*Journal of Organometallic Chemistry*, 93 (1975) 129—137

# COPPER(I) COMPLEXES FROM 1-BROMOPROPYN-3-OLS, DIMETHYLFORMAMIDE AND COPPER(I) CYANIDE AND THEIR CONVERSION TO HYDROXYACETYLENIC NITRILES AND HEXADIYNEDIOLS

STEPHEN R. LANDOR
*Department of Chemistry, Exeter University, Exeter EX4 4QD (Great Britain)*
BASIL DEMETRIOU, ROMAN GRZESKOWIAK and DOUGLAS F. PAVEY
*School of Chemistry, Thames Polytechnic, London SE18 6PF (Great Britain)*
(Received January 20th, 1975)

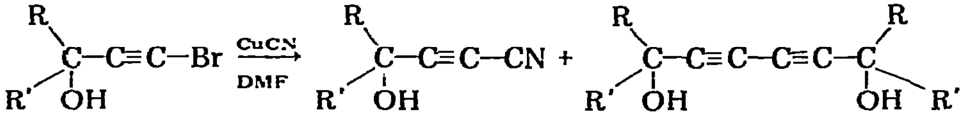
## Summary

Copper(I) complexes of approximate composition $(CuCN)_4 \cdot (DMF)_2 \cdot RR'C(OH)C{\equiv}CBr$ have been isolated from copper(I) cyanide and 1-bromopropyn-3-ols in dry dimethylformamide (DMF). Decomposition of these complexes with aqueous DMF gives 4-hydroxybutynenitriles in about 60% yield. For preparative purposes it is not necessary to isolate the complex, similar yields being obtained in a one step process. Decomposition of the isolated copper(I) complex with water gives the hexadiynediol as the only isolated product. Formation of the latter is completely suppressed by the presence of hydroxylammonium chloride in the one step process.

---

## Introduction

A general synthesis of allenic nitriles (60-70%) by treatment of 1-bromoallenes with copper(I) cyanide in dry dimethylformamide has been reported previously [1], and similar methods have been used to convert aliphatic and aromatic bromides to cyanides at elevated temperatures [2]. However, no report of the isolation of intermediate copper complexes and subsequent controlled decomposition has appeared in the literature. The method had been successfully used to synthesise 3-phenylpropynenitrile [3] and there was no reason to believe that it could not be used equally well for the synthesis of 4-hydroxybutynenitriles (II) which were required for our investigations. However, under these conditions 1-bromopropyn-3-ols (I) gave only 15-20% of 4-hydroxybutynenitriles (II) together with substantial amounts (ca. 20%) of coupled products, the hexa-2,4-diyne-1,6-diols (III). The coupling of 1-bromoalkynes in the presence of copper(I) salts had previously been observed [3,4]. A search for methods for suppressing the coupling reaction while still permitting nitrile formation showed that complexes of 1-bromopropyn-3-ols, copper(I) cyanide and dimethylformamide, initially assumed to exist only in solution, could be isolated as solids and decomposed under controlled conditions either to 4-hydroxybutynenitriles (II) or to hexa-2,4-diyne-1,6-diols (III):



(I) (II) (III)

## Results and discussion

A study of the effect of temperature and mole ratio of the reactants on the yield of products revealed that, (a) very little conversion to 4-hydroxybutynenitriles (II) occurs below 40° whereas above 80°C only coupled products (III) are isolated, albeit in poor yield (ca. 23%), (b) the optimum temperature range for the reaction is 45-50°C and (c) the optimum ratio of copper(I) cyanide to 1-bromopropyn-3-ol is near 4/1 (Table 1). Four different 1-bromo-3,3-dialkylpropyn-3-ols consistently gave yields of ca. 60% under these optimised conditions (method A, Table 2).

The intermediate complexes were isolated from reaction mixtures by method A simply by omitting the addition of water. The solids were filtered and washed with a small volume of dry ether but could not be recrystallised. Both microanalyses and thermogravimetric analyses led to the stoichiometric ratios for the complexes given in Table 3.

