

Unsaturated Hydrogen-Free Halogeno Cyano Compounds

II. Synthesis and General Properties of Bromocyanoacetylene

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Bromocyanoacetylene, m.p. 96°C, has been prepared by bromination of cyanoacetylene by means of a bromine/bromide complex and minor amounts of alkali. General properties of the highly volatile compound are described. The electric dipole moment was found to be 3.88 ± 0.05 Debye at 25.0°C.

The existence of iodocyanoacetylene¹ as a relatively stable, well-crystallising (high-melting) compound suggested that the synthesis of other members of this series, $\text{Hal}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, might be successful.

Of the possible procedures for the preparation of the bromine analogue, $\text{Br}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, the bromination of cyanoacetylene² was considered. As an agent for brominating ethynylic hydrogen, alkali hypobromite has been used.³⁻⁷

As strong alkaline conditions are required in this reaction, the method seemed rather doubtful in the case of cyanoacetylene, because its sensitivity towards alkali promotes polymerisation to insoluble, tar-like products.² In fact, an attempted bromination by this method resulted in a rapidly darkening mixture, the components of which could not be identified.*

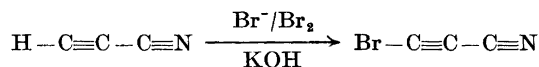
A modification of the above procedure would be to carry out the ethynylic bromination at an earlier stage which tolerates alkaline conditions. By successively building up the nitrile group by conventional methods, the final bromocyanoacetylene (bromopropionitrile) could be achieved.

For this purpose methyl bromopropiolate⁸ was prepared. Conversion of the ester to its acid amide, followed by treatment with phosphorus pentoxide, should result in the formation of bromopropionitrile. However, this procedure failed in the final steps, as the reaction product from preparation of the amide underwent decomposition when heated with phosphorus pentoxide.

* Bromination of cyanoacetylene by means of a Grignard reagent seemed less likely on account of the reactivity of the cyano group towards this reagent.

The possibility of ethynylic bromination by means of an alkali bromide/bromine solution under the influence of alkali has so far not been reported. Treatment with this reagent in the presence of *acid*, however, leads to an *addition* of bromine to the triple bond. Thus 3-methyl-3-hydroxy-butyne-1 in acetic acid gives *trans*-(CH₃)₂C(OH)CBr=CHBr, according to Nazarov and Bergel'son.⁹

To avoid the destructive effect of aqueous alkali on cyanoacetylene, the sequence of the added reagents was altered. An aqueous solution of potassium bromide, in which was dissolved an appropriate amount of bromine,¹⁰ was mixed with a neutral aqueous solution of cyanoacetylene. To this mixture was added small portions of potassium hydroxide solution. An excess of the bromide/bromine complex kept the reaction mixture acid during the alkali addition. A fine, heavy crystalline precipitate appeared, and the addition of alkali was continued until the reaction seemed to be complete. A rich, snow-white reaction product was isolated, which after sublimation under reduced pressure gave pure bromocyanoacetylene, m.p. 96.0–96.5°C (s.c.) without decomposition. The yield of purified product was 62 %.



Pure bromocyanoacetylene is relatively insensitive to air and light. Its high vapour pressure allows complete sublimation, leaving no trace of transformed material, in contrast to its iodine analogue. It has a sweetish odour and is strongly lachrymastic.

Bromocyanoacetylene appears in different crystal forms. By sublimation in the absence of water it deposits as clusters, which adhere strongly to the glass wall. Thin needles, more than 30 mm long, were obtained when the emptied reaction tube, still containing vapours of the reaction product, was left closed overnight.

Spectroscopic investigations have been undertaken in the infrared, ultraviolet and micro-wave^{9a} regions.

For examination of the *infrared* absorption spectra sodium chloride and calcium fluoride optics were used. With a rock salt prism the following bands were observed: 2275 s, and 2110, 2035, 1052, 958, 948 and 797 cm⁻¹, all weak (carbon disulphide solution). The first of these bands was observed at 2277 cm⁻¹ using calcium fluoride optics and carbon tetrachloride as a solvent.

