CHLOROSULFONATION OF 2-PYRIDONES

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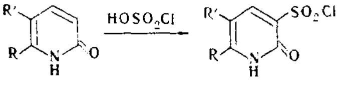
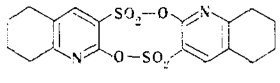
Chlorosulfonlyl-substituted 2-pyridones were obtained for the first time. The ability of 2-pyridone-3-sulfonyl chlorides to undergo conversion to sulfonylides of the pyridine series by the action of bases is shown in the case of 5,6,7,8-tetrahydro-2-quinolone-3-sulfonyl chloride.

In a continuation of our investigation of electrophilic substitution reactions in the 2-pyridone sèries [1, 2], in the present paper we have for the first time studied the chlorosulfonation of 2-pyridones and some properties of the sulfonyl chlorides obtained. We used 5,6,7,8-tetrahydro-2-quinolone (I), 5,6-dimethyl-2-pyridone (II), and 1-methyl-2-pyridone (III) as the starting 2-pyridones.

5,6-Disubstituted 2-pyridones I and II were chlorosulfonated by heating with a fivefold excess of chlorosulfonic acid to 110-120°C for 10 h.



I, II IV, V



VIII

I, IV R–R'=$(CH_2)_4$; II, V R=R'=CH_3

The structure of sulfonyl chlorides IV and V was confirmed by the IR spectra, which contain amide C=O absorption (1660 cm^{-1}) and intense absorption bands at 1163 and 1377 cm^{-1}, which are characteristic for the chlorosulfonyl group [3, 4].

Thus, 2-pyridones are chlorosulfonated under considerably more severe conditions than benzene and toluene, but are nitrated more readily than the latter [1].

Sulfonyl chloride IV was characterized by the preparation of m-toluidide VI and sulfonic acid VII (by hydrolysis). In an attempt to obtain the amide by the action of concentrated ammonium hydroxide on sulfonyl chloride IV, we isolated a compound (in 55% yield) to which we assigned sulfonylide structure VIII on the basis of the results of elementary analysis, the mass spectrum (M^+ 422), and the IR spectrum (the presence of the absorption of a pyridine ring at 1590, 1200, and 1040 cm^{-1}). Compound VIII was obtained in higher yield (88%) by the action of aqueous 2 N sodium hydroxide on sulfonyl chloride IV. The formation of the previously unknown sulfonylide of the pyridine series* can be explained by the intermolecular interaction of the chlorosulfonyl groups of IV with the oxygen atom of the α-pyridone ring.

Sulfonyl chloride VIII is cleaved by refluxing in 20% sodium hydroxide solution to give sodium 5,6,7,8-tetrahydro-2-quinolone-3-sulfonate (IX), from which sulfonic acid VII was obtained by treatment with KU-2 cation-exchange resin.

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* Sulfonylides were previously obtained from the corresponding sulfonyl chlorides of phenols and cresols [5, 6].

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1-Methyl-2-pyridone (III) is not chlorosulfonated under the conditions described above, but 1-methyl-2-pyridone-3,5-disulfonyl chloride (X) was obtained in 15% yield under more severe conditions (by heating with a tenfold excess of chlorosulfonic acid to 140-145° for 20 h).

EXPERIMENTAL

5,6,7,8-Tetrahydro-2-quinolone-3-sulfonyl Chloride (IV). A 4.3-g (0.93 mole) sample of 5,6,7,8-tetrahydro-2-quinolone was added gradually with cooling (cold water) to 17.6 g (0.15 mole) of chlorosulfonic acid, and the mixture was stirred and heated to 110-120° for 10 h. It was then poured over 100 g of ice, and the resulting precipitate was removed by filtration and washed to neutrality with cold water to give 3.6 g (51%) of sulfonyl chloride IV with mp 183-184° (from methylene chloride). IR spectrum, ν, cm^{-1}: 1660 (amide CO), 1163, and 1375 (SO_2Cl). Found, %: C 43.9; H 4.1; Cl 14.1. $C_9H_{10}NClSO_3$. Calculated, %: C 43.6; H 4.0; Cl 14.3.

5,6-Dimethyl-2-pyridone-3-sulfonyl Chloride (V). This compound, with mp 187-188° (from methylene chloride), was obtained in 42% yield by the method described above. IR spectrum, ν, cm^{-1}: 1660 (amide CO), 1163, and 1375 (SO_2Cl). Found, %: C 38.1; H 3.5; Cl 16.1; N 6.4; S 14.7. $C_7H_8ClNO_3S$. Calculated, %: C 38.0; H 3.6; Cl 16.0; N 6.3; S 14.4.

