Reaction of Copper(I) Hydride with Organocopper(I) Compounds

Sir:

A number of important transition metal catalyzed organic syntheses are carried out in solutions containing mixtures of intermediate transition metal hydrides and \( \sigma \)-alkyls. The reactivity of transition metal hydrides toward metal alkyls has not been defined. However, the facility with which nontransition metal hydrides react with many \( \sigma \)-organometallic compounds suggests that analogous reactions of transition metal hydrides might be important in the catalytic transition metal systems.

As part of a study of the mechanism(s) of thermal decomposition of copper(I) alkyls, we have prepared copper(I) hydride and examined its reactivity toward organocopper(I) compounds. The reactivity of copper hydride toward copper alkyls is of particular interest as a model for the reactivity of other transition metal hydrides and alkyls: since copper hydride does not catalyze olefin isomerization or deuterium exchange under the conditions used in this study, the structures of hydrocarbon products formed in the presence of copper hydride can be determined without ambiguity. Here we wish to report that hydridic and \( \sigma \)-organometallic derivatives of copper(I) react readily with one another, and that the mechanism of this reaction does not involve intermediate organic free radicals.

Copper(I) hydride was prepared by treating 1 equiv of copper(I) bromide dissolved in 100 equiv of pyridine with 1.1 equiv of diisobutylaluminum hydride (20% in heptane) at \(-50^\circ\text{C}\). Vigorous mixing produced a homogeneous, dark brown solution, from which copper(I) hydride could be precipitated by dilution with \(~300\) equiv of ether. Centrifugation, separation of the supernatant liquid, and repeated washing of the precipitate with ether, all at \(-78^\circ\text{C}\), permitted isolation of copper(I) hydride as a brown solid in greater than 90% yield. The ratio of hydride to copper in this material is 0.96 \pm 0.04; it contains less than 0.5% aluminum or bromine but retains \(~25\) % pyridine, based on copper.

Pure, anhydrous copper(I) hydride decomposes to hydrogen and metallic copper above \(-20^\circ\text{C}\); it is indefinitely stable at \(-78^\circ\text{C}\). Suspensions of copper(I) hydride in ether are relatively air insensitive; the dry solid is pyrophoric. Tri- \( n \)-butylphosphine and copper(I) hydride form a 1:1 complex, the high solubility of which has prevented its isolation. Attempts to detect a metal–hydrogen stretching vibration in the solution IR spectrum of copper hydride, or a hydride resonance in its NMR spectrum, have so far been unsuccessful.

Hydrido(tri- \( n \)-butylphosphine)copper(I) reduces primary, secondary, and tertiary alkyl-, vinyl-, and arylcopper(I) compounds to the corresponding hydrocar-

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bons in high yield under very mild conditions. We have explored the intermediary of free radicals in these reductions by examining the stereochemistry of the products obtained upon reduction of endo-2-norbornyl-(tri-$n$-butylphosphine)copper(I) (2) and of cis- and trans-2-butenyl-(tri-$n$-butylphosphine)copper(I) (1) with derivatives of CuH. In each of the reactions studied the result obtained was that, within our limits of detection, the reduction of the organocopper compound occurred with complete retention of configuration at carbon. Under these conditions, HCuPBu$_3$ does not reduce norbornene or 1- or 2-butene.

Typically, 2 was prepared by reaction of endo-2-norbornylmagnesium bromide (1) with bromo(tri-$n$-butylphosphine)copper(I) in ether at $-78^\circ$ (Scheme I). The stereochemistry of 2 could be established by conversion to the corresponding methyl ate complex 3 on treatment with 3-5 equiv of methyl lithium, followed by oxidative coupling by reaction with nitrobenzene at $-78^\circ$ to yield 2-methylnorbornane (98% endo, 2% exo). Thus, reaction of 2 with DCuPBu$_3$ must take place by a non-radical pathway.

The conclusion that free organic radicals are not intermediates in the reduction of organocopper(I) compounds by HCuPBu$_3$ is supported by two related observations: first, reduction of either cis- or trans-2-butenyl(tri-$n$-butylphosphine)copper(I) in ether at $-30^\circ$ produces norbornane-2-dr with high stereoselectivity, presumably with retention of configuration in each step. Treatment of 2 ($>98\%$ endo) with a limiting amount of deuterio(tri-$n$-butylphosphine)copper(I) in ether at $-30^\circ$ yielded norbornane-2-dr ($>98\%$ endo). Reduction of a mixture of endo- and exo-2-norbornyl-(tri-$n$-butylphosphine)copper(I) (60% endo) under similar conditions produced norbornane-2-dr ($>60\%$ endo). Thus, reduction of 2 to 5 takes place with retention of stereochemistry. Since the intermediary of a free 2-norbornyl radical in this reaction would lead to products with loss of stereochemistry at the 2 position, reaction of 2 with DCuPBu$_3$ must take place by a non-radical pathway.

The epimeric compositions of the norbornane-2-dr from the reduction mixtures were determined by comparison of their ir spectra with spectra of mixtures of endo- and exo-norbornane-2-dr of known epimeric composition. The presence of norbornane-2-dr among the reaction products made it impossible to use the fingerprint region for these analyses, and the relative insensitivity of the C-D stretching region to changes in the ratio of endo- to exo-norbornane-2-dr limited the accuracy of ir analysis to $\pm 5\%$ in samples containing $>90$ mole % endo epimer.

The epimeric compositions of the norbornane-2-dr reduce the product mixture of 1 to 2, and of 3 and 4 to 6, take place with high stereoselectivity, presumably with retention of configuration in each step.
of configuration;\(^{17}\) and second, reduction of neophyl-
(tri-\(n\)-butylphosphine)copper(I) under similar condi-
tions leads to \(t\)-butylbenzene, with no observable rear-
rangement to isobutylbenzene.

The detailed nature of the C–H bond forming step in
these reductions has not been established, although it
could plausibly proceed by intramolecular reaction of
hydrido and alkyl ligands coordinated to a common
cluster of copper(I) atoms.\(^{17,18}\) Studies of the mecha-
nism of this and related reactions, and of the role of
copper hydride in the thermal decomposition of alkyl-
copper(I) reagents, will be discussed in later papers.

\(^{17}\) For a discussion of the stereochemical consequences expected
from a free 2-butenyl radical in the related thermal decomposition of
these compounds, see G. M. Whitesides and C. P. Casey, \textit{J. Amer.

\(^{18}\) A. Cairncross and W. A. Sheppard, Abstracts, 157th National
Meeting of the American Chemical Society, Minneapolis, Minn.,
April 1969, ORGN 118.

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