

Unsaturated Hydrogen-Free Halogeno Cyano Compounds

IV Synthesis and Properties of Chlorocyanoacetylene

ELSE KLOSTER-JENSEN

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

Chlorocyanoacetylene, m.p. 42°C, has been prepared by the reaction of lithium cyanoacetylide with molecular chlorine. Chemical and physical characteristics of the highly volatile compound are described.

The successful preparation of iodocyanoacetylene¹ and bromocyanoacetylene² encouraged a synthetic approach to further members of the halogenocyanoacetylene series. The physical characteristics of the two compounds mentioned indicate that the analogue, chlorocyanoacetylene, would appear as a relatively volatile, low-melting or liquid compound of some stability. In that case the moderate size of the halogen attached to the straight-chained molecule would offer extended possibilities for critical investigations by various physical methods.

The present paper reports a study of synthetic methods for the preparation of chlorocyanoacetylene. Starting from cyanoacetylene³ a procedure was sought for replacing the ethynyl hydrogen by chlorine under neutral or slightly acid reaction conditions. As earlier experience had shown,^{3,1,2} cyanoacetylene undergoes polymerisation to insoluble, tar-like products under the influence of alkali. In an attempt to prepare its sodium salt in liquid ammonia the intensely violet solution turned dark and deposited destructed material. Chlorination methods involving sodamide or sodium hypochlorite were therefore rejected. The direct chlorination of cyanoacetylene by means of a halogen/halide complex, which proved convenient for the preparation of iodo¹ and bromocyanoacetylene,² was also discarded, as the concentration of the chloro complex in equilibrium with its components is too small.⁴

Since it possesses an ethynyl grouping cyanoacetylene was expected to undergo Grignard reactions. By interaction of the Grignard intermediate with an appropriate chlorination agent neutral reaction conditions would be maintained. However, the presence of the cyano group in the molecule actually represents a second centre of attack by the Grignard reagent, although less active. The reaction course was therefore checked by an experiment, in which *p*-toluenesulphonyl chloride⁵ was used for the chlorination: Cyano-

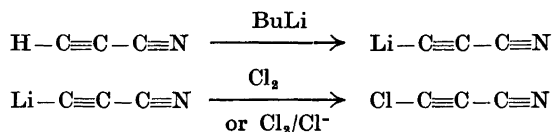
acetylene was brought to react with ethyl magnesium bromide or methyl magnesium iodide, and the reaction mixture was then treated with *p*-toluenesulphonyl chloride, with the expectation thus to obtain chlorocyanoacetylene. When the reaction was carried out at sufficiently low temperatures, a colourless Grignard complex was formed in both cases. However, when ethyl magnesium bromide was used, no reaction product could be isolated from the final reaction mixture, which turned dark on standing, and deposited black solids when the temperature was allowed to rise. On the other hand, by the reaction involving methyl magnesium iodide substantial amounts (45 %) of a stable crystalline material was produced, which proved indistinguishable from *iodocyanoacetylene*; no chlorocyanoacetylene was formed. An alternative approach to the preparation of the Grignard intermediate by reacting *iodocyanoacetylene* with metallic magnesium failed.

The experiments above revealed an extraordinary high reactivity of cyanoacetylene towards Grignard reagents. The production of *iodocyanoacetylene* in considerable amounts confirms a preferred reactivity of the ethynyl part of the molecule, leaving the cyano group intact by the Grignard reagent. The formation of the *iodo* analogue is surprising. However, other workers⁶ also find that Grignard iodide reagents on acetylenes tend to encourage side reactions.

p-Toluenesulphonyl chloride acts on alkali salts of acetylenes to give chloroacetylenes in good yields.⁵ In the case of lithium acetylides their preparation can also be performed through *neutral* paths, and exploratory experiments on the preparation of lithium cyanoacetylide were undertaken. A vigorous and destructive reaction between phenyl lithium and cyanoacetylene took place at moderately low temperatures. However, in a dilute solution of ether cooled by solid carbon dioxide, lithium cyanoacetylide was formed and could be kept at this temperature for a very limited time (darkened after about a quarter of an hour). No reaction occurred, however, on successive treatment with *p*-toluenesulphonyl chloride; when the temperature was raised, the mixture rapidly darkened and black solids deposited. Apparently, the low temperature necessary for the preparation of the lithium acetylide rendered the chlorination agent inactive.

