ACTA CHEMICA SCANDINAVICA 17 (1963) 1866–1874

Unsaturated Hydrogen-Free Halogeno Cyano Compounds

III. Preparation and Properties of Halogenocyanoethylenes

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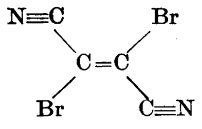
Dibromofumaronitrile and di-iodofumaronitrile have been prepared by addition of the respective halogens to dicyanoacetylene. Physical evidence for their *trans* ethylene configuration is given. Two likewise unknown nitriles, tribromocyanoethylene and tri-iodocyanoethylene, have been prepared by prolonged action of the halogenation agent on cyanoacetylene during preparation of bromocyanoacetylene [2] and iodocyanoacetylene.[3] A very low C=C stretching mode at 1495 cm^{-1} was observed in tri-iodocyanoethylene.

Moureu and Bongrand in their work on dicyanoacetylene [1] reported that a decolouration occurred when a solution of equimolecular amounts of dicyanoacetylene and bromine was allowed to stand in diffuse light for a couple of days. They suggested that bromine had been added to the carbon-carbon triple bond during formation of 1,2-dibromo-1,2-dicyanoethylene; however, the reaction was never proved. The action of bromine as well as iodine on dicyanoacetylene has now been examined, and dibromofumaronitrile and diiodofumaronitrile have been prepared. The expected *trans* configuration of the reaction products has been verified from spectroscopic and X-ray investigations and by electric dipole moment determinations. Further, two trihalogenocyanoethylenes, likewise unknown, have been prepared, namely tribromoacrylonitrile and tri-iodoacrylonitrile. Their preparation was achieved simply by continuing the halogenation reaction of cyanoacetylene during the intended preparation of bromocyanoacetylene [2] and iodocyanoacetylene.[3]

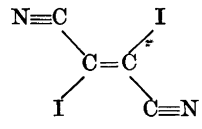
1,2-Dibromo- and 1,2-di-iododicyanoethylene

Dicyanoacetylene was brought to react with molecular bromine by keeping a solution of the reactants at room temperature for three days.[1] During this time rich amounts of a partly crystalline, reddish product separated from the chloroform-ether solution. Recrystallisation and sublimation under reduced

pressure afforded coarse, transparent prisms of dibromodicyanoethylene (I), m.p. 110—111°C (s.c.). Yield 57 %.



I



II

Molecular iodine reacts with acetylenes much less readily than does either chlorine or bromine. Early studies on iodination of simple acetylenic compounds like acetylene mono- and dicarboxylic acid,[4] tetrolic acid,[5] and phenylpropiolic acid,[6] revealed that addition of iodine to the triple bond could be effected by heating the reagents in a sealed tube at about 100°C for several hours. Alternatively, the catalytic action of anhydrous ferrous iodide [6] was able to bring about the reaction, although slowly, at room temperature.

By the aid of the iodine carrier mentioned,[6] considerable amounts of solid reaction product were obtained when a solution of dicyanoacetylene and iodine was exposed to diffuse light at room temperature for a period of ten days. Carbon disulphide [6] was chosen as a solvent, although the solubility of the catalyst in this medium is poor.

In the course of two days a compact, glittering, crystalline product deposited on the finely divided catalyst. From an ether extract of the solid material a rather pure reaction product was isolated, a microanalysis of which corresponded to di-iododicyanoethylene (II). The melting (m.p. 188.5—189.5°C, s.c.) was accompanied by evolution of iodine.

Additional amounts of highly contaminated reaction product were isolated from the liquid phase at the end of ten days. Total yield of pure reaction product was 38 %.