It should be noted that the stability of these complexes is not high. Prolonged washing with ether gradually removes the acetylenic ligand and, to some extent, the base (DMF) from the complex. For this reason complexes of constant and definite stoichiometry could not be isolated and average analysis values from three preparations are quoted here (Table 3). These intermediate complexes have the same composition irrespective of the ratio of copper(I) cyanide to 1-bromopropyn-3-ol initially used to prepare them and the stoichio-

TABLE 1

YIELDS OF NITRILE, $MeEtC(OH)C{\equiv}C{-}C{\equiv}N$ AND DIYNEDIOL, $[MeEtC(OH)C{\equiv}C{-}]_2$ FOR DIFFERENT MOLAR RATIOS OF CuCN AND $MeEtC(OH)C{\equiv}C{-}Br$ AT 50°C

| Concentration (moles) | | Yield (%) | |
|---|---|---|---|
| CuCN | $RR'C(OH)C{\equiv}CBr$ | Nitrile | Diynediol |
| 1 | 1 | 25 | 18 |
| 2 | 1 | 40 | 15 |
| 3 | 1 | 55 | 14 |
| 4 | 1 | 61 | 6 |
| 5 | 1 | 62 | 5 |
| 6 | 1 | 61 | 5 |

TABLE 2

YIELD OF PRODUCTS BY METHOD A ($CuCN / RR'C(OH)C\equiv CBr$ = 4/1), METHOD B ($CuCN / RR'C(OH)C\equiv CBr$ / HYDROXYLAMMONIUM CHLORIDE = 3/2/3) AND METHOD C (FROM ISOLATED COMPLEX WITH WATER)

| From $RR'C(OH)C\equiv CBr$ | | Yield (%) | | | |
|---|---|---|---|---|---|
| | | Method A | | Method B with hydroxylamine | Method C from complex with $H_2O$ |
| R | R' | Nitrile | Diynediol | Nitrile | Diynediol |
| Me | Me | 60 | 2 | 56 | 28 |
| Me | Et | 62 | 6 | 56 | 36 |
| Me | Pr | 62 | 2 | 60 | 39 |
| Me | t-Bu | 60 | 2 | 55 | 49 |

metries are in accord with the observation that optimum yields are obtained for a ratio of copper(I) cyanide to bromocarbinol of 4/1. This tends to support the view that the controlled reaction of the isolated complex is similar to the reaction of the corresponding species in solution in the one step process. The fact that the isolated intermediate complex with aqueous DMF gives nitrile (II) and diol (III) in practically the same ratio as that obtained by method A further supports this view.

The presence of excess DMF during the hydrolysis of the complex is an essential prerequisite for formation of the nitrile (II). Thus, when the isolated complex is hydrolysed by the addition of water only, nitrile formation is completely suppressed and diol (III) formed as the sole product.

An alternative procedure which uses hydroxylammonium chloride as an extra ligand led to improved yields of nitriles (II) and completely suppressed the self-coupling reaction (method B, Table 2). Equimolar quantities of 1-bromopropyn-3-ols, copper(I) cyanide and hydroxylammonium chloride in DMF at 60°C gave 55-60% of 4-hydroxybutynenitriles (II). However, solid complexes could not be isolated from the reaction involving hydroxylammonium chloride (method B) but complexation of this species with copper(I) cyanide undoubtedly occurs and is shown by a change in colour of the reaction mixture on addition of this reagent. Furthermore, hydroxylammonium chloride suppresses self-coupling of bromopropynols only when it is introduced at the beginning of the reaction but has little effect when added during the hydrolysis stage.

A probable structure for the isolated intermediate complexes is shown in Fig. 1. This is analogous to the structure of $Cu(CN)_2^-$ in the $KCu(CN)_2$ complex [5], which consists of polymeric CuCN chains formed by coordination of nitrogen to a neighbouring copper atom; a second $CN^-$ group at each copper atom

TABLE 3

STOICHIOMETRIC RATIOS FOR THE COMPLEXES

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | CuCN | : | 0.54 | DMF | : | 0.28 | $Me_2C(OH)C\equiv CBr$ |
| 1 | CuCN | : | 0.50 | DMF | : | 0.28 | $MeEtC(OH)C\equiv CBr$ |
| 1 | CuCN | : | 0.50 | DMF | : | 0.22 | $Me\text{-}n\text{-}PrC(OH)C\equiv CBr$ |
| 1 | CuCN | : | 0.58 | DMF | : | 0.21 | $Me\text{-}t\text{-}BuC(OH)C\equiv CBr$ |

