424. (*Methyl isocyanide*)*copper*(I) *Iodide.*

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A very stable compound of cuprous iodide and methyl isocyanide has been prepared from the components and by the interaction of cuprous cyanide with methyl iodide in acetonitrile at 100°. The homologues CuI,EtNC and CuI,Pr^{n}NC, and the compound CuBr,MeNC were prepared in a similar way.

Whereas the interaction of cuprous cyanide and methyl iodide at 100° gives an unstable adduct, 3CuCN,MeI, Hartley[1] stated that "in the presence of excess of pure dry acetonitrile the reaction proceeds differently and a compound CuNC,MeI is formed which . . . . crystallises in white needles." When heated with an aqueous solution of potassium cyanide the compound evolved methyl isocyanide. Attempts to determine its molecular weight ebullioscopically in acetonitrile "gave a high value corresponding to about 3(CuNC,MeI)."[1]

Hartley gave no further experimental details. We have found that when the components are heated in a sealed tube very little of his compound is formed if the duration is less than 12 hours or if the concentration of methyl iodide in the solvent, acetonitrile, falls much below 35% (v/v). A greyish non-crystalline solid, insoluble in water, acetonitrile, and all common solvents, separates intermediately. This contains no iodine and dissolves in aqueous potassium cyanide with the evolution of methyl isocyanide. It appears to be a mixture of cuprous cyanide with an adduct CuCN,MeNC. On continued heating in the presence of excess of methyl iodide a homogeneous, dark brown liquid is obtained from which the desired compound separates on cooling, accompanied by an oily by-product from which it is readily separated.

It seemed probable from its reactions that Hartley's compound, CuNC,MeI, should really be formulated as a complex of cuprous iodide and methyl isocyanide, *viz.*, as [MeNC$\rightarrow$CuI]. This was confirmed by its direct synthesis from methyl isocyanide and

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[1] Hartley, *J.*, 1928, 780.

cuprous iodide (*a*) when the latter is dissolved in concentrated potassium iodide, or (*b*) suspended in acetonitrile, or (*c*) in the absence of any solvent. The homologues [EtNC→CuI] and [Pr^nNC→CuI] and the compound [MeNC→CuBr] were prepared similarly.

EXPERIMENTAL

Preparation of (*Methyl isocyanide*)*copper*(I) *Iodide.*—(a) *By Hartley's method.* Many experiments were carried out in which various proportions of methyl iodide, acetonitrile, and cuprous cyanide (prepared in 95% yield by Barber's procedure [2]) were heated in sealed tubes at 100° for different times. The liquid in the vicinity of the cuprous cyanide soon became dark and oily in appearance and the cyanide slowly went into solution. If the contents of the tube were shaken, the solution became homogeneous at a certain stage and when it was allowed to cool a light grey substance separated which was insoluble in water and all common solvents. It contained no iodine and liberated methyl isocyanide when warmed with aqueous potassium cyanide (Found: C, 22·1; H, 1·1; N, 18·3; Cu, 50·1. Calc. for [MeNC→CuCN]: C, 27·6; H, 2·3; N, 21·4; Cu, 48·7. Calc. for CuCN: C, 13·4; N, 15·6; Cu, 70·9%).

If the contents of the tube were heated at least twice as long as was needed to dissolve the initial cuprous cyanide a dark brown homogeneous solution resulted from which crusts of white crystals embedded in a brown oily matrix separated on cooling. The solid was thoroughly washed with acetone and recrystallised twice from hot acetonitrile, (methyl isocyanide)-copper(I) iodide being obtained as fine white needles which had scarcely any odour of isocyanide (Found: C, 10·2; H, 1·0; Cu, 26·8. Calc. for C_2H_3NICu: C, 10·4; H, 1·3; Cu, 27·4%).

The best yield of pure product (about 2 g., 13%) was obtained by heating cuprous cyanide (6·0 g.; 1 mol.), redistilled methyl iodide (19·5 g., 2 mol.), and acetonitrile (26 ml.) in a sealed tube at 100° for 15 hr. With shorter times of heating or with concentrations of methyl iodide below about 35% (v/v) the yield was greatly reduced.

(b) *From cuprous iodide and methyl isocyanide.* (i) As in Mann, Purdie, and Wells's procedure [3] for the preparation of tetrakis(monoiodotrialkylarsinecopper), excess of methyl isocyanide (prepared by the action of aqueous potassium cyanide upon the adduct MeNC,AgI) [4] was distilled into a solution of cuprous iodide (2 g.) in saturated aqueous potassium iodide (20 ml.). (Methyl isocyanide)copper(I) iodide separated immediately as a flocculent, white, microcrystalline precipitate which was collected and recrystallised from boiling acetonitrile. (ii) Excess of methyl isocyanide was distilled on to dry cuprous cyanide, and the mixture warmed in a sealed tube. The iodide went into solution and, on cooling, (methyl isocyanide)-copper(I) iodide separated as white needles (Found: Cu, 27·9%). (iii) A sealed tube containing redistilled methyl isocyanide (2·34 g., 1 mol.) was placed in a flask containing cuprous iodide (10·8 g., 1 mol.) and acetonitrile (100 ml.). The flask was stoppered and shaken to break the sealed tube. Slight heat was developed, and during intermittent shaking for 1 hr. all the cuprous cyanide had dissolved and the smell of isocyanide was no longer perceptible. The mixture was heated to its b. p. on the water-bath and filtered hot. On cooling, (methyl isocyanide)copper(I) iodide separated as white needles which were analysed without further purification (Found: C, 10·5; H, 1·9; N, 6·1; Cu, 27·2, 26·7, 27·2. Calc. for C_2H_3NICu: C, 10·4; H, 1·3; N, 6·1; Cu, 27·4%). The complex is insoluble in water, methanol, ethanol, pentanol, ethers, light petroleum, benzene, and carbon tetrachloride. It dissolves readily in boiling acetonitrile and propionitrile.

