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Preliminary communication

COPPER(I) ALKYLBOROHYDRIDES FROM ALKENES USING THE CuCl/NaBH$_4$ REAGENT SYSTEM

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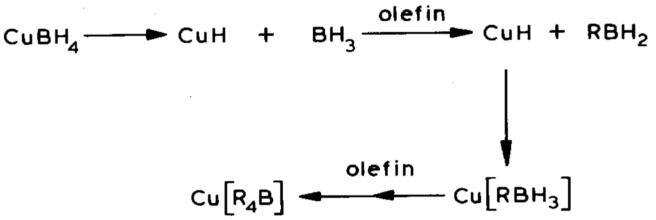
Summary

A 1/1 mixture of CuCl and NaBH$_4$ in THF reacts with alkenes to give copper(I) alkylborohydrides.

A decade ago, Suzuki and his coworkers reported that copper(I) methyltrialkylborates, Cu[CH$_3$BR$_3$], prepared by the reaction of methyllithium with trialkylboranes followed by treatment with copper(I) halides, undergo a variety of reactions characteristic of organocopper reagents [1–5]. In 1952, it was reported that CuBH$_4$, prepared from LiBH$_4$ and copper(I) halides, decomposes to give Cu, H$_2$ and B$_2$H$_6$ [6]; it was suggested that the decomposition in ether solvents takes place through "CuH" and "BH$_3$" intermediates [6,7]. It seemed to us that if this were the case then it should be possible to prepare the copper(I) alkylborates by carrying out such reactions in the presence of olefins, to initiate a hydroboration-comproportionation sequence (Scheme 1).

Such a method should be very attractive, since the synthesis of the copper(I) alkylborates would be achieved without the use of carbanionic organometallic reagents such as RLi and RMgX. We report here our preliminary observations on this new method of making copper(I) alkylborohydrides, Cu[BH$_m$R$_n$] and on some of their reactions.



SCHEME 1

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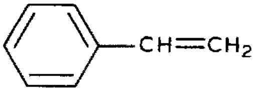
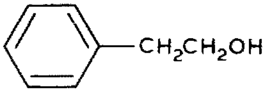
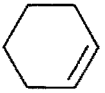
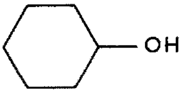
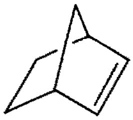
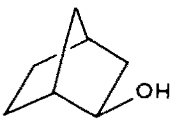
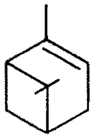
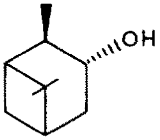
TABLE 1

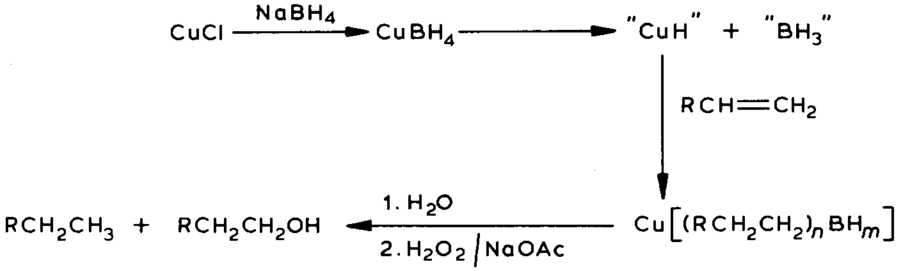
REACTION OF THE CuCl/$NaBH_4$ REAGENT WITH ALKENES [a]

Substrate	Product [b]	Yield (%) [c]
$CH_3(CH_2)_7CH{=}CH_2$	$CH_3(CH_2)_7CH_2CH_2OH$	75 [d,e]
		75 [f]
		65
		68 [d]
		60 [d]
$CH_2{=}CH(CH_2)_8COOCH_3$	$HOCH_2CH_2(CH_2)_8COOCH_3$	70 [d,g]

[a] The reactions were carried out by the addition of $NaBH_4$ (10 mmol) to a mixture of CuCl (10 mmol) and alkene (20 mmol) in THF (80 ml). The reaction temperature and time are given in the text. [b] Products isolated after hydrolysis at 0°C and oxidation with $H_2O_2/NaOOCCH_3$. [c] Yields are of the distilled products based on Scheme 2. [d] The ^{13}C NMR spectrum of the distilled product does not show signals corresponding to the isomeric/epimeric alcohols thus the amount of the isomeric alcohol (if any) could not exceed 5%. [e] Decane (10%) was also isolated; the yield in this case is based on the assumption that only one equivalent of the alkene or hydride in the borate complex would undergo hydrolysis. [f] Up to 17% of the isomeric 1-phenylethanol is present (^1H NMR). [g] Methyl undecanoate (15%) was also isolated; the products were isolated by chromatography (silica gel, hexane/$CHCl_3$).

A solution of CuCl (10 mmol) and the olefin (20 mmol) in THF (80 ml) was cooled to −10°C (bath temperature) and $NaBH_4$ (10 mmol) was added under nitrogen [8]. The temperature was raised to 25°C during 2 h and the mixture was stirred at this temperature for 24 h (12 h in the case of 1-decene). Alcohols were isolated after hydrolysis at 0°C and oxidation with $H_2O_2/NaOOCCH_3$ following the procedure described for the oxidation of organoboranes [9,10]. The reaction was found to occur with a range of representative alkenes (Table 1). In the case of the reaction with 1-decene, 10% of the decane was isolated along with the 1-decanol (75%). In the reaction with methyl-10-undecenoate (Table 1) methylundecanoate (15%) was isolated besides methyl-11-hydroxyundecanoate (70%).