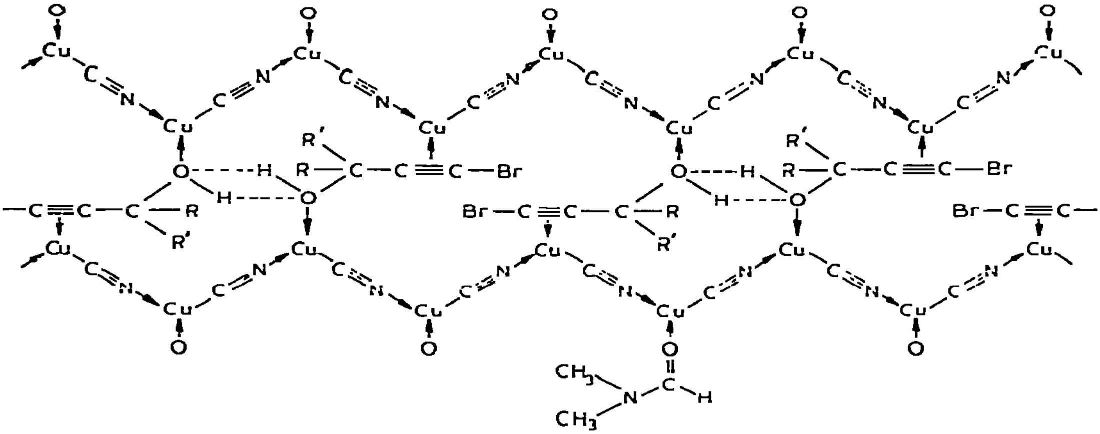


Fig. 1. Proposed polymeric structure of intermediate complex Cu(CN)$_4$·(DMF)$_2$·RR'C(OH)C≡CBr.

gives a coordination number of three. In the DMF—bromopropynol complex shown in Fig. 1, two chains of CuCN are linked together by bromopropynol acting as a bidentate ligand with DMF at alternate copper atoms. In this structure each copper atom has a coordination number of three. The structure is compatible with the stoichiometry of the complex and the shifts observed for certain characteristic bands in the infrared region of both organic ligands. DMF is coordinated to copper(I) through the carbonyl oxygen causing a shift of the carbonyl stretching frequency from 1675 cm$^{-1}$ (in free DMF) to about 1650 cm$^{-1}$ (in complexed DMF) and a hypsochromic shift (ca. 22 cm$^{-1}$) for the N—C=O deformation. Similar observations were made by Jungbauer [6], who studied complexes of DMF with other transition metals. The proposed structure is also supported by (a) the presence in the IR spectrum of sharper bands which are shifted to higher frequencies for the stretching vibration of the hydroxyl group and (b) the absence of a band at around 2200 cm$^{-1}$ corresponding to the C≡C stretching mode. The fact that the C≡C stretching band is also absent from complexes of copper(I) bromide, DMF and bromopropynols [7] may be taken as strong indication of π-coordination between the acetylene group and copper(I) atoms.

Any mechanistic scheme for the formation of hydroxybutynenitriles from 1-bromopropyn-3-ols and copper(I) cyanide in DMF will have to account for the following facts:

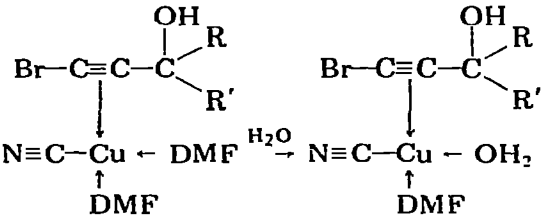
(*i*). Water is essential for the formation of product. In the absence of water only copper complexes are isolated. Hydrolysis with aqueous DMF (or other donors such as DMSO) yields the nitrile as the major product. However, the corresponding hexadiynediols are formed exclusively by treatment of the isolated complex with water only.

(*ii*). In all cases studied, about 90% of the bromine from the bromopropynols is present in the mother liquor as Br$^-$.

(*iii*). The analysis of the residue which is left after hydrolysis and extraction of products gives a clear indication that cyanide groups used to form the hydroxybutynenitrile are replaced by hydroxyl groups on the copper. The residue does not contain bromine. On this basis any mechanism [2,7] involving formation of a 4-centre transition state between ≡C—Br and CuCN which subsequently collapses to nitrile and copper(I) bromide can be excluded.

(*iv*). Addition of strong complexing agents like hydroxylamine to the reaction mixture in DMF and hydrolysis of the resulting soluble complex gives nitrile as the sole product.