Addition of bromine to an acetylene affords *cis* and/or *trans* isomers of dibromo ethylenes, depending on the conditions chosen to provide a radical or ionic reaction course. Dimethyl acetylenedicarboxylate, for example, under conditions of a radical addition gives an equimolecular mixture of isomeric dibromo ethylene esters. With lithium bromide, which promotes a nucleophilic addition course, mainly the *trans* isomer is obtained.[7] Illumination counteracts the LiBr effect. On the other hand, 3-methyl-3-hydroxybutyne-1 with small amounts of potassium bromide in 70 % acetic acid yields the *trans* dibromobutene, whereas a solution in petrol ether in the presence of dibenzoyl peroxide under illumination gives the *cis* dibromo isomer.[8]

Addition of iodine to a triple bond is of little preparative interest, and the relatively few examples described [9] usually omit steric considerations (unsubstituted acetylene gives *trans* di-iodoethylene [10]).

In the actual halogen addition reactions a *trans* configuration of the reaction product would be expected in the case of iodine because the presence of ferrous iodide supports formation of an ionic iodide complex, thus effecting a nucleophilic addition reaction. Further, the space-consuming iodine substituent would tend to demand the *trans* configuration. The latter consideration loses its relevance for bromine, by the fact that *cis* dibromoethylene is a more stable

configuration than the *trans* dibromoethylene [11] (an isomeric mixture usually being formed). In the bromine reaction, chloroform as a polar solvent may induce polarisation of the bromine-bromine bond, thus promoting an ionic bromine addition. On the other hand, addition of molecular bromine to an ester from the actual nitrile in the same solvent was shown to give both isomers.[7]

The presence of the *trans* dihalogenodicyanoethylenes I and II was supported in part by spectroscopic investigations. The lack of infrared absorption in the ethylene region, associated with the presence of a centre of symmetry, is in accordance with the *trans* ethylene configuration (see below).

Containing electron-attracting as well as electron-repelling centres in the molecule, crystals of these compounds might be expected to contain intermolecular nitrogen-halogen bonds, presumably of the charge transfer type.

A crystal structure determination of the bromo compound has been undertaken by Hassel and Römming,[12] using X-ray diffraction technique. Preliminary results give a strong indication of a *trans* configuration of the reaction product. X-Ray examinations of crystals of the iodo compound showed that the space group is *Pbca* with four molecules per unit cell. This proves the molecules to possess a centre of symmetry, which excludes the presence of the *cis* isomer.

During investigations of the latter, difficulties arose in obtaining crystals of high quality. In order to provide alternative evidence for a definite assignment of the configuration of the iodo compound, the electric dipole moment of the compounds were determined. For di-iododicyanoethylene a surprisingly high moment of 1.33 Debye was found (in benzene solution). For comparison, dibromodicyanoethylene exhibited a moment of 0.54 Debye. Under the same conditions a similar value (0.57 Debye) was found for the electric dipole moment of tetrabromomethane. The dipole moment of *cis* di-iododicyanoethylene (di-iodomaleonitrile) has been roughly estimated to be about 4.0 Debye by calculation from bond moments. An explanation of the appreciable moment observed for the iodo compound is left open (association effects would hardly come into play at the very dilute solutions actually measured (weight fractions $\sim 10^{-4}$)).

The foregoing physical evidence supports the view that the halogenated products exist as dibromofumaronitrile (I) and di-iodofumaronitrile (II).

Tribromo- and tri-iodocyanoethylene

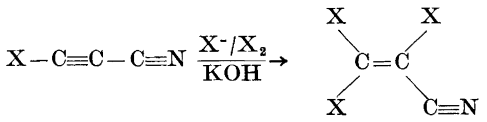
Along with investigations of suitable reaction conditions for bromine substitution in cyanoacetylene it was found that an *acid* reaction medium favoured the formation of Br—C≡C—C≡N.[2] This was achieved merely by altering the sequence of the reagents added, keeping cyanoacetylene in an excess of a potassium bromide/bromine solution during the addition of alkali.

