THE VILSMEIER COMPLEX AS A DEHYDRATING AGENT IN THE SYNTHESIS OF 2,6-DICYANOPYRIDINE

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The dehydration of dipicolinic acid diamide (I) to 2,6-dicyanopyridine (II) under the influence of phosphorus oxychloride is realized under severe conditions [1], is accompanied by considerable resinification, and gives the product in low yield when the scale of the operations is increased. We have found that the high  $\pi$ -deficient character of the pyridine ring in I and II makes it possible to use the Vilsmeier complex in dimethylformamide (DMF) for the dehydration of amide I.\* The reaction proceeds rapidly at room temperature, leads to dinitrile II in high yield (close to quantitative), and is satisfactorily reproduced when the amounts of reagents are increased.

$$H_2NOC$$
 $N$ 
 $CONH_2$ 
 $+ (CH_3)_2NC$ 
 $-OPOCI_2CI$ 
 $NC$ 
 $N$ 
 $CN$ 

The electrophilic Vilsmeier complex III evidently detaches a hydroxy group from the imino hydroxy forms of I that are formed in the transition state with subsequent deprotonation of the resulting imonium cations. The process is carried out by dissolving 10 g (67 mmole) of diamide I with gentle heating in 150 ml of DMF, cooling the solution to room temperature, adding 31 g (0.2 mole) of phosphorus oxychloride with stirring, and subsequently stirring the mixture at room temperature for 4 h. The low basicity of dinitrile II and its poor solubility in water simplify workup of the reaction products substantially. After dilution of the mixture with methylene chloride, the acidic substances and the bulk of the DMF were extracted with water, the solvent was evaporated, and the residue was washed with water and dried to give 6.2 g (90%) of dinitrile II with mp 120-121.5°C (mp 123-124°C after recrystallization from isopropyl alcohol [1]).

## LITERATURE CITED

- 1. R. Lukes and M. Pergal, Chem. Listy, <u>52</u>, 68 (1958).
- 2. T. M. Bargar and C. M. Riley, Synth. Commun., 10, 479 (1980).

<sup>\*</sup>The dehydration of amides to nitriles in the presence of the Vilsmeier reagent for compounds of the heterocyclic series was previously described in [2].

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