It is conceivable that the polymeric structure (Fig. 1) proposed for the isolated intermediate complex is cleaved by donor solvents such as DMF to an intermediate stage containing species IV which is converted to V on addition of water. Both IV and V show copper(I) with a coordination number of 4 which is preferred for solutions.



(IV) (V)

$Br^- + NC{-}C{\equiv}C{-}C(OH)RR'$

$H_3O^+ + DMF \cdot Cu(OH)$

$(\text{or } DMF \cdot Cu_2O \cdot H_2O)$

(VI)

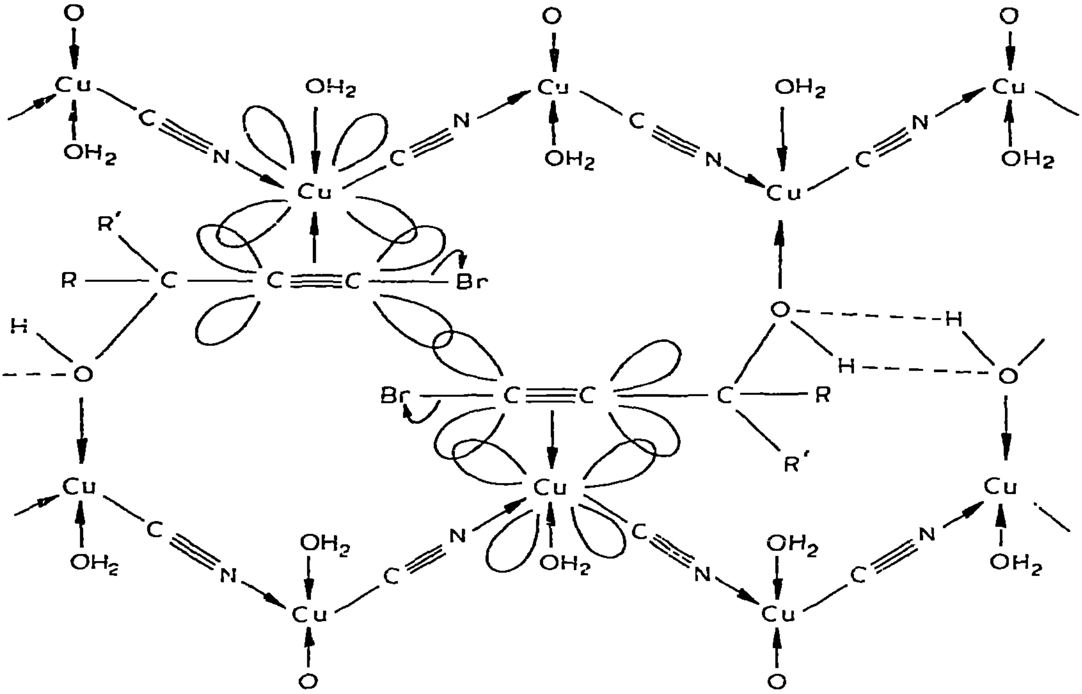
Formation of diynediol as the sole product on treatment of the isolated complex with water only, would seem to suggest that the preservation to some degree of the polymeric structure of the complex is a necessary condition for the coupling reaction to take place. The same conclusion may also be drawn from the fact that the presence of hydroxylamine completely prevents diynediol formation. This ligand may well disrupt or prevent polymer formation and the resulting complex remains in solution, probably in a monomeric form (VI, $NH_2OH$ replacing DMF). It thus precludes the possibility of two bromopropynol molecules, $RR'C(OH)C{\equiv}CBr$ being sufficiently close in the complex for self-coupling to occur. The formation of diynediol from the proposed polymeric structure (Fig. 1) is rationalised in Scheme 1 by coordination of water to give a 4-coordinate copper(I) polymer which gives rise to carbon—carbon bond formation as shown.

This scheme accounts for the fact that 90% of bromine is found in solution as $Br^-$, the absence of bromine in the solid residue and the presence of copper(II) in the solution to the extent of only 4-5% could well be due to aerial oxidation. A 3*d* electron is transferred from copper to the carbon atom bearing the bromine and at the same time a bromide anion is expelled. The two acetylenic radicals thus formed are held in close proximity to each other in the proposed polymeric structure and immediately link up to form the hexadiynediol (III). The hydrated copper(II) species formed during the coupling process, unstable in the presence of cyanide ions, is reduced to copper(I) cyanide*. By contrast, copper(II) and bromide ions are found in amounts equivalent to the diynediol formed in the aqueous hydrolysates obtained from the self-coupling reaction of 1-bromopropyn-3-ols (I) and copper(I) bromide [7].

