)]. The latter react with perchloric acid in dioxane to give complexes I, whereas in ether or glacial acetic acid they give perchlorates III, which are reversibly deprotonated by treatment with water.

IR spectra of complexes I (mineral oil): Ia: 3085 (NH), 1720 (C=O), and 1585, 1545, 1300, and 1085 cm^{-1} (ClO_4^-); Ib: 3120, 1730, 1590, 1545, 1300, 1105, and 1055 cm^{-1}. PMR spectra of complexes I: Ia (CF_3COOD): 3.8 (4H, s, OCH_2CH_2O) and 7.47-8.40 ppm (9H, m, aromatic protons); Ib (CF_3COOH): 3.6 (4H, s, OCH_2CH_2O), 4.34 (2H, s, CH_2), 7.1 (5H, s, C_6H_5), and 7.30-8.35 ppm (4H, m, phenylene).

Perchlorate IIIa, with mp 246°C (dec., from glacial AcOH), was obtained in 97% yield. Perchlorate IIIb, with mp 188°C (dec., from glacial AcOH), was obtained in 75% yield. IR spectra of perchlorates III (mineral oil): IIIa: 3085 (NH), 1695 (C=O), and 1585, 1520, 1300, and 1085 cm^{-1} (ClO_4^-); IIIb: 3130, 1730, 1585, 1540, 1300, 1100, and 1045 cm^{-1}.

The results of elementary analysis of the synthesized I and III were in agreement with the calculated values.

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SYNTHESIS OF 4-(1-METHYL-4-HYDROXY-4-PIPERIDYL)QUINOLINE AND 4-(1-METHYL-4-HYDROXY-4-PIPERIDYL)-1,2-DIHYDROQUINOLINE

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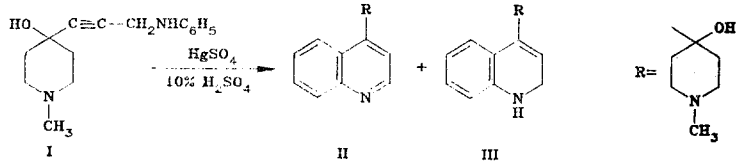
We have established that 1-methyl-4-(3-anilino-1-propynyl)-4-piperidol (I) undergoes cyclization to give new, difficult-to-obtain, 4-substituted quinoline derivatives II and 1,2-dihydroquinoline III when it is heated in sulfuric acid in the presence of catalytic amounts of mercuric sulfate.



1-Methyl-4-(3-anilino-1-propynyl)-4-piperidol (I) was obtained by the reaction of 107 mmole of 1-methyl-4-piperidone and 107 mmole of N-propargylaniline in 200 ml of absolute ether in the presence of 214 mmole of KOH for 7-8 h at 0-5°C. The yield of piperidol I, with mp 113-114°C [from benzene–petroleum ether (1:1)], was 70%. IR spectrum (KBr): 1600 (benzene ring), 2170 (C≡C), 3100-3150 (OH), and 3315 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 2.06 (3H, s, NCH_3), 3.8 (2H, d, J = 4 Hz, CH_2NH), 4.62 (1H, broad s, OH), and 6.5-7.35 ppm (5H, m, aromatic protons).

4-(1-Methyl-4-hydroxy-4-piperidyl)quinoline (II) and 4-(1-methyl-4-hydroxy-4-piperidyl)-1,2-dihydroquinoline (III) were formed by heating 84 mmole of piperidol I in 100 ml of 10% H_2SO_4 in the presence of 1 g of $HgSO_4$ for 5 h at 70-80°C. The precipitate that formed after cooling and neutralization of the reaction mixture was removed by filtration and separated with a column packed with aluminum oxide (the eluent was $CHCl_3$ saturated with NH_3) to give 60% of quinoline II with mp 181-182°C (from benzene). IR spectrum ($CHCl_3$): 1580 and 1590 (quinoline ring); 3590 cm^{-1} (OH). PMR spectrum ($CDCl_3$): 2.03 (3H, s, NCH_3), 5.05 (1H, s, OH), 6.87 (1H, d, J = 4 Hz, 3-H), 7.37 (2H, m, 6-H and 7-H), 7.87 (1H, d, J = 8 Hz, 5-H), 8.30 (1H, d, J = 4 Hz, 8-H), and 8.79 ppm (1H, d, J = 7 Hz, 2-H). The yield of dihydroquinoline III, with mp 120-121°C (from benzene), was 10%. IR spectrum ($CHCl_3$): 1685 (benzene ring), 1610 (C C), 3460 (NH), and 3585 cm^{-1} (OH). PMR spectrum (d_6-DMSO): 2.16 (3H, s, NCH_3), 3.32 (2H, d, J = 4 Hz, 2-H), 3.91 (1H, s, OH), 5.75 (1H, t, J = 3 Hz, 4-H), and 6.50-7.35 ppm (4H, m, 5-H, 6-H, 7-H, 8-H). The results of elementary analysis of I-III were in agreement with the calculated values.

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