A chlorination agent capable of reacting with lithium cyanoacetylide at the low temperatures required, was found in molecular chlorine.⁷ Admixture of controlled amounts of chlorine was obtained by adding a solution of the gas in an organic solvent. As an inert, non-solidifying, readily vapourisable liquid with good solvent properties, fluorotrichloromethane ("Freon 11") was selected. The lithium cyanoacetylide was prepared from butyl lithium and cyanoacetylene at -70°C . On addition of the chlorine solution a reaction obviously took place, as the colourless precipitate of the lithium cyanoacetylide disappeared and an almost clear solution remained. When the temperature was allowed to rise, large amounts of a colourless, fine, heavy precipitate spontaneously deposited. The reaction mixture was kept at -20°C for 15 h, and a clear, slightly coloured solution could be decanted from the deposited lithium chloride. The solution was directly fractionated under reduced pressure at -35°C . A crystalline material was isolated, mainly from the last fraction, and purification by gas liquid chromatography yielded a snow-white product of

m.p. 42°C. The yield of chlorocyanoacetylene was *ca.* 30 %. A nonvolatile, oily residuum in substantial amounts was not further examined.



In preliminary experiments an unexpected reaction during the chlorination procedure took place. A high-melting compound was the only reaction product when phenyl lithium was first used in the preparation of lithium cyanoacetylide. From the melting point (95°C) and gas chromatographic retention values the product proved identical with bromocyanoacetylene. The yield (22 %) was somewhat less than when chlorocyanoacetylene was produced. The explanation of the reaction path is that, by formation of phenyl lithium from bromobenzene and metallic lithium, lithium bromide is produced, which is readily soluble in ether and remains in solution. During addition of chlorine the bromide ions are oxidized to molecular bromine, which then — perhaps as an interhalogen complex — reacts with lithium cyanoacetylide to give bromocyanoacetylene. By preparing the lithium intermediate from butylchloride and lithium, the interfering presence of bromide ions was avoided.

A distressing experience during the preparation of the chlorine agent may be worth mentioning. In lack of chlorine from a gas bomb the gas was prepared on a small scale from potassium permanganate⁸ and concentrated hydrochloric acid. The chlorine solutions from this source caused spontaneous destruction of the freshly prepared lithium cyanoacetylide, which deposited rich amounts of light, intensively black solids (readily soluble in water). In contrast, chlorine from manganese dioxide and hydrochloric acid caused no complications. Minor amounts of free oxygen⁹ liberated by the action of the acid on permanganate may have destroyed the rather sensitive cyanoacetylide.

Chlorocyanoacetylene, like iodo- and bromocyanoacetylene appears in different crystal forms. Sublimation at moderately low temperatures furnishes fine, long needles, which disintegrates to a fine powder at higher temperatures. The compound is rather insensitive to light and sublimes readily at room temperature. A vapour pressure of about 52 mm Hg at 24°C was measured. A solution of the compound in carbon tetrachloride was heated at 60°C for several hours without destruction of the material. Chlorocyanoacetylene is a stronger lachrymator than bromocyanoacetylene.

Spectroscopic investigations of the compound have been undertaken in the ultraviolet, infrared, and micro-wave regions. The absorption features were found to be much the same as those observed in iodo- and bromocyanoacetylene.

The *ultraviolet* spectrum exhibited strong absorption maxima at *ca.* 221 $m\mu$ and 228 $m\mu$. Weak shoulders were observed at 240 and 244 $m\mu$. It is not surprising that the longest-wave-length absorptions which appeared in the iodo and bromo analogues, are scarcely observable in the chloro substituted compound.

The *micro-wave* spectrum has been examined in the $J = 8 \rightarrow 9$ and $J = 9 \rightarrow 10$ region. Beyond reasonable doubt the molecule is linear. The value of the ground state rotational constant B_0 from these preliminary investigations agree with expectation and is in accordance with investigations¹⁰ on bromo-cyanoacetylene.

For examination of the *infrared* absorption spectra calcium fluoride, sodium chloride and potassium bromide optics were used. In the 2000–2300 cm^{-1} region fundamental absorptions were observed at 2293 (vs) and 2146 (m) cm^{-1} (calcium fluoride prism, carbon tetrachloride solution); 2283 (vs) cm^{-1} (carbon disulphide). Maximal absorptions were further observed at 1100 (vs), 963 (s), 815 (vw), 785 (w), 762 (vw), 667 (s) cm^{-1} (sodium chloride, carbon disulphide), and 737 (s), 680 (m), 660 (vw), 532 (w) and 484 (s) cm^{-1} (potassium bromide, carbon disulphide). The three bands at 2293 (2283), 2146 and 1100 cm^{-1} may be assigned to the $\text{C}\equiv\text{N}$, $\text{C}\equiv\text{C}$, and $\text{C}-\text{C}$ stretching modes, respectively. No absorption indicating ethynylic hydrogen was observed (gaseous $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ exhibits strong absorption at 3328 cm^{-1} ^{11,12}).