(*Ethyl isocyanide*)*copper*(I) *iodide* was prepared similarly by heating cuprous iodide (3 g.), acetonitrile (15 ml.), and excess of ethyl isocyanide for a short time. Brownish-yellow needles which separated when the mother-liquor was allowed to evaporate were collected and washed well with acetone, the *complex* being obtained as colourless needles (Found: C, 14·4; H, 2·1; Cu, 25·7. C_3H_5NICu requires C, 14·7; H, 2·1; Cu, 25·9%). The *n-propyl analogue*, prepared similarly in very poor yield, formed dirty white needles (Found: Cu, 24·9. C_4H_7NICu requires Cu, 24·5%).

(*Methyl isocyanide*)*copper*(I) *Bromide.*—Methyl isocyanide (1·50 g., 1 mol.), cuprous bromide (5·25 g., 1 mol.), and acetonitrile (75 ml.) were heated to boiling. A green colour developed and almost all the solid went into solution. The mixture was filtered, and the filtrate cooled, where-

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[2] Barber, *J.*, 1943, 79.
[3] Mann, Purdie, and Wells, *J.*, 1936, 1903.
[4] Hartley, *J.*, 1916, **109**, 1296.

upon white crystals (3·0 g.) separated. These were analysed after being washed with acetone and dried in the air (Found: Cu, 34·1. C_2H_3NBrCu requires Cu, 34·4%).

Action of 2,2′-Bipyridyl on (Methyl isocyanide)copper(I) *Iodide.*—2,2′-Bipyridyl (0·50 g.) and (methyl isocyanide)copper(I) iodide (0·74 g.), separately dissolved in warm acetonitrile (40 ml. in all), were mixed; orange-red crystals separated (Found: C, 33·6; H, 3·6; Cu, 19·0. Calc. for $C_{20}H_{16}N_4Cu_2I_2$: C, 34·6; H, 2·3; Cu, 18·4%). Evaporation of the mother-liquor gave a greenish-yellow powder smelling strongly of isocyanide: this was not further investigated.

DISCUSSION

Hartley's compound is formally similar to the crystalline complexes of cuprous iodide with tertiary arsines or phosphines. These are now known to be tetrameric, $[R_3As(\text{or } P)\rightarrow CuI]_4$, with structures in which the four copper atoms are arranged at the apices of a tetrahedron: the four iodine atoms are located centrally above the four faces, and the arsenic (or phosphorus) atoms lie beyond the copper atoms to which they are co-ordinated on the elongation of the axes joining these to the centre of the tetrahedron.[3] The hypothesis that the isocyanide complexes might have a similar structure proved to be false. For, whereas the value of n in $[R_3As(\text{or } P)\rightarrow CuI]_n$ always lay within the range 3·6—4·2 irrespective of the alkyl group (R = Et, Pr^n, Bu^n, or $n\text{-}C_5H_{11}$), the solvent (acetone, benzene, or ethylene dibromide), or the method of determination (cryoscopy or ebulliometry), yet the value of n in the formula $[MeNC\rightarrow CuI]_n$ when obtained by ebulliometric measurements in acetonitrile ranged from 1·1 to 2·1 and varied with the concentration. No weight could be attached to these results, for at the b. p. of acetonitrile (82°) the complex was definitely dissociated and the hot solution smelled strongly of isocyanide (b. p. 60°). On the other hand, the vapour pressure of isocyanide over the solid complex is very low, for a sample prepared by Hartley in 1926 and kept since then in a loosely stoppered weighing bottle had only a faint smell and was perfectly colourless and analytically pure 30 years later. Since cuprous iodide dissolves in acetonitrile and is solvated thereby, the possibility of such dissociation equilibria in boiling acetonitrile as

$$4[MeNC\rightarrow CuI]_n + 2nx\,MeCN \rightleftharpoons n[2MeNC,CuI]_2 + 2n[CuI,x\,MeCN]$$

cannot be overlooked and is consistent with the structure now found for the isocyanide complex.[6] The complex $[2MeNC,CuI]_2$ would be an analogue of Arbusov's compound $2PEt_3,CuI$,[5] which Mann *et al.* have suggested is a dimer, bridged through the two iodine atoms.[3]

A red compound formed by the action of 2,2′-bipyridyl on Hartley's compound is probably the bridged complex bisbipyridyl-μ-di-iododicopper first prepared by Tartarini and later studied by Mann, Purdie, and Wells.[3] Its formation affords no real clue to the structure of the complex $[MeNC\rightarrow CuI]_n$, which appears from *X*-ray crystallography to be quite unlike the formally analogous complexes of tertiary arsines or phosphines and of a quite unusual character with infinite double chains of copper atoms linked through iodine atoms: the isocyanide groups are attached in pairs to half the metal atoms.[6]

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[5] Arbusov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 293.
[6] Fisher, Taylor, and Harding, this issue, paper no. 461.