Use of the bromide/bromine complex in combination with an *acid*, on the other hand, supports an addition of bromine to the triple bond, as already mentioned.[8]

By the above modified application of the alkali hypohalite reagent extensive halogen substitution in cyanoacetylene took place (yields about 60 %). Continuation of this halogenation reaction, which actually occurred under

acid conditions, led to an *addition* of halogen to the acetylenic bond, which had apparently succeeded the ethynylic substitution. A trihalogenated ethylenic nitrile, free from monohalogenated product, could be isolated as a second reaction product.

The absence of *di*halogenated ethylenic product suggested that addition of halogen had taken place at the halogeno-substituted rather than at unsubstituted cyanoacetylene.



III: X = Br
IV: X = I

When the spontaneously precipitating halogenocyanoacetylene had been removed from the reaction mixture, additional amounts of hypohalite reagent were mixed with the filtrate. After keeping a bromination mixture at 0°C for 20 h a heavy, yellowish crystalline product had deposited. Purification by sublimation at 60°C under 10 mm Hg pressure over phosphorus pentoxide gave tribromocyanoethylene (tribromoacrylonitrile), III, m.p. 88.0—89.0°C (s.c.). The yield was 8.0 %, calculated from residual, unreacted cyanoacetylene.

Similarly, the action of hypoiodite on cyanoacetylene yielded a second reaction product, although much more slowly. After storage for about two months in the cold, a very heavy, yellow, fine precipitate had separated. Recrystallisation gave pure tri-iodocyanoethylene (tri-iodoacrylonitrile), IV, m.p. 179.5—180.5°C (s.c.). The yield was lower than for its bromine analogue.

Tribromoacrylonitrile is a fairly volatile, almost odourless compound, forming coarse, transparent, slightly yellowish crystals, which endures heating far above their melting point (150°) without discolouration. The non-volatile tri-iodoacrylonitrile appears in mustard-yellow tiny needles, decomposing at melting with evolution of iodine.

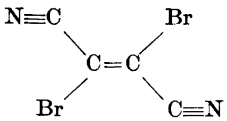
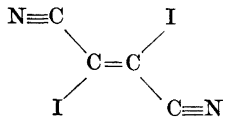
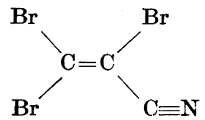
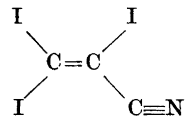
Spectroscopic investigations

Spectroscopic investigations of the compounds have been undertaken in the infrared and ultraviolet regions.

Infrared spectra. For examination of the infrared absorption spectra sodium chloride and calcium fluoride optics were used. Spectra of the compounds were recorded in solutions, nujol mulls or potassium bromide pellets. The absorption characteristics are listed in Table 1.

Among these bands the distinct absorption present in all the compounds around 2225 cm^{-1} can be related to the C≡N stretching frequency. With calcium fluoride optics dibromofumaronitrile and di-iodofumaronitrile absorb at equal wave-numbers, 2228—2229 cm^{-1} (carbon tetrachloride; chloroform). This is slightly lower than the nitrile absorption of unsubstituted fumaronitrile at 2240 cm^{-1} (chloroform) as reported by Kitson and Griffith,[13] and 2242 cm^{-1} by Felton and Orr.[14] For maleonitrile the former reported a weaker doublet at

Table 1. Infrared absorption bands of halogenocyanoethylenes (cm^{-1}).

No.	Compound	Sodium chloride prism				Calcium fluoride prism	Phase
I		(2230 w)	—	1050 s	740 vs		CS_2
						2228 w 2200 vw 2182 vw	CCl_4
II		(2220 w)	—	1035 w	677 s		CS_2
			1607 w			2229 m	$CHCl_3$
		(2225 m)	—				Nujol
		(2225 m)	—	1033 s	826 w 682 vs		KBr
III		2225 m	1533 m	1064 m	855 s 825 w 708 s		KBr
IV		2220 m	1495 m	1015 w	778 m		KBr