---

[*] Cyanogen is thought to be formed but its presence has not been established.

SCHEME 1



## Experimental

DMF was dried by azeotropic distillation with benzene. GLC was carried out with a nitrogen flow rate of 40 ml min$^{-1}$; infrared spectra were determined with a Perkin—Elmer 257 spectrophotometer for liquid films and for Nujol mulls; ultraviolet spectra for absolute ethanolic solutions with a Unicam SP800 spectrophotometer.

1-Bromoprop-1-yn-3-ols were prepared as detailed by Greaves, Kalli, Landor and Landor [9]. Analyses for copper(II) and bromide ions in solution were carried out by standard titrimetric procedures [10].

*4-Hydroxy-4-methylpent-2-ynenitrile*

(*a*). Anhydrous copper(I) cyanide (49 g, 0.56 mol) and 1-bromo-3-methylbut-1-yn-3-ol (22.3 g, 0.14 mol) were added to dry DMF (100 ml) under nitrogen; the temperature was not allowed to rise above 50°C. The mixture was stirred for 2 h at 50°, allowed to cool and then poured into vigorously stirred water (500 ml). Stirring was continued until the solid was no longer sticky. After filtration, the aqueous solution was extracted with ether (4 × 50 ml). The solid was stirred with ether (3 × 50 ml) and filtered. The ethereal solution was washed with water (5 × 100 ml), dried ($MgSO_4$) and distilled to give the nitrile (9.15 g, 60%), b.p. 62.4°C/1.5 mmHg. (Found: C, 66.1; H, 6.6; N, 12.8. $C_6H_7NO$ calcd.: C, 66.1; H, 6.5; N, 12.8%.) GLC on silicone oil at 80°C showed only one peak, $R_t$ 6.8 min; $\nu_{max}$ 3380 (OH), 2290 (C≡N), 2220 cm$^{-1}$ (C≡C). The residue from the distillation gave 2,7-dimethylocta-3,5-diyne-2,7-diol (0.3 g, 2%), m.p. 129-130°C (lit. [11] 129-131°), $\lambda_{max}$ 253, 240, 227 nm ($\epsilon$ 245, 358, 338) on recrystallisation from chloroform.

(*b*). Copper(I) cyanide (20 g, 0.23 mol) and hydroxylammonium chloride (16 g, 0.23 mol) were added to dry DMF (75 ml) and the mixture was heated to 50°C. 1-Bromo-3-methylbut-1-yn-3-ol (22.3 g, 0.14 mol) was added whilst maintaining the temperature at 50°. The mixture was stirred at this temperature for a further 2 h and worked up as in (*a*). Distillation gave 4-hydroxy-4-methylpent-2-ynenitrile (10.2 g, 56%), b.p. 58-59°C/1 mmHg with an IR spectrum identical with that of the nitrile from (*a*).

*4-Hydroxy-4-methylhex-2-ynenitrile*

(*a*). Copper(I) cyanide (56 g, 0.6 mol) and 1-bromo-3-methylpent-1-yn-3-ol (26.8 g, 0.15 mol) in dry DMF (100 ml) at 50°C for 2 h under nitrogen gave (i) the nitrile (11.4 g, 62%), b.p. 72°C/1.5 mmHg. (Found: C, 68.1; H, 7.5; N, 11.3. $C_7H_9NO$ calcd.: C, 68.2; H, 7.4; N, 11.4%.) GLC on silicone oil at 100° showed one peak, $R_t$ 6.6 min; $\nu_{max}$ 3420 (OH), 2290 ($C\equiv N$), 2220 cm$^{-1}$ ($C\equiv C$), and (ii) 3,8-dimethyldeca-4,6-diyne-3,8-diol (0.8 g, 6%), m.p. 86-87°C (lit. [12] 89-91°), $\lambda_{max}$ 253, 241, 229 nm ($\epsilon$ 251, 367, 350).

(*b*). Copper(I) cyanide (20 g, 0.23 mol), 1-bromo-3-methylpent-1-yn-3-ol (26.8 g, 0.15 mol) and hydroxylammonium chloride (16 g, 0.23 mol) in DMF (75 ml) at 50°C gave the nitrile (9.6 g, 56%); b.p. and spectra identical to those of the product from (*a*).

