Notes A department for short papers of immediate interest.

N-Methylpyrrolidone as Solvent for Reaction of Aryl Halides with Cuprous Cyanide[1]

Melvin S. Newman and Herbert Boden

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The reaction of aryl chlorides and bromides with cuprous cyanide to yield nitriles is a useful reaction which has been carried out in the presence and absence of solvents.[2] The advantage of using *N*-methylpyrrolidine as a reaction medium because of its ability to dissolve cuprous cyanide has been pointed out.[3] Although we have not studied this method in great detail, we report our findings now because of their possible utility.

As can be seen from the results summarized in Table I, the yields are generally near 90%. One advantage in the use of *N*-methylpyrrolidone is the shorter time needed.[4] Most runs were carried out with about 0.1 mole[5] of halide and an 80% excess of cuprous cyanide in 100 ml. of *N*-methylpyrrolidone at reflux (202°). Other studies[5] showed that the amount of *N*-methylpyrrolidone can be decreased markedly. Lower temperatures than that of refluxing solvent (202°) can be used (see Footnotes *f*, *g*, and *h* in Table I) but this variable has not been much studied. 1-Chloronaphthalene afforded a high yield[6] but insufficient work was done with chloro compounds to generalize.

To our knowledge, the synthesis of cinnamononitrile represents the first conversion of a vinylic halide to a nitrile by this method.

We hope to utilize the fact that cuprous cyanide dissolves in *N*-methylpyrrolidone at about 90° to carry out relative rate measurements on a series of aryl halides.

TABLE I

Reactions of Aryl and Heterocyclic Halides with Cuprous Cyanide in *N*-Methylpyrrolidone

Halide[a]	Reaction Time (hr.)	Yield,[b] %
1-Bromonaphthalene	3	89
1-Bromonaphthalene	3	60[c]
1-Chloronaphthalene	24	87
2-Bromonaphthalene	3	90[d]
2-Bromonaphthalene	3	88[e]
2-Bromonaphthalene	3	85[f]
2-Bromonaphthalene	11	84[g]
9-Bromophenanthrene	4.5	92
β-Bromostyrene	2	92
2-Bromothiophene	19	67[h]
2-Chloroquinoline	4.5	42
4-Bromoisoquinoline	2.5	90
1-Bromobenzo[c]-phenanthrene	1.5	83
Methyl 2-chloro-3,5,6-trimethylbenzoate	3	82

[a] All experiments in Table I involved 0.1 mole of halide and 0.18 mole of cuprous cyanide in 100 ml. of distilled *N*-methylpyrrolidone[7] at reflux (202°) unless otherwise noted. [b] Yield represents per cent of material, distilled or recrystallized, agreeing well with the properties described in the literature for the pure substances. All products after sodium fusion gave negative tests for halogen. [c] In refluxing (165°) dimethylacetamide.[8] [d] The yield in a 0.5-mole run (4 hr. heating, 100 ml. of *N*-methylpyrrolidone) was 95%. [e] Only 0.15 mole of cuprous cyanide used. [f] Same as *e* except temperature held at 180°. [g] Same as *e* except temperature held at 155 ± 5°. [h] In a similar run at 180–190° for 34 hours the yield was 55%.

McPherson University Laboratory
Ohio State University
Columbus 10, Ohio

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[2] For a review see L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961). In this paper the advantage of using ferric chloride solution in working up the reaction mixture is pointed out.

[3] M. S. Newman and D. K. Phillips, *J. Am. Chem. Soc.*, **81**, 3667 (1959).

[4] For example, M. Newman, *Org. Syntheses*, Coll. Vol. III, 633 (1955) reports a yield of 82–90% of 1-naphthonitrile from 1-bromonaphthalene after fifteen hours of heating.

[5] In every case in which a run considerably larger than 0.1 mole was made, the yield of purified product was over 90%. For example, Dr. M. V. George prepared pure *p*-tolunitrile in 95% yield from *p*-bromotoluene (85.5 g.) in a *N*-methylpyrrolidone (100 ml.) by heating for two hours at reflux.

[6] Only one experiment with 1-chloronaphthalene was made. The long reaction time (twenty-four hours) might be unnecessary.

[7] We acknowledge with thanks a generous gift of *N*-methylpyrrolidone from the Antara Chemical Co.

[8] We acknowledge with thanks a generous gift of *N*,*N*-dimethylacetamide from the du Pont Company.

A Convenient Synthesis of Water-Soluble Carbodiimides

John C. Sheehan,[1,2] Philip A. Cruickshank,[2] and Gregory L. Boshart[1]

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The utility of the carbodiimide procedure for formation of the amide bond has been well established by the synthesis of many complex pep-