A New Route to Lipophilic Onium Inorganocuprates(I)

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In connection with an investigation on the microbicidal activity of copper(I) compounds, the question of new ways to synthesize Cu(I) complexes arose. In this respect the tetrabutylammonium dihalocuprates(I), recently described by Nilsson,[1] were interesting compounds to study. During the microbiologically oriented investigation, we found a novel route for the synthesis of these compounds, which is presented in this communication.

It is well known that Cu(I) halides are almost insoluble in water but soluble in the presence of excess halide ions due to the formation of dihalocuprate(I) anions [eqn.(1)].

$$CuHal + Hal^- \rightarrow CuHal_2^- \quad (1)$$

The dihalocuprate(I) ions form lipophilic ion pairs with typical phase transfer reagents (Q^+) such as tetrabutylammonium ions and are readily extracted into solvents like dichloromethane or chloroform, eqn. (2),

$$CuHal_2^- + Q^+HSO_4^- \rightarrow Q^+CuHal_2^- + HSO_4^- \quad (2)$$

which forms the basis for the synthetic procedure.[1]

The use of Cu(I) halide as a starting material, however, is sometimes associated with inconveniences; the copper(I) halide should be pure and it should be added as a finely powdered solid. We have found, that these problems can be overcome if Cu(II) is used in the form of halide or sulfate together with a reducing agent like ascorbic acid or sodium sulfite, all of which are readily soluble in water. In this way the dihalocuprate ion is immediately formed and is subsequently transferred into the organic phase by a suitable transfer agent [eqn.(3)].

$$Cu^{2+} + 2Cl^- \xrightarrow{Na_2SO_3} CuCl_2^- \xrightarrow{Q^+} Q^+ CuCl_2^- \quad (3)$$

The reaction is carried out in one step with a moderate excess of reducing agent and usually gives good yield of product after a single recrystallization. Some typical results are given in Table 1.

X-ray studies have established that the coordination of Cu(I) in crystalline dihalocuprates(I) is highly dependent upon the nature of the cation as well as of the halide ion.[2] Thus, the formation of discrete monomeric $CuHal_2^-$ species in the solid state is favoured by large cations with a highly screened charge and by decreasing halide radii.[3] Tetraphenylphosphonium and -arsonium dichloro- and dibromocuprates(I) have also been reported to crystallize with monomeric anions.[4] Some representatives of these compounds are included in Table 1 to demonstrate the general applicability of the synthetic procedure described. ^{13}C spectral data are given in Table 2 for compounds *1* and *5*. The $^{31}P-^{13}C$ coupling constants were used for the ^{13}C chemical shift assignment and are in accordance with earlier published data.[5]

Experimental. Preparation of tetrabutylammonium compounds (*1–4*): Tetrabutylammonium hydrogen sulfate (3.4 g, 10 mmol) and copper(II) sulfate pentahydrate (2.5 g, 10 mmol) were dissolved in 5 and 8 ml of water, respectively. Sodium halide (20–40 mmol) and sodium sulfite (20–40 mmol), dissolved in minimal amounts of water, were then mixed with the two other solutions by shaking in a separatory funnel containing 10 ml of dichloromethane. The organic phase was isolated and combined with a 10 ml portion of dichloromethane from a second extraction.

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Table 1. Compounds prepared according to eqn. (3).