*4-Hydroxy-4-methylhept-2-ynenitrile*

(*a*). Copper(I) cyanide (35.8 g, 0.4 mol), 1-bromo-3-methylhex-1-yn-3-ol (19.1 g, 0.1 mol) in DMF (100 ml) at 50° for 2 h under nitrogen gave (i) the nitrile (8.5 g, 62%), b.p. 95°C/2 mmHg. (Found: C, 70.0; H, 8.2; N, 10.9. $C_8H_{11}NO$ calcd.: C, 70.0; H, 8.1; N, 10.2%.) GLC (silicone oil) at 120°C gave a single peak, $R_t$ 6.6 min; $\nu_{max}$ 3420 (OH), 2290 ($C\equiv N$), $\nu_{sh}$ 2220 cm$^{-1}$ ($C\equiv C$), and (ii) 4,9-dimethyldodeca-5,7-diyne-4,9-diol (0.22 g, 2%), m.p. 112-4°C; $\lambda_{max}$ 253, 241, 230 nm ($\epsilon$ 255, 370, 259).

(*b*). Copper(I) cyanide (13.4 g, 0.15 mol), 1-bromo-3-methylhex-1-yn-3-ol (19.1 g, 0.1 mol), hydroxylammonium chloride (10.5 g, 0.15 mol) in DMF (75 ml) at 50°C gave the nitrile (8.2 g, 60%); b.p. and spectra identical to those of the nitrile from (*a*).

*4-Hydroxy-4,5,5-trimethylhex-2-ynenitrile*

(*a*). Copper(I) cyanide (35.8 g, 0.4 mol), 1-bromo-3,4,4-trimethylpent-1-yn-3-ol (20.5 g, 0.1 mol) in dry DMF (75 ml) at 50°C for 2 h under nitrogen gave (i) the nitrile (9.1 g, 60%), b.p. 79°C/1 mmHg. (Found: C, 70.4; H, 8.7; N, 9.1. $C_9H_{13}NO$ calcd.: C, 71.4; H, 8.7; N, 9.2%.) GLC (silicone oil) at 100°C gave a single peak, $R_t$ 12.4 min; $\nu_{max}$ 3480 (OH), 2290 ($C\equiv N$), $\nu_{sh}$ 2220 cm$^{-1}$ ($C\equiv C$), and (ii) 2,2,3,8,9,9-hexamethyldeca-4,6-diyne-3,8-diol (0.25 g, 2%), m.p. 132-4°C; $\lambda_{max}$ 253, 242, 231 nm ($\epsilon$ 260, 374, 363).

(*b*). Copper(I) cyanide (13.4 g, 0.15 mol), 1-bromo-3,4,4-trimethylpent-1-yn-3-ol (20.5 g, 0.1 mol), hydroxylammonium chloride (10.5 g, 0.15 mol) in dry DMF (75 ml) at 50°C gave the nitrile (7.8 g, 55%) with b.p. and spectra as in (*a*).

TABLE 4

ANALYTICAL RESULTS FOR COMPLEXES OF $Cu^{I}CN$ WITH DMF AND RR'C(OH)C≡CBr

| R | R | Yield (%) | Found (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | Cu | C | H | N | Br |
| Me | Me | 29 | 35.0 | 27.2 | 2.3 | 11.9 | 12.8 |
| Me | Et | 32 | 35.1 | 27.6 | 2.9 | 11.5 | 12.4 |
| Me | n-Pr | 34 | 34.6 | 26.2 | 3.0 | 11.4 | 12.1 |
| Me | t-Bu | 30 | 32.7 | 27.1 | 3.7 | 11.4 | 11.9 |

### *Complexes CuCN·0.5 DMF·0.25 RR'C(OH)C≡CBr*

All the intermediate complexes were prepared as follows: the 1-bromopropyn-3-ol, RR'C(OH)C≡CBr (0.1 mol) was added to a stirred suspension of copper(I) cyanide (0.4 mol) in dry DMF (75 ml) under nitrogen. Throughout the addition of the bromopropynol and the subsequent stirring for 2 h, the temperature of the reaction mixture was maintained at 50°C. GLC of the resulting solution showed that the bromopropynol had completely disappeared but no peak for nitrile or diol could be detected. The brown solid (yields 29-34%) which separated on cooling was filtered, washed with dry ether and dried in vacuo. The addition of ether precipitated further crops of impure complex. Microanalyses are listed in Table 4.

