The structure of 2-methyl-2-butene-1,4-diamine was confirmed by reduction with hydrogen and platinum to 2-methylbutane-1,4-diamine, which formed a picrate, m.p. 228° C. A mixed melting point with the picrate of authentic 2-methylbutane-1,4-diamine, m.p. 227–228° C., was not lowered.

DISCUSSION

The authors became interested in finding a relatively simple method of preparing allylic diamines from the corresponding dihalides, specifically the diamines derived from *trans*- and *cis*-1,4-dibromo-2-butene and from 1,4-dibromo-2-methyl-2-butene. Allylic diazides rearrange extensively and, therefore, would not provide a suitable route for the synthesis of diamines since a mixture would be formed on reduction of the diazides (*9*). Also, the addition of 1,4-dibromo-2-methyl-2-butene to ammonia in ethanol produced only white polymeric material.

On the other hand, preliminary investigations on the reaction of *trans*-1,4-dibromo-2-butene with liquid ammonia contained in an open, round-bottomed flask, indicated that moderate yields of diamines could be obtained under greatly simplified conditions. Since *trans*- and *cis*-1,4-dibromo-2-butene could be obtained in pure form, their reactions in liquid ammonia were studied in detail. The results of these studies show that *trans*-1,4-dibromo-2-butene reacts with liquid ammonia to give the corresponding diamine in approximately the same yield as reported by DeTar and LePome (*5*).

In contrast to this, *cis*-1,4-dibromo-2-butene gave only a low yield of 3-pyrroline and not more than a trace of diamine, as indicated by gas chromatographic analysis. No explanation can be given for the fact that the cis dibromide failed to give diamine. The dibromide definitely seemed to react, inasmuch as a white solid remained when the ammonia had evaporated, and there was no indication of the intensely lachrymal effect of the dibromide. Conceivably, 3-pyrroline is formed initially which then reacts with more starting dihalide to form 5-azaspiro[4.4]-nona-2,7-dienium bromide, similar to the chloride reported by Amundsen, Bobbit, and Steiner (*1*).

Similar studies on the amination of 1,4-dibromo-2-methyl-2-butene showed that the corresponding diamine was formed, but in lower yield.

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Synthesis of Some *N*-Cyano and *N,N'*-Dicyanobenzamidines Using Cyanogen Bromide

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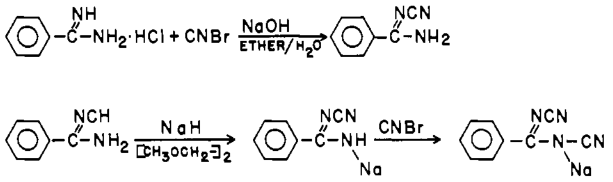
A convenient procedure to convert some benzamidine hydrochlorides to *N*-cyanobenzamidines using cyanogen bromide is given. The latter are converted to sodium *N,N'*-dicyanobenzamidines (I) using cyanogen bromide and sodium hydride in an aprotic solvent.

A COURSE of investigation required a small amount of potassium *N,N'*-dicyanobenzamidine (II). This compound has been prepared in one step by the reaction of cyanogen chloride and benzamidine hydrochloride in the presence of potassium hydroxide using acetone as a solvent (*4*). Several attempts to prepare II from the more readily available and more easily handled cyanogen bromide under the same reaction conditions gave only a very small amount of *N*-cyanobenzamidine and no II. Apparently, a strongly competing hydrolysis reaction (*5*) takes place when cyanogen bromide and sodium hydroxide are in contact with each other. Cyanogen chloride seems to be less reactive and more selective under the same conditions. Compound II could not be prepared from *N*-cyanobenzamidine, cyanogen bromide, and potassium hydroxide using acetone as the solvent. The authors decided to pursue this system to determine if II could be prepared from cyanogen bromide under other conditions. Equations 1 and 2 summarize a two step method which appears to be general for benzamidines—I is obtained rather than the potassium salt.



I

The first step is a modification of the method of Goerdeler and Loevenich (*1*) and gave *N*-cyanobenzamidines in good yield. These workers used cyanogen bromide and dry benzamidine free base in an anhydrous ether system with powdered sodium hydroxide. The method shown in Equation 1 uses benzamidine hydrochlorides (the typical product of the Pinner synthesis) and a two-phase ether-water system, with sodium hydroxide, and avoids an anhydrous system and the need to isolate the amidine free base. The cyanogen bromide was protected from any competing reaction with hydroxide ion by remaining in the ether layer, and most benzamidines have at least fair ether solubility to allow the desired reaction to occur in a reasonable time. A few attempts to extend this procedure to an aliphatic amidine hydrochloride, acetamidine hydrochloride, were not successful. This was undoubtedly due to the very low solubility of the free base in ether.

The second step involved the conversion of an *N*-cyanobenzamidine to its sodium salt by the use of sodium hydride in an aprotic solvent. This salt was then treated with cyanogen bromide to yield I. All of the dicyanoamidine salts gave characteristic green precipitates (*4*) with aqueous copper sulfate.

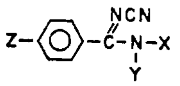
The infrared spectrum of *N*-cyano-*p*-toluamidine (a new compound) as well as the other two *N*-cyanoamidines showed absorption bands reported (*2*) for this type of compound: strong amino group absorption at 2.9 to 3.0, 3.1 to 3.2, and near 6.0 microns; carbon nitrogen double bond at 6.3 to 6.5 microns and strong nitrile doublet centered near 4.55 microns. Characteristic spectra were also exhibited by the three dicyanobenzamidine salts; strong nitrile doublet centered near 4.67 microns and a very strong band near 6.65 microns associated with conjugated nitriles (*4*). The compounds prepared are shown in Table I with pertinent data.

