

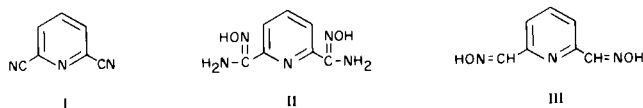
Improved Synthesis of 2,6-Dicyanopyridine (I)

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As part of a continuing investigation of amidoximes and their use in the formation of coordination compounds with transition metal ions, it was decided to synthesize 2,6-dicyanopyridine (I) for conversion to pyridine-2,6-diamidoxime (II), a potential tridentate ligand. The preparation of I by the dehydration of pyridine-2,6-dialdoxime (III) with acetic anhydride is possible; however, a commercial source of III could not be found and its synthesis appeared more difficult than that of I. Compound I has been prepared by the dehydration of pyridine-2,6-dicarboxamide with phosphorus pentoxide (4) or phosphorus oxychloride (5); however, yields in this laboratory never exceeded 10%. Previous work with the reaction of copper(I) cyanide and bromothiophenes (6) indicated that this route offered the best possibility for the preparation of the title compound.



EXPERIMENTAL

All melting points were determined using a Thomas-Kofler micro hot stage. A Varian T-60 nmr spectrometer and a Perkin-Elmer model 257 infrared spectrometer were used to determine the respective spectra. The 2,6-dibromopyridine was used as received from Aldrich Chemical Company. Elemental analyses were performed by PCR, Inc., Gainesville, Florida.

2,6-Dicyanopyridine (I).

A suspension of 9.48 g. (0.04 mole) of 2,6-dibromopyridine, 8.0 g. (0.09 mole) of copper(I) cyanide and 50 ml. of dimethylformamide was gently heated to affect solution in a 125-ml. three-necked round bottom flask fitted with a reflux condenser, glass plug, and a mechanical stirrer. (A stirring bar was ineffective due to the formation of chunky material during the course of the reaction). The dark solution was refluxed 3.5 hours after which 25 ml. of dimethylformamide were distilled from the reaction mixture, and the remainder was poured while still hot into 400 ml. of water. The reaction flask was washed and scraped clean using water and dichloromethane and the brown suspension was filtered. The filtrate was made slightly alkaline with dilute aqueous ammonia

solution and 100 ml. additional dichloromethane was added. The mixture was shaken in a separatory funnel saving the dichloromethane layer. The aqueous layer was again extracted with 100 ml. of dichloromethane and then discarded. The brown solid from the filtration was dissolved in 1:1 ammonia-water solution, filtered, and the dark blue filtrate extracted with three 100 ml. portions of dichloromethane. The dichloromethane extracts were combined and were themselves extracted with dilute aqueous ammonia solution until the blue color was removed from the dichloromethane and further extracted with 300 ml. portions of water until the aqueous layer was neutral. The dichloromethane was dried over anhydrous magnesium sulfate and removed by distillation leaving a white solid which was recrystallized from benzene to give 2.25 g. (44%) of I. A vacuum sublimed sample gave a m.p. of 125-126°; lit. (4) m.p. 123°; (5) m.p. 126°; ir: 2252 cm^{-1} ($\text{C}\equiv\text{N}$); nmr (deuteriochloroform): δ 8.09 (multiplet, 3H, A₂B pattern).

Anal. Calcd. for $\text{C}_7\text{H}_3\text{N}_3$: C, 65.11; H, 2.34; N, 32.56. Found: C, 65.21; H, 2.43; N, 32.69.

Pyridine-2,6-diamidoxime (II).

To a solution of 1.29 g. (0.01 mole) of I in 100 ml. of methanol was added 25 ml. of an aqueous solution containing 1.74 g. (0.02 mole) of hydroxylamine hydrochloride neutralized with 1.00 g. (0.025 mole) of sodium hydroxide. The reaction mixture was heated to 70° and stirred for 0.5 hour giving on cooling 1.74 g. (89%) of II, m.p. 214° dec.; ir (cm^{-1} potassium bromide): 3534(sh), 3472(sh) N-H; 3300, O-H (oxime); 1653, C=N; 956, N-O; nmr (DMSO- d_6): δ 9.84 (s, 2H, NOH); δ 7.83 (multiplet, 3H, pyridine ring H); δ 6.29 (multiplet, 4H, NH₂). The nmr signals at δ 9.84 and 6.29 disappear on deuteration.

Anal. Calcd. for $\text{C}_7\text{H}_9\text{N}_5\text{O}_2$: C, 43.05; H, 4.65; N, 35.89. Found: C, 42.98; H, 4.51; N, 35.78.

REFERENCES

- (1) This work was supported by a grant (GP 26524) from the National Science Foundation.
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- (4) R. Graf, G. Perathoner and M. Tatzel, *J. Prakt. Chem.*, **146**, 88 (1936).
- (5) R. Lukes and M. Pergal, *Chem. Listy*, **52**, 68 (1958).
- (6) J. Wisowaty and D. W. H. MacDowell, *J. Org. Chem.*, **36**, 3999 (1971).