Of the absorption bands in the 2000 cm⁻¹ region the strong band at 2277 cm⁻¹ may be assigned to the C≡N stretching frequency; the same value was also found in iodocyanoacetylene.¹ One of the weaker bands at 2110 or 2035 cm⁻¹ is attributable to the C≡C stretching mode. The weak absorption in the 1050–950 cm⁻¹ region may be related to the C–C stretching frequency; for comparison I–C≡C–C≡N has a single band in this region at 1027 cm⁻¹.¹

In the *ultraviolet* region bromocyanoacetylene showed four maxima at 262 sh (log ε 2.47), 245 sh (log ε 3.20), 233 (log ε 3.39) and 222 μ (log ε 2.40) (cyclohexane solution). As compared to iodocyanoacetylene the absorptions are shifted towards shorter wave-lengths by *ca.* 10 μ. A hypsochromic displa-

cement in this system can be expected on account of the less electron releasing bromine substituent as compared to iodine.

For bromocyanoacetylene as well as for its iodine analogue, a considerable degree of polarity would be expected, and the electric dipole moment of the compound was measured. The value $\mu = 3.88$ Debye was found. As compared to the dipole moment of cyanogen bromide, 2.94 Debye,¹¹ the difference for this bromine couple of approximately 0.9 Debye is thus of the same magnitude as the difference in the case of the corresponding iodine couple, iodocyanoacetylene and cyanogen iodide, 4.59¹ and 3.71¹² Debye, respectively.

EXPERIMENTAL

Preparation of bromocyanoacetylene. To an ice-cooled solution of cyanoacetylene^{2,1} (1.16 g, 0.023 mole) in water (50 ml) was added a cold potassium bromide/bromine solution (45 ml). The latter was prepared in an ice-bath by adding bromine (3.0 ml, 0.06 mole) slowly to a solution of potassium bromide (7.5 g, 0.065 mole) in water (50 ml).¹⁰ By dropwise addition of half-normal potassium hydroxide to this mixture under shaking a fine, heavy precipitate soon appeared. The addition was continued until precipitation ceased (40 ml), as proved by addition of more alkali to a filtrated sample. From the partially decolourized, acid reaction mixture a rich, snow-white crystalline product was isolated by filtration (1.24 g), m.p. 86–90°C (s.c.) under decomposition. Sublimation at 32°C/10 mm (in portions) over phosphorus pentoxide gave pure bromocyanoacetylene in 62 % yield, melting at 96.0–96.5°C (s.c.) without decomposition. (Found: C 28.00; N 10.94; H 0. Calc. for C₃NBr: C 27.71; N 10.77). The high volatility of the compound complicated microanalysis, which failed on bromine.

Attempted synthesis of bromocyanoacetylene from methyl bromopropiolate. Methyl bromopropiolate⁸ (2.0 ml), prepared from bromopropiolate,⁴ was added slowly to liquid ammonia¹³ (10 ml), and the mixture was left overnight at dry ice temperature. The main quantity of ammonia was allowed to evaporate at low temperatures, and residual volatiles were driven off *in vacuo* in the cold until the vapour pressure was constant (5 mm Hg/–23°C; 15 mm Hg/–11.5°C, the same as measured for pure methanol. Methanol liberated from the ester could thus hardly be removed from the reaction product).

The residue (1.5 g) of odourless, partly crystallising, yellow liquid (solidifying at cooling; insoluble in chloroform, ether, acetone, fairly soluble in ethanol, very soluble in water) was mixed thoroughly with sand (25 g) and phosphorus pentoxide (12 g). The mixture was evacuated at dry ice temperature, and the temperature was allowed to raise to room temperature. After immersing the reaction tube into an oil bath at 120°C no reaction product could be collected in the cooled trap (dry ice). During additional heating to 220°C the contents of the reaction tube had swelled to four times its original volume.

Methyl propiolate by the same treatment gave a crystalline propiolic acid amide in 94 % yield and a pure propionitrile in 80 % yield. No swelling was observed during heating.

The infrared spectra were recorded on a Perkin-Elmer Infrared Spectrometer Model 21 (NaCl and CaF₂ prisms) in solutions of carbon tetrachloride and carbon disulphide.

The ultraviolet spectra were recorded on a Beckman DK-1 Recording Spectrometer, using cyclohexane as a solvent.

The dipole moment measurements were carried out by use of the same apparatus and technique as employed for iodocyanoacetylene.¹ A value of $\mu = 3.88 \pm 0.05$ Debye in benzene solution at 25.0°C was found.

The melting points (uncorrected) were measured on a Hoover Capillary Melting Point Apparatus in sealed capillaries (abbreviated s.c.).

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