EXPERIMENTAL

Melting points were run either in open capillaries (m.p. < 280° C.) or using a Fisher-Johns melting point apparatus and are uncorrected. The infrared spectra were determined on a Perkin-Elmer Model 137 Infracord. All of the intermediate benzamidine hydrochlorides required for these syntheses were prepared by standard methods (*3*). Sodium hydride, 50% oil dispersion, was obtained from Alfa Inorganics Inc., and cyanogen bromide was obtained from Distillation Product Industries and was used without further purification. The procedures used to prepare both types of compounds listed in Table I are illustrated by the preparation of the following two new compounds.

N-Cyano-p-toluamidine. One half of a solution of 12 grams (0.03 mole) of sodium hydroxide in 30 ml. of water was added dropwise to a stirred slurry of 25.5 grams (0.15 mole) of *p*-toluamidine hydrochloride in 30 ml. of water and 300 ml. of ethyl ether, the temperature being held at −7° to −5° C. The mixture was stirred for an additional 5 minutes at −10° C. after completion of addition. Then one half of a solution of 18 grams (0.17 mole) of cyanogen bromide in 60 ml. of ethyl ether was added dropwise at −5° to +3° C. After the mixture was stirred for an additional 5 minutes at 0° to 3° C., the remaining sodium hydroxide solution was added, followed by the remaining cyanogen bromide solution, in the same manner and at the same respective temperature intervals as given previously. After the external cooling bath had been removed, the mixture was stirred for an additional 5 hours, filtered, pressed damp dry, and then stirred with 200 ml. of water. Filtration, followed by air drying, yielded 21.4 grams (90%) of crude product, m.p. 208° to 210° C. An analytical sample was obtained by recrystallization from methanol, m.p. 214° to 216° C. In the preparation of *N*-cyanobenzamidine approximately one third of the crude product was in the ether layer.

Table I. *N*-Cyano and *N,N′*-Dicyanobenzamidines



Cmpd.	*X*	*Y*	*Z*	M.P., ° C.[a]	Yield, %[b]	Analyses Nitrogen, % Calcd.	Analyses Nitrogen, % Found
1	H	H	H	141-3[c]	72		
2	H	H	Cl	263-4[d]	50		
3	H	H	CH_3	214-16	90	26.4	26.4
4	CN	Na	H	322-4 dec.[e]	87	29.2	29.5
5	CN	Na	Cl	368-72 dec.[e]	94	24.7	25.0
6	CN	Na	CH_3	345-6 dec.	98	27.2	27.1

[a] Melting points are for recrystallized products. [b] Yields are for crude solids and are based on benzamidine hydrochlorides for the *N*-cyanobenzamidines and on sodium hydride for the *N,N′*-dicyanobenzamidine salts. [c] Reference (*1*) gives m.p. 142-142.5° C. [d] Reference (*1*) gives m.p. 265° C. [e] Recrystallized from *n*-propyl alcohol.

Sodium N,N′-Dicyano-p-toluamidine. Although the stoichiometry of Equation 2 requires two moles of sodium hydride and one mole of cyanogen bromide for complete conversion of one mole of *N*-cyanoamidine, the best conversion to dicyanoamidine salt resulted when only 1 mole of sodium hydride and 1 mole of cyanogen bromide (excess) were used per mole of *N*-cyanoamidine. Since dicyanoamidines are moderately strong acids, this resulted in half of the intermediate *N*-cyanomidine salt being neutralized and recoverable, at least in theory. Recoveries of *N*-cyanoamidines varied from 72 to 92%.

A stirred mixture of 8.0 grams (0.05 mole) of *N*-cyano-*p*-toluamidine in 150 ml. of dry 1,2-dimethoxyethane contained in a moisture-free system was treated in portions with 2.4 grams (0.05 mole) of a 50% oil dispersion of sodium hydride (prewashed with 60° to 110° C. boiling-range petroleum ether). The temperature, which had been maintained at −5° to +3° C. during the addition, was allowed to rise to 15° C. over a period of 1 hour of vigorous stirring. After the thick mixture cooled to 0° C., it was treated dropwise at 0° to 2° C. with a solution of 5.3 grams (0.05 mole) of cyanogen bromide in 25 ml. of 1,2-dimethoxyethane. After stirring for an additional hour at 2° C., and then overnight at room temperature, the mixture was filtered, and the filtrate was evaporated in vacuo to yield an orange residue. The residue was triturated with 50 ml. of ice water and filtered after adjusting the pH to about 7 with 2 drops of 5% sodium hydroxide. The filter cake, 3.7 grams, proved to be crude *N*-cyano-*p*-toluamidine (92% recovery). The filtrate on vacuum evaporation to dryness yielded a residue almost completely soluble in 125 ml. of acetone. Filtration to remove the small amount of inorganics and vacuum evaporation to dryness yielded 5.1 grams (98%) of the crude desired product, m.p. 343° to 345° C. decomposed. Recrystallization from *n*-propyl alcohol gave an analytical sample, m.p. 345° to 346° C. decomposed.

The workup of sodium *p*-chloro-*N,N′*-dicyanobenzamidine differed slightly from that just given in that the entire reaction mixture was first evaporated to dryness in vacuo. The residue was then triturated with 200 ml. of ice water, and after adjusting the pH to 7, was filtered and processed as above.

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