Tetrabutylammonium Inorganocuprates(I) * — $Bu_4N^+CuCl_2^-$, $CuBr_2^-$, CuI_2^- and $Cu(CN)_2^-$

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The dichlorocuprate(I) ion, $CuCl_2^-$, is important in the Sandmeyer [2] and Meerwein [3] reactions. It is also kinetically relevant in halogen exchange, especially that of 2-bromonitrobenzenes.[4,5] Similarly, cyanocuprate(I) ions are used in the displacement of diazonium groups by cyanide.[2] Sodium dicyanocuprate(I) has been used as a alternative to copper(I) cyanide for the replacement of aromatic or vinylic halogen by cyanide.[6]

The reactions may be summarised by a general equation for copper-promoted nucleophilic substitutions (1).[7,8] The equation also summarises several organocopper reactions.

Y is generally a soft atom or group, which forms a complex or a compound with copper(I), eqn. (1). The importance of the cuprate(I) ions mentioned above calls to mind the manifold uses of lithium diorganocuprates [9] in additions and in substitutions.

$$Ar-X+Y^- \xrightarrow{Cu^I, CuY \text{ or } CuY_2^-} Ar-Y+X^- \quad (1)$$
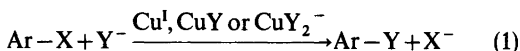
The increased use of phase transfer catalysis and the high reactivity of many anions in ion pairs with, for example, tetrabutylammonium (TBA) cation in suitable solvents [10,11] made it of interest to check the existence and behaviour of TBA dihalo- and dicyanocuprates(I).

Several TBA salts of transition metal anions have been described; in the present context, TBA dicyanoargentate(I) and TBA dicyanoaurate [12] as well as TBA perfluoroorganoaurates [13] are especially interesting. The $TBA^+PdCl_3^-$ has been used to catalyse the addition of organomercurials to α,β-enones in a phase transfer system.[14]

Tetrabutylammonium dichlorocuprate(I) was obtained in good yield in a water−dichloromethane system from tetrabutylammonium hydrogen sulfate, sodium chloride and copper(I) chloride. The cuprate was extracted into the organic phase while contaminating copper(II) remained in the aqueous phase. The salt was recrystallised from ethyl acetate

and formed colourless crystals, m.p. 71−72 °C, which were rather stable in the air and sparingly soluble in water (analysis C,H,Cl,Cu,N). It was very soluble in haloalkanes, halogenoarenes, ketones *etc.*, moderately soluble in other arenes, and little soluble in alkanes.

Tetrabutylammonium dibromocuprate(I), m.p. 88 −89 °C, was obtained when copper(I) bromide was dissolved in a tetrabutylammonium−dichloromethane solution. Recrystallisation from ethyl acetate gave beautiful crystals which took on a very faint lilac tint (analysis C,H,Br). Tetrabutylphosphonium bromide in dichloromethane dissolved at least two mol of copper(I) bromide, giving a compound, m.p. *ca.* 85 °C, with the approximate composition $Bu_4P\ Cu_2Br_3$, which was not stable, however; copper(I) bromide precipitated on attempted recrystallisation.

One mol of finely ground copper(I) iodide dissolved rather rapidly in a TBA iodide solution (one mol) giving a crystalline *TBA diiodocuprate(I)* on evaporation. On recrystallisation from ethyl acetate the salt had a strong tendency to precipitate as an oil, but from dilute solution colourless prisms m.p. 98−100 °C (analysis C,H,I) were obtained.

The preparation of *tetrabutylammonium dicyanocuprate(I)* gave some complications. Copper cyanide dissolved only slowly in tetrabutylammonium cyanide−dichloromethane. Mixing of an aqueous solution of sodium dicyanocuprate (from sodium cyanide and copper cyanide) with an equivalent amount of tetrabutylammonium hydrogen sulfate and sodium hydroxide in water gave a voluminous precipitate, which largely was dissolved in dichloromethane. The rapidly dried organic phase was evaporated and, on treatment with acetone, gave the desired TBA $Cu(CN)_2$ as a solid, which could be recrystallised from acetone (analysis C,H,Cu,N). The salt melted at 158−159 °C, giving off the characteristic odour of (butyl)isocyanide. The IR spectrum (KBr) showed a double cyanide band, 2190 and 2210 cm^{-1}, similarly to what is described [12] for potassium dicyanocuprate(I). Attempts to wash the crude cyanocuprate with water gave heavily hydrated crystals, which gradually gave off water from *ca.* 70 °C and could be dried at 120 °C, again giving evolution of isocyanide. During work-up and purification a higher-melting and sparingly soluble compound was obtained. The compound was also formed when dichloromethane solutions of TBA dicyanocuprate were dried, and also on attempted recrystallisation from acetonitrile. It melted at 249−252 C giving off the isocyanide odour. The composition, according to analysis (C,H,Cu,N), roughly corresponded to $Bu_4NCu(CN)_2 - BuNCCuCN$, but its IR spectrum gave only one peak in the cyanide region, at 2110 cm^{-1}.

* See Ref. 1.

The dihalocuprates should provide possibilities of halogen exchange. Iodobenzene and TBA dichlorocuprate at *ca.* 180 °C slowly gave chlorobenzene, which could be distilled off during a day. A closer, kinetic study of the halogen exchange with activated halogenoarenes is under way.[15] The present reagents may provide new combinations for halogen exchange as compared to the methods employing copper(I) halide and complexing solvent or other ligands.[16-18]

Preliminary experiments were made on reactions of aromatic halides and TBA dicyanocuprate. With bromobenzene (at 150 °C), no bromide – cyanide exchange took place. Some isonitrile was evolved and GLC showed also the formation of tributylamine. The thermal stability of the cyanocuprate was limited, and on distillation (around 200 °C) decomposition giving tributylamine *etc.* was extensive. The reaction with iodobenzene and TBA dicyanocuprate also gave some isonitrile formation, but here benzonitrile was also formed. Further work is in progress, and it will be interesting to see whether the new reagent may provide the possibility of halogen – cyanide exchange under phase-transfer conditions.

The mechanisms of copper-catalysed reactions, organocopper and organocuprate reactions are still unclear. Single electron transfer mechanisms including formation of copper(II) species and also copper(III) species are presently favoured in the discussion.[18,19] There are, however, several other possibilities including two-electron transfers, copper acting as a nucleophile to provide copper(III) species, and also other possibilities of oxidative addition – reductive elimination.[20-24]

The TBA inorganocuprates may make it possible to investigate some copper-promoted reactions under different conditions than used previously. This may provide new information and also new preparative possibilites. For example, it seems as if the dihalocuprates in dichloromethane solution form CT complexes with electron-deficient substrates such as 1,3,5-trinitrobenzene and α,β-enones (*cf.* Ref. 25). Structural investigations, now under way,[26] may provide some information regarding bond lengths and thereby indications of the nucleophilicity of the central copper atom.

Experimental. The new compounds were analysed by Novo Microanalytical Laboratory, Bagsvaerd, Denmark. Halogen and cyanide exchange reactions were checked with an HP 5880 A gas chromatograph. Infrared spectra were recorded on a Perkin Elmer model 197 instrument.

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