The high vapour pressure of crystalline chloroacetylene allowed infrared absorption studies to be undertaken also in the gaseous state. A complete assignment of the infrared spectrum of chloroacetylene will be published separately.¹³

No attempt on a micro analysis of the reaction product was made, as already the analysis of the less volatile bromoacetylene caused trouble.² However, the physical characteristics described above are regarded as sufficient proof of identity.

EXPERIMENTAL

The cyanoacetylene (b.p. 42.5°C)⁸ used in the experiments was prepared by a synthesis in four steps, from acetylenedicarboxylic acid monopotassium salt as described in part 1.¹ Improved yields of the propiolic amide intermediate were achieved by reacting the methyl propiolate with liquid ammonia.¹⁴

Portions of cyanoacetylene were sublimed under reduced pressure from a reservoir into a tared vacuum tube cooled by carbon dioxide. The weighed quantity was then dissolved in dry ether.

Preparation of chloroacetylene. Butylchloride (2.68 g) in dry ether (5 ml) was added slowly under an atmosphere of nitrogen to a suspension of lithium (0.500 g) in ether. After addition was complete, the solution was stirred for another hour. The diluted solution (ca. 40 ml) was then passed through a tube loosely plugged with glass wool into a deep reaction tube previously flushed with nitrogen. The milky solution was cooled in a carbon dioxide/alcohol bath, and a solution of cyanoacetylene (0.980 g) in ether (10 ml) was added under vigorous stirring during a period of 10 min. A white precipitate formed immediately upon addition. The mixture was stirred for additional 10 min, and a solution of molecular chlorine in dry fluorotrichloromethane (17.5 g, see below) cooled at -70°C was added during 15 min. The initial darkening of the mixture soon ceased. The precipitated material disappeared, and the addition was discontinued, when a sample of the reaction mixture no longer was alkaline after addition of water. A sample of the yellowish solution immediately deposited fine, heavy, crystalline solids as soon as the temperature was raised. The mixture was stirred for additional 40 min. The precipitate dissolved readily in additional amounts of ether as well as in water (lithium chloride). Less rapid precipitation was achieved by keeping the reaction mixture at -20°C overnight.

A clear solution was decanted from compact deposited material, and excess of chlorine was removed under reduced pressure at about -35°C . The volatility of the reaction product allowed concentration by direct fractionation of the solution at -35°C under a

pressure of 10 mm Hg (static vacuum, magnet stirrer). Gas liquid chromatography of the fractions (*ca.* 5–10 ml) unveiled considerable amounts of unreacted cyanoacetylene in the first fractions. Chlorocynoacetylene was concentrated mainly in the last fraction, distilled at room temperature (6 ml). To the residuum was added a few ml of ether; on distillation, residual amounts of reaction product could be isolated. Concentration of the two last fractions and purification of solid material by gas liquid chromatography (in carbon tetrachloride solution) furnished a snow-white crystalline substance (0.490 g) of m.p. 42.0–42.5°C. The yield of isolated pure chlorocynoacetylene was 26.5 %.

A nonvolatile, partly oily, coloured residuum in substantial amounts was not examined further.

During sublimation of the reaction product under reduced pressure (10 mm Hg) into a tube cooled at -70°C the product deposited as a compact layer on the cooled glass wall, above which fine long needles of the substance was formed. At lower or higher temperatures the crystals transformed to a fine powder.

Preparation of the chlorine reagent. Fluorotrichloromethane, ("Freon 11", b.p. 23°C , m.p. -111°C , Du Pont de Nemours & Co., 139.5 g), distilled over phosphorus pentoxide, was cooled in a trap (fitted with a glass joint and stop cocks) placed in a carbon dioxide/alcohol bath. Chlorine gas from a flask was passed through a tower filled with phosphorus pentoxide and conducted through the liquid, which soon turned yellow. The uptake of chlorine was followed by weighing the trap from time to time. The increase of weight by saturation was 23 g, corresponding to about 14 % of dissolved chlorine.