2251 and 2231 cm^{-1} (chloroform). Tribromoacrylonitrile and tri-iodoacrylonitrile exhibit absorptions at 2225 and 2220 cm^{-1}, respectively (potassium bromide pellets, sodium chloride prism), which represent a similar, small low-frequency shift as compared to the value given by the authors mentioned above. Acrylonitrile itself absorbs at 2230 cm^{-1} (lithium fluoride prism).[13,14] As compared to the C≡N stretching absorption at 2277 cm^{-1} of the acetylenic nitriles iodocyanoacetylene [3] and bromocyanoacetylene,[2] the described ethylenic nitriles absorb by about 50 cm^{-1} towards lower wave-numbers.

The absence of absorption in the C=C stretching region would be good evidence for the *trans* ethylene structure of the first two compounds. No absorption around 1600 cm^{-1} was found in dibromofumaronitrile. In di-iodofumaronitrile a weak band appeared at 1607 cm^{-1} in chloroform solution. However, this region was empty when II was run in nujol mull or potassium bromide pellet. A similar absorption in chloroform solution has been observed for fumaronitrile at 1612 cm^{-1}, and dimethylfumaronitrile at 1645 and 1615 cm^{-1}.[14] However, these findings have not been supplemented by investigations in the solid state.

Tribromoacrylonitrile and tri-iodoacrylonitrile, on the other hand, had sharp absorption bands at 1533 and 1495 cm^{-1}, respectively, to be assigned to

C=C stretching modes. Substitution of heavy halogen at the ethylenic bond and conjugation to the nitrile group may be responsible for the rather strong low-frequency shift of these bands. The absorption at 1495 cm^{-1} of tri-iodocyanoethylene may probably represent the lowest infrared absorption known for a C=C stretching frequency. In good agreement with the observation of a band at 1533 cm^{-1} in tribromocyanoethylene is the C=C absorption at 1557 cm^{-1} in tribromoethylene, as reported by Evans and Bernstein.[15] As one would expect, unsubstituted acrylonitrile absorb at considerably higher wavenumbers, 1647 and 1610 cm^{-1}.[14]

In the 1000 cm^{-1} region the bands at 1050, 1035, 1064 and 1015 cm^{-1} can be related to the C—C stretching mode of the respective compounds. Of the lowest-frequency bands about 700—800 cm^{-1} the strong absorption at 708 cm^{-1} in tribromocyanoethylene may be attributable to a C—Br stretching mode. A strong band at 704 cm^{-1} was observed in tribromoethylene by the same authors.[15]

Ultraviolet spectra. In the ultraviolet region the spectral features of the bromine-iodine couple I—II resembled to a considerable extent those of III—IV. The absorption characteristics are summarized in Table 2.

Table 2. Ultraviolet absorption maxima of halogenocyanoethylenes. Shoulders in brackets.

Dibromofumaronitrile I [a]		Di-iodofumaronitrile II [a]		Tribromoacrylonitrile III [b]		Tri-iodoacrylonitrile IV [b]	
λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
283	4.03	325	3.89	(264)	(3.69)	283	4.03
275	4.03	317	3.87	(253)	(3.92)	(~280)	(~4.01)
(263)	(3.86)	271	3.58	246	3.98	253	3.83
		(230)	(3.83)	242	3.99	240	3.88
		(222)	(4.06)				

a in methanol solution.
b in cyclohexane solution.

Dibromofumaronitrile exhibited a double maximum at 283 and 275 mμ of high intensity (log ε 4.03), with a slightly weaker shoulder at 263 mμ. In di-iodofumaronitrile the main absorption peak had a similar shape, but was situated at considerably longer wave-lengths. Separated by the same distance, 8 mμ, the double maximum was here found at 325 and 317 mμ; the intensity was reduced by about 25 %. A bathochromic displacement of *ca.* 40 mμ of the longest wavelength band is ascribable to the replacement of bromine by more easily polarizable iodine atoms. A second, flat, lower-intensity band appeared at 271 mμ (log ε 3.58). As in the bromine analogue the absorption raised steeply towards shorter wave-lengths; two weak shoulders were obtained at 230 (log ε 3.83) and 222 mμ (log ε 4.06).