The observations can be accounted for in terms of Scheme 2, which involves the formation of copper(I) alkylborohydride species via hydroboration and subsequent



SCHEME 2

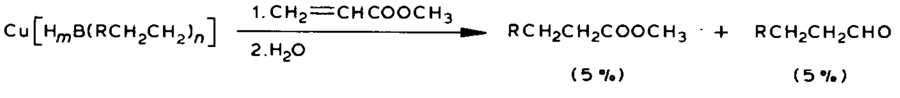
complexation of the resulting organoboron intermediates with CuH species (Scheme 2).

Although unchanged olefin remained when more than 20 mmol of olefins were used, it is not certain that the reaction gives the dialkylborate species cleanly. Moreover, the copper alkyl borohydride may be polymeric rather than the discrete species shown in Scheme 2 [12,13].

We found that the addition of water at 0 °C to the copper(I) alkylborohydride species also gives some reduction products: 10% of decane in the reaction with 1-decene and 15% of methylundecanoate in the reaction with methyl-10-undecenoate. Organoboranes are relatively stable towards water under the reaction conditions (0 °C), but tetraalkyl organoborates would undergo hydrolytic cleavage of one of the alkyl–boron bonds [14]. Thus the formation of the reduction products indicates that the CuCl/$NaBH_4$ reagent system gives copper(I) alkylborohydrides with alkenes.

In order to examine the reactions of such copper(I) alkylborohydrides, we carried out the following experiments.

The copper(I) decylborohydride was prepared by adding $NaBH_4$ (10 mmol) to a mixture of 1-decene (20 mmol) and CuCl (10 mmol) in THF (80 ml) at −10 °C (bath temperature). The reaction mixture was stirred further for 8 h at this temperature and methylacrylate (10 mmol) was added. The mixture was further stirred for 2 h at −10 °C. After hydrolysis, oxidation with H_2O_2/$NaOOCCH_3$ and work-up (ether extraction etc.), methyltridecanoate (5%) and tridecanal (5%) were isolated by chromatography on silica gel (hexane/chloroform as eluent), along with polymeric materials containing ester and decyl groups.



The yields of the conjugate addition products in the present experiment are very low compared to the yields (45–70%) obtained by use of Suzuki's reagent, $Cu(CH_3BR_3)$ [1]. It is possible that transfer of the hydride dominates over that of the alkyl group in the present case. It seemed possible that if the 'borane unit' could be separated using Bu_3P as unreactive alkylborane-PBu_3 complex then alkyl transfer reaction might be favoured, but when the conjugate addition was carried out after addition of Bu_3P (10 mmol), only a 1/1 mixture of eicosane (RR) and decane (RH) were isolated along with Bu_3P-borane complexes (B–H, strong IR absorption at 2350 cm^{-1}).

$$Cu\left[H_mBR_n\right] \xrightarrow{Bu_3P} \underset{\text{(mixture)}}{Bu_3PBH_xR_y} + \underbrace{RR + RH}_{(20\%)}$$

It has been reported that $[P(Bu)_3]_nCuR$ complexes decompose to give RR and RH species [15] and so our results can be rationalized in terms of the formation of $(Bu_3P)_nCuR$. We are continuing our study on the utilization of the $CuCl/NaBH_4$ reagent system.

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References

1 N. Miyaura, M. Itoh and A. Suzuki, Tetrahedron Lett., (1976) 255.
2 N. Miyaura, M. Itoh and A. Suzuki, Synthesis, (1976) 618.
3 N. Miyaura, N. Sasaki, M. Itoh and A. Suzuki, Tetrahedron Lett. (1977) 173.
4 N. Miyaura, N. Sasaki, M. Itoh and A. Suzuki, Tetrahedron Lett., (1977) 3369.
5 N. Miyaura, M. Itoh and A. Suzuki, Bull. Chem. Soc. Jpn., 50 (1977) 2199.
6 E. Wiberg and W. Henle, Z. Naturforschung. B, 7 (1952) 582.
7 K.B. Gilbert, S.K. Boocock and S.G. Shore, In G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 6.
8 If the temperature is immediately raised to 25°C, considerable decomposition of the hydride takes place, as indicated by evolution of hydrogen.
9 H.C. Brown, Organic Synthesis via Boranes, Wiley-Interscience, New York, 1976.
10 The oxidation using $H_2O_2/NaOH$ was rather vigorous, but it was relatively smooth with $H_2O_2/NaOAc$.
11 With other olefinic substrates the reduction products could not be isolated in sufficient quantities for identification.
12 Another complication is the further reaction of CuCl with diborane to give Cu, H_2 and BCl_3, as reported in ref. 13. We are undertaking a detailed investigation on the utilization of the hydride species produced by use of various ratios of CuCl.
13 G.W. Schaeffer, J.S. Roscoe and A.C. Stewart, J. Am. Chem. Soc., 78 (1956) 729.
14 A. Pelter and K. Smith, Organoborate Salts, in D.H.R. Barton and W.D. Ollis (Eds.), Comprehensive Organic Chemistry, Pergamon Press, Oxford, 1979, Vol. 3.
15 J. Schwartz, Tetrahedron Lett., (1972) 2803.