

## KRATKA SAOPĆENJA

## SHORT COMMUNICATIONS

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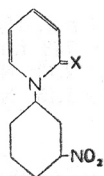
### The Preparation of Some 1-(Nitrophenyl)-2-pyridones and -thiopyridones

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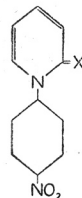
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In connection with a study of certain reactions of furfural with *m*- and *p*-nitroaniline, to be published later, samples of the hitherto undescribed 1-(3'-nitrophenyl)-2-pyridone (I) and 1-(4'-nitrophenyl)-2-pyridone (II) were prepared for purposes of comparison.



I X = O  
III X = S



II X = O  
IV X = S

The two 1-(nitrophenyl)-2-pyridones (I and II) have been prepared in a manner similar to that described by Tschitschibabin and Jeletzky for the synthesis of 1-phenyl-2-pyridone<sup>1</sup>. By condensation of dry 2-pyridone potassium<sup>2</sup> with 3-bromonitrobenzene and 4-chloronitrobenzene respectively in presence of catalytic amounts of active copper powder<sup>3</sup> at 240—260°, I and II were obtained in a satisfactory yield. The pure products were almost colourless crystalline substances, slightly soluble in hot water, better in methanol, ethanol or benzene, insoluble in ether.

The prepared pyridones could easily be converted to the corresponding 1-(nitrophenyl)-2-thiopyridones (III and IV) by means of phosphorus pentasulfide, following the excellent procedure described by Klingsberg and Papa<sup>4</sup>. On refluxing a solution of equimolecular amounts of pyridone and phosphorus pentasulfide in pyridine for two hours and pouring the reaction mixture into warm water, a high yield of the corresponding thiopyridone was obtained. The purified products (III and IV) are well crystallized yellow coloured substances, soluble in most organic solvents, sparingly soluble in hot water.

## EXPERIMENTAL

All melting points are uncorrected. The analytical samples were dried with phosphorus pentoxide *in vacuo* at 100° for two hours.

*Materials.*

2-Pyridone (2-hydroxypyridine) has been prepared from 2-aminopyridine following the method described by Adams and Schrecker for the preparation of 6-methyl-2-pyridone<sup>5</sup>. From 9.4 g. (0.1 mole) of 2-aminopyridine in 100 ml. of 20% aqueous sulfuric acid and 7.3 g. (0.106 mole) of sodium nitrite, 7.1 g. (75%) of pure 2-pyridone was obtained.

The potassium salt of 2-pyridone (2-pyridone potassium) was obtained by the method of Binz and Rāth<sup>2</sup> in form of the monohydrate melting at 269—273° (reported<sup>2</sup> m. p. 274—275°). In the following experiments 2-pyridone potassium has been previously dried at 105° to constant weight.

*1-(3'-Nitrophenyl)-2-pyridone (I)*

A mixture of 6.0 g. (0.045 mole) of dry 2-pyridone potassium, 36.2 g. (0.18 mole) of *m*-bromonitrobenzene and 0.3 g. of freshly prepared active copper powder<sup>3</sup> was heated on a sand bath in a 150 ml. round-bottomed flask, fitted with an ascendant air condenser at 240—260° for four hours. The excess of *m*-bromonitrobenzene was removed by steam-distillation, 26.8 g. (0.13 mole) of the material being regenerated in this way. The remaining content of the flask was repeatedly extracted with boiling water, until there was no further deposit from the cooled extraction liquid. From the united aqueous extracts (about 1500 ml.) 6.1 g. (63%) of crude pyridone I was obtained in form of pale brown crystals melting at 180—181°. After crystallization from 170 ml. of ethanol 5.2 g. of almost colourless needles, m. p. 183—184°, was obtained. The analytical sample, obtained after two more crystallizations, melted at 184—185°.

*Anal.* 21.425 mg. subst.: 48.2 mg. CO<sub>2</sub>, 6.6 mg. H<sub>2</sub>O  
 2.198 mg. subst.: 0.255 ml. N<sub>2</sub> (25°, 753 mm)  
 C<sub>11</sub>H<sub>8</sub>O<sub>3</sub>N<sub>2</sub> (216.2) calc'd: C 61.11; H 3.73; N 12.96%  
 found: C 61.40; H 3.45; N 13.17%

*1-(4'-Nitrophenyl)-2-pyridone (II)*

This product was synthesized in a manner analogous to that described for the preparation of I. By heating the mixture of 2 g. (0.015 mole) of 2-pyridone potassium, 9.5 g. (0.06 mole) of *p*-chloronitrobenzene and 0.1 g. of active copper powder<sup>3</sup> at 245—260° for four hours, steam-distillation of the excess of *p*-chloronitrobenzene (6.8 g., i. e. 0.043 mole, being regenerated) and extraction of the product with boiling water (total volume of extracts 300 ml.), 1.62 g. (50%) of crude II, light yellow crystals melting unsharply at 172—179°, was obtained. A single crystallization from 20 ml. of ethanol gave yellowish prismatic crystals, m. p. 187—188°. The analytical sample was obtained, after two recrystallizations, in the form of almost colourless needles, m. p. 188—189°.