In the acrylonitrile couple III—IV the same type of differences were observed; however, as less extended conjugated systems they absorbed at considerably shorter wave-lengths. The bromo substituted III showed only one

short-wavelength, closer double absorption maximum at 242 and 246 mμ (log ε ~ 4.00), with a marked shoulder at 253 mμ (log ε 3.92). Additionally, a weak shoulder was seen at 264 mμ (log ε 3.69). The iodine analogue IV, like II, exhibited three absorption maxima, one highest-intensity double peak at 283 and 280 mμ (log ε ~ 4.02) and two flat maxima at 253 and 240 mμ of almost equal intensity (log ε ~3.85). Again, a bathochromic shift of about 40 mμ of the longest wave-length band had taken place by changing from bromine to iodine substitution. The intensity in this case remained almost unchanged.

The basic compounds fumaronitrile [16] and acrylonitrile [17] exhibit one single absorption maximum at 220 (log ε 4.2) and 215.5 mμ (log ε 1.69), respectively (ethanol solution).

EXPERIMENTAL

Dibromofumaronitrile. The cyanoacetylene used was prepared from dimethyl acetylenedicarboxylate by conversion of the ester to its amide and treatment of the amide with phosphorus pentoxide after Moureu and Bongrand.[1]

From a reservoir dicyanoacetylene (312 mg, 0.004 mole) was distilled *in vacuo* into a reaction tube cooled in dry ice. Under an atmosphere of nitrogen it was dissolved in ether (10 ml) in an ice bath. A solution of bromine (0.22 ml, 0.0043 mole) in chloroform (10 ml) was added in portions to the ether solution and the reaction mixture was allowed to stand at room temperature in diffuse light for three days.

The solvents were removed *in vacuo* in the cold, leaving a rich, yellow-red, partly crystalline residue. By recrystallisation from chloroform/petrol ether an almost colourless, well-crystallising product (200 mg) precipitated, m.p. 110°C. Concentration of the mother liquor gave additional amounts (354 mg) of a less pure crystalline product. The residual red oil (50 mg) was non-crystallisable. Repeated sublimation at 50°/10 mm yielded coarse, transparent crystals, m.p. 110.0—111.0°C (s.c.) without decomposition. Yield 57 %. (Found: C 20.42; H 0; N 11.95; Br 68.00. Calc. for $C_4N_2Br_2$: C 20.36; N 11.88; Br 67.75.)

Di-iodofumaronitrile. Freshly distilled dicyanoacetylene (see above) (300 mg, 0.004 mole) was dissolved in carbon disulphide (7 ml) under an atmosphere of nitrogen in an ice bath. A solution of iodine (1.0 g, 0.004 mole) in carbon disulphide (10 ml) was added to the dicyanoacetylene solution. The mixture was supplied with finely powdered, anhydrous ferrous iodide (100 mg) and kept at room temperature in diffuse light for ten days.

After two days considerable amounts of heavy crystalline material had deposited on the catalyst. The solids were filtered off, and another 100 mg of ferrous iodide was added to the solution to stimulate further crystal formation.

From isolated solids, organic material was extracted by ether. The colourless extracts were concentrated *in vacuo*, leaving a very pure crystalline product (417 mg), m.p. 182—184°C (s.c.). Recrystallisation from petrol ether gave fine, yellow plates of m.p. 187.0—188.0°C (s.c.).

