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# THE PREPARATION OF DICYANODIACETYLENE

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## ABSTRACT

The preparation of dicyanodiacetylene as reported by Moureu and Bongrand has been investigated more fully and a procedure developed whereby yields as high as 36% have been obtained.

## INTRODUCTION

In 1920 Moureu and Bongrand (1) reported what was undoubtedly the first synthesis of dicyanodiacetylene. By the action of aqueous potassium ferricyanide on the cuprous derivative of propriolonitrile (cyanoacetylene) they obtained trace quantities of a solid with characteristic properties. This preparation has been investigated more fully and a procedure developed whereby yields as high as 36% have been obtained. The product was characterized as dicyanodiacetylene ($C_6N_2$) by elementary analysis and molecular weight determinations and by conversion on hydrogenation to hexamethylenediamine. Although the yield of hexamethylenediamine (isolated as the picrate) was low (8.5%), this low yield appeared to be due to decomposition of the dicyanodiacetylene in the presence of the hydrogenation catalyst (Adams' platinum oxide).

Dicyanodiacetylene is an unstable, volatile, white solid with a marked irritating odor. By sublimation in a stream of carbon dioxide gas it may be obtained as fine, elongated crystals melting at 64.5–65.5°C. X-ray diffraction lines obtained from a single crystal rotation pattern are listed in Table I, together with their estimated relative intensities.

TABLE I

X-RAY* DIFFRACTION PATTERN DATA ON DICYANODIACETYLENE

| Spacing, $d$ (Å) | Intensity, $I/I_1$ | Spacing, $d$ (Å) | Intensity, $I/I_1$ |
|---|---|---|---|
| 5.10 | 30 | 2.62 | 10 |
| 4.09 | 60 | 2.57 | 10 |
| 3.98 | 5 | 2.39 | 20 |
| 3.52 | 5 | 2.35 | 10 |
| 3.43 | 30 | 2.16 | 10 |
| 3.24 | 100 | 2.09 | 20 |
| 3.19 | 80 | 2.05 | 10 |
| 3.10 | 80 | 1.88 | 10 |
| 3.05 | 80 | 1.84 | 20 |
| 2.88 | 20 | 1.76 | 10 |
| 2.83 | 20 | 1.58 | 10 |

*Wave length 1.5418 Å.

Attention should be drawn to the unusual composition and structure of dicyanodiacetylene. Being composed solely of carbon and nitrogen it can be

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considered as a subnitride of carbon. It is also one of the longest, completely linear molecules described and should be a very interesting compound for structural study.

## EXPERIMENTAL

### *Preparation of Cuprous Propriolonitrile*

Cuprous chloride (9.9 gm., 0.10 mole) was dissolved in 10 cc. of 14% aqueous ammonia under an atmosphere of nitrogen and diluted with 900 ml. of water. To this solution at approximately 25°C. was added with agitation propriolonitrile (1) (1.5 gm., 0.029 mole) over a three minute period. After being stirred for an additional five minutes the olive green precipitate was separated by decantation and filtration and washed twice with 30 ml. of 1.5% aqueous ammonia. The product after drying under vacuum, first over sulphuric acid and finally over phosphorus pentoxide, weighed 3.7 gm. (110% yield on propriolonitrile). Cuprous propriolonitrile is subject to detonation by heat and shock.

### *Preparation of Dicyanodiacetylene*

A solution of 7.8 gm. (0.0234 mole) potassium ferricyanide in 20 ml. of water was added over a five minute period to a stirred suspension of cuprous propriolonitrile (1.5 gm., 0.012 mole) in 25 ml. of water and 25 ml. of benzene. The temperature of the reaction mixture was maintained at 5 to 6°C. throughout. Agitation was continued for two minutes after addition was complete and the reaction mixture then centrifuged, the centrifuge bottles and cups being chilled before use in an ice-water bath. After centrifuging for five minutes at 2000 r.p.m., the benzene layer (17 ml.) was removed. The lower aqueous layer and a heavy sludge-like precipitate were again cooled, extracted with a further 20 ml. of benzene, and the centrifuging procedure repeated. Owing to the formation of a fine black precipitate at this stage, only 10 ml. of benzene extract could be separated by this means. By filtration of the residual mixture through filter-aid, a further 15 ml. of extract was obtained. The combined benzene extracts were dried over sodium sulphate and most of the benzene removed by fractionation at atmospheric pressure through a short (8 cm.) Vigreux column. The resulting dark brown concentrate (2 ml.) was taken to dryness in a slow stream of carbon dioxide, the condensate being collected in a small ice-cooled receiver. After removal of all the benzene, dicyanodiacetylene was sublimed from the residue by continuing the volatization procedure. The sublimate was further purified by resublimation in a stream of carbon dioxide. The white crystalline product thus obtained, m.p. 64.5–65.5°C., weighed 0.180 gm. (30.5% yield). Calc. for $C_6N_2$: C, 72.0; N, 28.0; mol. wt., 100. Found: C, 72.15; N, 27.42; mol. wt. (depression of f.p. of benzene) 97. An additional 0.035 gm. of product, m.p. 64–64.5°C., was obtained by distilling most of the solvent from the benzene distillates using a column packed with glass spirals and working up the concentrate as described above. The total yield isolated was 0.215 gm. (36% yield on cuprous propriolonitrile).