*Anal.* 20.596 mg. subst.: 45.9 mg. CO<sub>2</sub>, 6.7 mg. H<sub>2</sub>O  
 2.692 mg. subst.: 0.316 ml. N<sub>2</sub> (29°, 759 mm)  
 C<sub>11</sub>H<sub>8</sub>O<sub>3</sub>N<sub>2</sub> (216.2) calc'd: C 61.11; H 3.73; N 12.96%  
 found: C 60.82; H 3.64; N 13.25%

*1-(3'-Nitrophenyl)-2-thiopyridone (III)*

To the solution of 2.2 g. (0.01 mole) of I in 10 ml. of dry pyridine, 2.2 g. (0.01 mole) of powdered phosphorus pentasulfide was added and the mixture refluxed for two hours, gentle boiling being maintained all the time. The reaction mixture was then poured into a beaker containing 50 ml. of warm water. After cooling overnight in an ice-box, the yellow solid formed was filtered off. The crude thiopyridone (yield 1.96 g., i. e. 84%) melted unsharply at 171—175°, but after crystallization from 70 ml.

of hot benzene the melting point rose to 191—192°. After several crystallizations from the same solvent, the pure product, yellow platelets melting at 199—200°, was obtained.

Anal. 21.385 mg. subst.: 44.8 mg. CO<sub>2</sub>, 6.4 mg. H<sub>2</sub>O  
 3.829 mg. subst.: 0.412 ml. N<sub>2</sub> (23°, 755 mm)  
 C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>N<sub>2</sub>S (232.27) calc'd: C 56.88; H 3.47; N 12.06%  
 found: C 57.17; H 3.35; N 12.33%

#### 1-(4'-Nitrophenyl)-2-thiopyridone (IV)

The mixture of 1.1 g. (0.005 mole) of II in 8 ml. of dry pyridine with 1.1 g. (0.005 mole) of phosphorus pentasulfide was refluxed for two hours and treated in the same manner as described for III, to give 0.85 g. (73%) of crude thiopyridone IV, light yellow crystals melting at 148—151°. After crystallization from 15 ml. of benzene the melting point rose to 166—168°. The analytical sample was obtained after two recrystallizations in form of yellow prisms, m. p. 174—175°.

Anal. 23.230 mg. subst.: 48.5 mg. CO<sub>2</sub>, 7.0 mg. H<sub>2</sub>O  
 2.397 mg. subst.: 0.256 ml. N<sub>2</sub> (23°, 751 mm)  
 C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>N<sub>2</sub>S (232.27) calc'd: C 56.88; H 3.47; N 12.06%  
 found: C 56.98; H 3.37; N 12.17%

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#### IZVOD

#### Pripravljjanje nekih 1-(nitrofenil)-2-piridona i -tiopiridona

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Opisuje se sinteza 1-(3'-nitrofenil)-2-piridona (I) i 1-(4'-nitrofenil)-2-piridona (II) iz 2-piridon-kalija<sup>2</sup> i *m*-bromnitrobenzena odnosno *p*-klornitrobenzena, uz aktivni praškasti bakar<sup>3</sup> kao katalizator. Reakciona smjesa zagrijavana je 4 sata kod 240—260°, a suvišak halogenitrobenzena izdvojen je destilacijom s vodenom parom. Na taj je način pripravljen spoj I s iskorištenjem od 63%; nakon tri kristalizacije iz etanola dobivene su gotovo bezbojne iglice sa talištem 184—185°. Spoj II je nastao, uz iste uvjete, s iskorištenjem od 50%; gotovo bezbojni igličasti kristali (iz etanola), t. t. 188—189°.

Obradom sa fosfornim pentasulfidom prevedeni su spojevi I i II u odgovarajuće 1-(nitrofenil)-2-tiopiridone (III i IV) po metodi Klingsberga i Pape<sup>4</sup>. Ekvimolekularne količine piridona i fosfornog pentasulfida u piridinu zagrijavane su 2 sata do ključanja, a zatim je reakciona smjesa izlivena u toplu vodu. Tako su dobiveni 1-(3'-nitrofenil)-2-tiopiridon (III), iskorištenje 84%, nakon višekratne prekriztalizacije iz benzena žute pločice, t. t. 199—200°, i 1-(4'-nitrofenil)-2-tiopiridon (IV), iskorištenje 73%, žute prizme iz benzena, t. t. 174—175°.

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