

## 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  $\text{KBu}^s_3\text{BH}$  (2 mol. equiv.) (**1**)<sup>1</sup> in tetrahydrofuran (THF) to  $\text{CuI}$  produces a novel hydride species (2; 1 reagent) as a dark grey mixture. This reagent, presumably  $(\text{KCuH}_2)_n$  (*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.<sup>2</sup> 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.

The thermal stability and commercial availability of (1)

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, (CuH)<sub>n</sub>, CuBu<sub>3</sub>BH (2). Since the copper(I) hydride prepared by Whitesides<sup>4</sup> 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*<sup>2</sup> hybridized organic halides presumably *via* an oxidative addition-reductive elimination

TABLE  
Reaction condition

Substrate	Reaction condition			Substrate-reagent ratio	Product	Yield (%) <sup>a</sup>
	Temp (t/°C)	Time/h				
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	<i>Z</i> -Dec-5-ene	94 <sup>b</sup>
Cyclohexanone .. ..	0	0.5		1:1.5	Cyclohexanol	84
Methyl benzoate .. ..	25	12		1:1.5	Benzyl alcohol	35

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

(from Aldrich, as K-selectride) makes the present procedure more convenient than related procedures<sup>3</sup> developed recently. Use of LiEt<sub>3</sub>BH<sup>2</sup> 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 KBu<sub>3</sub>BH

sequence,<sup>5</sup> coupled with the inertness of trialkylborohydride reagents towards these halides,<sup>2</sup> the formulation (KCuH<sub>2</sub>)<sub>n</sub> appears to be reasonable for the 2:1 reagent.

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† To CuI (30 mmol) was added KBu<sub>3</sub>BH (0.55M; 60 mmol) in tetrahydrofuran at -50° under N<sub>2</sub>. The mixture was warmed to 0° over 2 h [240 ml (32% of the total hydride) of a gas (presumably H<sub>2</sub>) was evolved] and 4-bromobenzoic acid (10 mmol) was added. After 3 h at room temperature, the mixture was quenched with 3*N*-HCl and the organic layer was examined by g.l.c. after silylation with Me<sub>3</sub>SiCl. Benzoic acid (trimethylsilyl ester) was obtained as the only product in 86% yield.

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