A Novel Copper-containing Hydride Species and its Application to the Reduction of Organic Substances

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Summary Addition of 2 equiv. of potassium tri-s-butylborohydride to copper(I) iodide produces a novel hydride species, which reduces both sp^3 and sp^2 hybridized organic halides in addition to various other organic functional groups.

ADDITION of $KBu^s{}_3BH$ (2 mol. equiv.) (**1**)[1] in tetrahydrofuran (THF) to CuI produces a novel hydride species (2:1 reagent) as a dark grey mixture. This reagent, presumably $(KCuH_2)_n$ (*vide infra*), reduces readily not only sp^3 hybridized organic halides but also sp^2 hybridized organic halides, a class of compounds that cannot be readily reduced by the parent trialkylborohydride reagents.[2] Experimental results are summarized in the Table.

It is noteworthy that the 2:1 reagent reacts even with a simple acetylene, *i.e.* dec-5-yne, to produce predominantly the corresponding *Z*-olefin ($Z:E = 88:12$). Whether or not the corresponding alkenyl copper is formed as an intermediate remains to be established. Reduction of 4-bromobenzoic acid† to benzoic acid without destruction of the aromatic system indicates advantages of the present method over reduction with metals.

Table

Substrate	Reaction condition Temp (t/°C)	Time/h	Substrate-reagent ratio	Product	Yield (%)[a]
1-Iodo-octane	0	0·1	1:1·5	Octane	100
1-Bromo-octane	0	0·25	1:1·5	"	95
1-Chloro-octane	25	36	1:1·5	"	46
Benzyl chloride	0	0·5	1:1·5	Toluene	98
1-Bromonaphthalene ..	25	1	1:1·5	Naphthalene	95
1-Bromonaphthalene ..	25	1	1:1	"	70
1-Chloronaphthalene ..	25	12	1:5	"	98
4-Bromoanisole	25	3	1:1·5	Anisole	72
4-Bromobenzoic acid ..	25	12	1:1·5	Benzoic acid	86
1-Iodohept-1-yne	0	0·25	1:1·5	Hept-1-yne	94
Dec-5-yne	0	3	1:3	*Z*-Dec-5-ene	94[b]
Cyclohexanone	0	0·5	1:1·5	Cyclohexanol	84
Methyl benzoate	25	12	1:1·5	Benzyl alcohol	35

[a] By g.l.c. [b] $Z:E = 88:12$. A minor apparently isomeric substance (<10%) appearing between *Z*- and *E*-dec-5-enes was also observable.

The thermal stability and commercial availability of (**1**) (from Aldrich, as K-selectride) makes the present procedure more convenient than related procedures[3] developed recently. Use of $\mathrm{LiEt_3BH}$[2] in place of (**1**) in the reduction of 1-bromonaphthalene resulted in a lower yield of naphthalene under comparable conditions.

In contrast to the 2:1 reagent, the reagent obtained by the reduction of CuI with 1 equiv. of (**1**) (1:1 reagent) does not reduce 1-bromonaphthalene, and neither does $\mathrm{KBu^{s}{}_3BH}$ alone. The contrasting behaviour of the 1:1 and 2:1 reagents suggests that CuI and (**1**) first produce the 1:1 reagent, which reacts further with (**1**) to form the 2:1 reagent as another distinct species, the rate of its formation being much slower than that of the 1:1 reagent. Reaction of CuI with (**1**) in a 1:1 ratio can produce either copper(I) hydride, $\mathrm{(CuH)}_n$, $\mathrm{CuBu^{s}{}_3BH}$ (**2**). Since the copper(I) hydride prepared by Whitesides[4] is reported to reduce aromatic halides, the 1:1 reagent is probably the complex (**2**). In view of the known ability of dialkylcuprate complexes to react with sp^2 hybridized organic halides presumably *via* an oxidative addition–reductive elimination sequence,[5] coupled with the inertness of trialkylborohydride reagents towards these halides,[2] the formulation $\mathrm{(KCuH_2)}_n$ appears to be reasonable for the 2:1 reagent.

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† To CuI (30 mmol) was added $\mathrm{KBu^{s}{}_3BH}$ (0·55M; 60 mmol) in tetrahydrofuran at −50° under N_2. The mixture was warmed to 0° over 2 h [240 ml (32% of the total hydride) of a gas (presumably H_2) was evolved] and 4-bromobenzoic acid (10 mmol) was added. After 3 h at room temperature, the mixture was quenched with 3N-HCl and the organic layer was examined by g.l.c. after silylation with $\mathrm{Me_3SiCl}$. Benzoic acid (trimethylsilyl ester) was obtained as the only product in 86% yield.

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