Q^+	Starting materials[a] X^-	Reducing agent	Molar ratio	Complex obtained	Yield %		M.p./°C		
					Crude product	Recryst.(solvent)	Crude product	Recryst.	
$Bu_4N^+HSO_4^-$	NaCl	Na_2SO_3	1:4:2	$Bu_4N^+CuCl_2^-$ (*1*)[6]	66	59 (EtOAc)	69–71	70–71	(71–72[1])
$Bu_4N^+HSO_4^-$	NaCl	asc.acid	1:4:2	$Bu_4N^+CuCl_2^-$ (*1*)[6]	71	53 (EtOAc)	70–72	72–73	(71–72[1])
$Bu_4N^+HSO_4^-$	NaBr	Na_2SO_3	1:4:2	$Bu_4N^+CuBr_2^-$ (*2*)[6]	81	68 (EtOAc)	–	87–88	(88–89[1])
$Bu_4N^+HSO_4^-$	NaBr	asc.acid	1:4:2	$Bu_4N^+CuBr_2^-$ (*2*)[6]	65	60 (EtOAc)	86–88	86–88	(88–89[1])
$Bu_4N^+HSO_4^-$	NaI	Na_2SO_3	1:4:2	$(Bu_4N^+)_2Cu_2I_4^{2-}$ (*3*)[7]	77	41 (EtOAc)	87–90	91–93	(98–100[1])
$Bu_4N^+HSO_4^-$	NaI	Na_2SO_3	1:2:4	$(Bu_4N^+)_2Cu_2I_4^{2-}$ (*3*)[7]	59	30 (EtOAc)	95–98	96–98	(98–100[1])
$Bu_4N^+HSO_4^-$	NaCN	Na_2SO_3	1:4:2	$(Bu_4N^+Cu(CN)_2^-)_n$(*4*)[8]	73	27[b]	–	153–155[b]	(158–159[1])
$Ph_4P^+Cl^-$	NaCl	Na_2SO_3	1:4:2	$Ph_4P^+CuCl_2^-$ (*5*)	63	–	190–192	–	–
$Ph_4P^+Br^-$	NaBr	Na_2SO_3	1:4:2	$Ph_4P^+CuBr_2^-$ (*6*)	60	–	192–193	–	(195[9])
$Ph_4As^+Cl^-$	NaCl	Na_2SO_3	1:4:2	$Ph_4As^+CuCl_2^-$ (*7*)	56	–	170–172	–	(176–178[9])
$Ph_4As^+Cl^-$	NaCl	Na_2SO_3	1:2:4	$Ph_4As^+CuCl_2^-$ (*7*)	62	–	164–170	–	(176–178[9])

[a] $CuSO_4$, $5H_2O$ was used as the Cu(II) source. [b] The crude product was obtained as an oil from which crystals separated upon treatment with an acetone – diethyl ether mixture.

Table 2. ^{13}C–NMR spectral data of compounds *1* and *5*.

Compound	^{13}C chemical shift/ppm	$J_{^{31}P-^{13}C}$/Hz	Assignment
$Bu_4N^+CuCl_2^-$ (*1*)	13.7	–	C_4
	19.7	–	C_3
	24.0	–	C_2
	58.9	–	C_1
$Ph_4P^+CuCl_2^-$ (*5*)	117.1	88.6	C_1
	130.5	12.2	C_3
	134.1	9.8	C_2
	135.5	2.4	C_4

After drying over magnesium sulphate, the filtered solution was evaporated to dryness, yielding a crystalline product. This product was then recrystallized from ethyl acetate or acetone.

The sodium sulfite could be replaced by ascorbic acid giving essentially the same results (Table 1). In this procedure the ascorbic acid (20mmol) was dissolved in 10 ml of 0.1 M sodium carbonate solution.

Preparation of tetraphenylphosphonium and -arsonium compounds (*5*–*7*): Tetraphenylphosphonium or -arsonium halide (0.5 mmol) was dissolved in *ca.* 2 ml of dichloromethane. Copper(II) sulfate pentahydrate (125 mg, 0.5 mmol), sodium halide (1.0–2.0 mmol) and sodium sulfite (1.0–2.0 mmol) were each dissolved in minimal amounts of water. The solutions were mixed and shaken in a separatory funnel, the dichloromethane phase isolated and then combined with a 2 ml portion from a second extraction. The subsequent procedure was as described above.

The NMR-spectra were recorded with a JEOL FX-100 FT-spectrometer.

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