### *Hydrolysis of complex Cu(I)CN·0.5 DMF·0.25 MeEtC(OH)C≡CBr*

*(i). With aqueous DMF.* The complex (15 g) was stirred with a solution of DMF (40 ml) in water (200 ml) until the resultant cream coloured solid became granular. Work up as above gave 4-hydroxy-4-methylhex-2-ynenitrile (1.6 g, 59%) and 3,8-dimethyldeca-4,6-diyne-3,8-diol (0.1 g, 4.7%).

The residual complex does not contain bromine or acetylenic ligand*; $\nu_{max}$ 2180 and 2120 (C≡N), 1680 and 1640 $cm^{-1}$ (C≡O). Analysis gave C, 17.9; H, 1.38; Cu, 59.5; N, 15.9%, and calculation showed that this solid contained oxygen in excess of that required by a CuCN—DMF complex.

*(ii). With water.* The complex (33 g) was stirred with water (200 ml) until a granular solid was formed. Work up as before gave 3,8-dimethyldeca-4,6-diyne-3,8-diol (1.7 g, 36%), m.p. 86-87°C. The residual copper(I) complex (Cu, 53.8%) contains bromine detectable by sodium fusion but not by adding a silver nitrate solution to the solution produced by digesting the complex with nitric acid. The result indicates the presence of 1-bromoprop-1-yn-3-ol in the complex. $\nu_{max}$ 3520 and 3420 (OH), 2120 and 2180 (C≡N), 1650 (C=O), 1480, 1380 $cm^{-1}$.

### *Hydrolysis of complex Cu(I)CN·0.5 DMF·0.25 Me-t-BuC(OH)C≡CBr*

The complex (15 g) treated with aqueous DMF, as described above, gave 4-hydroxy-4,5,5-trimethylhex-2-ynenitrile (1.7 g, 53%) and 2,2,3,8,9,9-hexamethyldeca-4,6-diyne-3,8-diol (0.5 g, 19%).

---

* Confirmed by using $(CH_3)_2{}^{14}C(OH)C{\equiv}CBr$ in these reactions followed by measurement of radioactivity at each stage.

## Conclusion

Unstable π-complexes of copper(I) cyanide and 1-bromopropyn-3-ols may be isolated and these react under controlled conditions to give either acetylenic nitriles or coupled products (diynediols).

## Acknowledgement

We thank the S.R.C. for a Studentship (to D.F.P.).

## References

1 P.M. Greaves, S.R. Landor and D.R.J. Laws, J. Chem. Soc. C, (1968) 291.
2 L. Friedmann and H. Schechter, J. Org. Chem., 26 (1961) 2522.
3 P.M. Greaves and S.R. Landor, unpublished work.
4 G. Eglington and W. McCrae, Advances in Organic Chemistry, Vol. 4, Interscience, New York, 1963, p. 274; P. Cadiot and W. Chodkiewicz, C.R. Acad. Sci., 241 (1955) 1055.
5 D.T. Cromer, J. Phys. Chem., 61 (1957) 1388.
6 M.A. Jungbauer and C. Curran, Nature (London), 202 (1964) 290.
7 B. Demetriou, R. Grzeskowiak, S.R. Landor, D.F. Pavey and (in part) R. Crafts, unpublished work.
8 R.G.R. Bacon and H.A. Hill, Quart. Rev., 19 (1965) 121; C.A. Buchler and D.E. Pearson, Survey of Organic Syntheses, Wiley—Interscience, London—New York, 1970, p. 934.
9 P.M. Greaves, M. Kalli, P.D. Landor and S.R. Landor, J. Chem. Soc. C, (1971) 667; cf. F. Strauss, L. Kollek and W. Heyn, Ber. Deut. Chem. Ges., 63 (1930) 1863, and W. Chodkiewicz, Ann. Chim. (Paris), 2 (1967) 819.
10 A.I. Vogel, Quantitative Inorganic Analysis, Longmans, London, 1962, pp. 267, 358.
1 A.E. Brown and R.T. Tedeschi, J. Org. Chem., 27 (1964) 2051.
2 H. Boden and M.S. Newmann, J. Org. Chem., 26 (1961) 2525.