5,6,7,8-Tetrahydro-2-quinolone-3-sulfonic Acid m-Toluidide (VI). A mixture of 0.75 g (3 mmole) of sulfonyl chloride IV, 2 g (22 mmole) of m-toluidine, and 15 ml of a 2% solution of sodium carbonate was stirred thoroughly for 30 min, after which the resulting oil was separated and treated with a small amount of acetone. The precipitated m-toluidide (VI) was removed by filtration to give 0.7 g (73%) of a product with mp 273-274° (decomp., from dioxane). IR spectrum, ν, cm^{-1}: 1650 (amide CO), 3300 (NH). Found, %: C 60.4; H 5.7; N 8.5. $C_{16}H_{18}N_2O_3S$. Calculated, %: C 60.4; H 5.6; N 8.8.

5,6,7,8-Tetrahydro-2-quinolone-3-sulfonic Acid (VII). A) A mixture of 1.4 g (5.6 mmole) of sulfonyl chloride IV and 12 ml of water was refluxed for 1.5 h, after which the hot solution was filtered, and the filtrate was evaporated to 3 ml and cooled. The resulting precipitate of the sulfonic acid (VII) was removed by filtration and washed with acetone to give 1.0 g (77%) of a product with mp ~ 250° (decomp.). IR spectrum, ν, cm^{-1}: 1640 (amide CO), 3200 (associated OH). Found, %: C 46.8; H 4.7; S 13.9. $C_9H_{11}NO_4S$. Calculated, %: C 47.1; H 4.8; S 14.0.

B) A 0.1-g sample of sulfonylide VIII was heated for 4 h with 5 ml of 20% sodium hydroxide solution, after which the mixture was filtered, and the filtrate was passed through a column filled with KU-2 cation-exchange resin. The water was removed from the eluate by distillation, and the residue began to crystallize to give 0.03 g (30%) of a product with mp ~250° (decomp.). No melting point depression was observed for a mixture of this product with the product obtained by hydrolysis of sulfonyl chloride IV.

Sulfonylide (VIII) of 5,6,7,8-Tetrahydro-2-quinolone-3-sulfonic Acid. A total of 4 ml of 2 N aqueous sodium hydroxide was added with ice-cooling and vigorous stirring to 1 g (4 mmole) of sulfonyl chloride IV, after which the mixture was stirred for 15 min. The precipitated sulfonylide (VIII) [0.75 g (88%)] was washed on the filter with small portions of cold water, dried, and crystallized from benzene to give a product with mp 251-252°. IR spectrum, ν, cm^{-1}: 1590, 1200, and 1040 (pyridine ring). Found, %: C 51.6; H 4.2; N 6.6; S 15.0; M 422 (mass spectrum). $C_{18}H_{18}N_2O_6S_2$. Calculated, %: C 51.2; H 4.2; N 6.6; S 15.1; M 422.

1-Methyl-2-pyridone-3,5-disulfonyl Chloride (X). An 8.5-g (0.08 mole) sample of 1-methyl-2-pyridone was added gradually with water cooling in the course of 30 min to 95 g (0.8 mole) of chlorosulfonic acid, and the mixture was heated at 120-140° for 20 h. It was then poured over 500 g of ice, and the resulting precipitate was removed by filtration and washed with cold water to give 2.5 g (15%) of disulfonyl chloride X with mp 227-230° (decomp., from dioxane). IR spectrum: 1670 cm^{-1} (amide ν_{CO}). Found, %: C 23.8; H 1.6; S 21.1. $C_6H_5Cl_2NO_5S_2$. Calculated, %: C 23.5; H 1.6; S 20.9.

1-Methyl-2-pyridone-3,5-disulfonic Acid S-Benzylthiuronium Salt (XI). A mixture of 0.2 g (0.65 mmole) of disulfonyl chloride X and 4 ml of water was refluxed for 1.5 h, after which the precipitated crystals of the disulfonic acid (0.15 g) were removed by filtration and dried, 0.2 g of S-benzylthiuronium chloride was added, and the mixture was treated by the method in [7] to give 0.21 g (63%) of S-benzylthiuronium salt XI with mp 215-216° (from water). IR spectrum, ν, cm^{-1}: 1660 (amide CO), 3250, and 3100 (NH). Found, %: C 43.7; H 4.6; S 21.4. $C_{22}H_{27}N_5O_7S_4$. Calculated, %: C 43.9; H 4.5; S 21.3.

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