Dicyanodiacetylene gradually turns brown at room temperature, but may be stored at 0°C. This discoloration is more rapid in the presence of water or

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in ether solution and occurs at once in alcohol. Petroleum ether, b.p. 28–35°C., may be used as an extraction solvent in place of benzene. Ether is unsatisfactory owing to the instability of dicyanodiacetylene in this medium and chloroform is not recommended since it is difficult to separate from the by-product sludge.

### *Hydrogenation of Dicyanodiacetylene to Hexamethylenediamine*

The hydrogenation was carried out in a small high pressure hydrogenation unit equipped with a 110 ml. glass liner. Dicyanodiacetylene (0.27 gm., 0.0027 mole) was dissolved in 20 ml. of acetic anhydride and Adams' platinum oxide (0.10 gm.) added just prior to the sealing up of the mixture in the hydrogenation unit. (Although dicyanodiacetylene is reasonably stable in acetic anhydride solution, decomposition occurs in the presence of Adams' catalyst as evidenced by the gradual appearance of a dark brown color.) After being flushed out with hydrogen, the apparatus was charged to a pressure of 800 p.s.i. and the shaker started. The pressure fell off to 725 p.s.i. in 15 min. and more slowly to 710 p.s.i. over a three and one-half hour period. No further drop in pressure had occurred at the five hour mark and the reaction was stopped. The reaction temperature remained at approximately 30°C. throughout the hydrogenation. The solvent was removed from the dark brown reaction mixture by vacuum distillation, and the residual oily gum, containing acetylated hexamethylenediamine, was hydrolyzed by refluxing for five hours with 20% aqueous sulphuric acid (5 gm.). The hydrolyzate was made alkaline to a pH of 13–13.5 with 20% aqueous sodium hydroxide to liberate hexamethylenediamine from its salt and the resulting solution distilled to dryness under aspirator vacuum. To the distillate was added 1.4% aqueous picric acid (40 ml.) and the precipitate of hexamethylenediamine picrate removed by filtration. The product, m.p. 219°C., weighed 0.13 gm. (8.5% yield on dicyanodiacetylene). After recrystallization from water, the material melted at 221–222°C. (lit. 220°C.). It was further identified as hexamethylenediamine

TABLE II

X-RAY* DIFFRACTION PATTERN DATA ON HEXAMETHYLENEDIAMINE PICRATE

| Spacing, $d$ (Å) | Intensity, $I/I_1$ | Spacing, $d$ (Å) | Intensity, $I/I_1$ |
|---|---|---|---|
| 11.3 | 50 | 2.89 | 2 |
| 8.25 | 2 | 2.70 | 2 |
| 7.47 | 80 | 2.58 | 5 |
| 6.40 | 15 | 2.50 | 3 |
| 5.54 | 20 | 2.44 | 3 |
| 5.20 | 15 | 2.31 | 2 |
| 4.64 | 40 | 2.25 | 2 |
| 4.37 | 30 | 2.13 | 2 |
| 4.21 | 80 | 2.06 | 2 |
| 3.91 | 20 | 1.97 | 2 |
| 3.54 | 100 | 1.92 | 2 |
| 3.35 | 40 | 1.86 | 2 |
| 3.30 | 40 | 1.76 | 2 |
| 3.17 | 50 | | |

**Wave length 1.5418* Å.

picrate by X-ray diffraction analysis (see Table II for list of diffraction lines from powder diagram and their relative intensities).

## ACKNOWLEDGMENT

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## REFERENCE

1. MOUREU, C. and BONGRAND, J. Ann. chim. 14: 47. 1920.

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