When chlorine gas was prepared from potassium permanganate or manganese dioxide and concentrated hydrochloric acid, the gas evolved was dried in two towers of concentrated sulphuric acid, followed by two towers of calcium oxide and phosphorus pentoxide, respectively, before it was collected in carbon tetrachloride (dried over phosphorus pentoxide). For the effect of these chlorine/carbon tetrachloride solutions on lithium cyanoacetylide, see above.

Carbon tetrachloride had to be discarded as a solvent because the vapour pressure of the reaction product proved to be of the same magnitude as that of the solvent. The relatively high melting point of the solvent as well (-23°C) made an effective isolation of the final product by freezing out the solution, impossible.

Attempted preparation of chlorocynoacetylene by means of bromobenzene/lithium and chlorine. Lithium cyanoacetylide from phenyl lithium (2.82 g bromobenzene and 0.278 g lithium) and cyanoacetylene (0.700 g) was prepared as described above. A 7.5 % solution (16.3 g) of chlorine in carbon tetrachloride was added slowly and the reaction mixture was kept at -20° overnight. A clear, yellow solution was decanted from deposited, crystalline material. The organic phase was washed three times with a saturated solution of ferrous sulphate, then three times with water saturated with sodium chloride and dried over magnesium sulphate. Fractionation (as above) gave minor amounts of crystalline material in the last fractions. However, a fine crystalline, yellowish residuum could be isolated (0.393 g) together with some oil. Recrystallisation once from chloroform/petrol ether gave colourless crystals of m.p. $95-96.5^{\circ}$ (s.c.). Gas liquid chromatography of the product exhibited retention values identical with a reference sample of bromocynoacetylene (m.p. 96°C). The yield was 22 %. No chlorocynoacetylene was observed.

Grignard reactions on cyanoacetylene

1. *With methyl magnesium iodide.* Cyanoacetylene (0.280 g) in ether was added to a stirred solution of methyl magnesium iodide (from 0.800 g methyl iodide and 0.130 g magnesium) in dry ether cooled at -70°C . A white precipitate spontaneously appeared. After admixture of a dilute solution of *p*-toluenesulphonyl chloride (1.0 g) in ether, the temperature was raised slowly to -20°C . A lively reaction took place under evolution of heat. At higher temperatures the reaction mixture turned slightly dark. The solution was filtered and the solvent removed under reduced pressure in the cold. A reddish crystalline residuum (0.551 g) with a iodoformlike odour showed m.p. $122-135^{\circ}\text{C}$. Sublimation once (0.441 g) gave m.p. $148-151^{\circ}\text{C}$. An infrared spectrum (CaF_2 prism, CCl_4 solution) exhibited band maxima at 2278 and 2139 cm^{-1} . In iodoacetylene¹ (m.p. 151°C) absorption bands were observed at 2277 and 2138 cm^{-1} ($\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{C}$ stretching modes, respectively). The yield of purified iodoacetylene was 45 %.

2. *With ethyl magnesium bromide.* A white precipitate was likewise formed by reaction of cyanoacetylene with ethyl magnesium bromide at -70°C . No reaction was observed after addition of *p*-toluenesulphonyl chloride. A black, sticky material had deposited after storing 4 days at -20°C . The reaction mixture was poured over pieces of ice and acidified by dilute sulphuric acid. Washing with water, drying and evaporation of the solvent yielded a crystalline residuum, which after recrystallisation once showed m.p. $64-66^{\circ}\text{C}$. *p*-Toluenesulphonyl chloride (m.p. 66°C) was recovered in 84 % yield.

3. *Iodocyanoacetylene and magnesium.* No reaction occurred between iodocyanoacetylene (dried over phosphorus pentoxide) and magnesium in diethyl ether or dibutyl ether. During prolonged influence of moderate heat iodocyanoacetylene partly decomposed. Metallic magnesium was recovered to an extent of 98 %.

The *gas liquid chromatograms* were performed on a Beckman GC-2 Gas Chromatograph, using a 3 m column with 25 % Apiezon L on Chromosorb W. At a temperature of 64°C and a flow-rate of helium of 60 ml/min the following retention values relatively to pentane were observed: Cyanoacetylene 0.36, chlorocyanoacetylene (m.p. 41°C) 2.19, and bromocyanoacetylene (m.p. 96°) 6.35.

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

The *infrared spectra* were recorded on a Perkin-Elmer Infrared Spectrometer Model 21 (CaF₂ and NaCl prisms) and on a Unicam Infrared Spectrometer Model SP 100 (NaCl and KBr prisms) in solutions of carbon tetrachloride and carbon disulphide.

For observations in the *micro-wave region* an equipment available at this institute was used.

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

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