By the end of ten days no additional precipitation of crystalline material had occurred. The catalyst was filtered off, and unreacted iodine in the carbon disulphide solution was removed by shaking with a concentrated solution of sodium thiosulphate. Drying over anhydrous sodium sulphate and evaporation of the solvent *in vacuo* gave a yellow, crude residue melting unsharply at 145°C (s.c.). On attempted recrystallisation from several organic solvents only heavy red oil precipitated. The solution from a treatment with acetone/petrol ether was decanted from the oil layer and volatiles removed *in vacuo*. Extraction of the residue three times with petrol ether and concentration of the collected extracts *in vacuo* gave a crystalline precipitate (73 mg), which on recrystallisation from petrol ether showed the same melting point as crystalline material first deposited on the catalyst.

According to a microanalysis the isolated product was di-iododicyanoethylene. (Found: C 14.47; H 0; N 8.77; I 76.40. Calc. for $C_4N_2I_2$: C 14.67; N 8.49; I 76.93.) The total yield of pure reaction product was 38 %.

On chromatography of the crude product on alumina (Woehler, neutral), the column became discoloured and slowly brown. Elution (petrol ether-benzene) of material failed compietely.

Tribromoacrylonitrile. The partly decolourized reaction mixture from isolated bromocyanoacetylene (starting from 1.16 g of cyanoacetylene [2]) was supplied with additional bromide/bromine solution (2 ml) and half-normal potassium hydroxide (10 ml) and left overnight at 0°C. A very heavy, yellow crystalline product precipitated. This was recovered by filtration and washed on the filter with a few drops of ethanol (6.02 g; m.p. 72–78°C (s.c.)). Sublimation over phosphorus pentoxide at 60°/10 mm gave coarse, transparent prisms of tribromocyanoethylene, m.p. 88.0–89.0°C (s.c.). Yield 0.407 g, *i.e.* 8.0 % calculated from unreacted cyanoacetylene. (Found: C 12.48; H 0; N 4.95; Br 82.86. Calc. for C_3NBr: C 12.43; N 4.83; Br 82.73.)

An ether extract of the aqueous phase contained no reaction product.

Tri-iodoacrylonitrile. The filtered reaction mixture (from conversion of 150 mg of cyanoacetylene to iodocyanoacetylene [3]) was mixed with additional amounts of iodide/iodine solution and half-normal potassium hydroxide and stored at 0°C. After two months small amounts of very heavy, yellow, fine crystalline substance had deposited. Isolated material (46 mg, m.p. 160–170°C) by recrystallisation once from a dilute benzene-petrol ether solution in the cold gave fine, yellow needles of tri-iodocyanoethylene (14 mg), m.p. 179.5–180.5°C (s.c.) under decomposition. By concentration of the mother liquor additional amounts (5 mg) of equally pure crystals were isolated. (Found: C 8.58; H 0; N 3.28. Calc. for C_3NI_3: C 8.36; N 3.25).

The infrared spectra were recorded on a Perkin-Elmer Infrared Spectrometer Model 21 (NaCl and CaF_2 prisms) in solutions (CS_2, CCl_4, $CHCl_3$), nujol mull, and KBr pellets.

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

The dipole moment measurements were carried out by use of the same apparatus and technique as previously employed.[2,3] For di-iodofumaronitrile and dibromofumaronitrile an electric dipole moment of $\mu = 1.33$ and 0.54 Debye, respectively, in benzene solution at 25.0°C was found. Tetrabromomethane under the same conditions exhibited a dipole moment of 0.57 Debye. Weight fractions in the range 10^{-4}–10^{-3} were measured. The values quoted are considered to be accurate within $\pm$ 0.05 Debye.

The dipole moment of di-iodomaleonitrile was roughly calculated from the values 0, 0, 1.2, and 3.5 Debye units taken, respectively, for the C=C, C–C, C–I and C≡N bond moments.[18] A bond angle of 180° was taken for the C–C≡N angle and 120° for the C=C–C angle. A value of μ of about 4.0 Debye was thus obtained.

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

Acknowledgements. The author is grateful to Mag.sc. Else Augdahl for measurements and discussion of the infrared absorption spectra. Thanks are due to Cand.real. A. Lindheim for his cooperation in determination of the electric dipole moments.

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Received April 9, 1963.