Reaction of Copper(I) Hydride with Organocopper(I) Compounds[1]

Sir:

A number of important transition metal catalyzed organic syntheses are carried out in solutions containing mixtures of intermediate transition metal hydrides and σ-alkyls.[2] The reactivity of transition metal hydrides toward metal alkyls has not been defined. However, the facility with which nontransition metal hyrides react with many σ-organometallic compounds[3,4] 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 σ-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°. Vigorous mixing produced a homogenous, dark brown solution, from which copper(I) hydride could be precipitated by dilution with ~300 equiv of ether. Centrifugation, separation of the super-

natant liquid, and repeated washing of the precipitate with ether, all at −78°, permitted isolation of copper(I) hydride as a brown solid in greater than 90% yield.[5] The ratio of hydride to copper in this material is 0.96 ± 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°; it is indefinitely stable at −78°. 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 unsuccesful.[3]

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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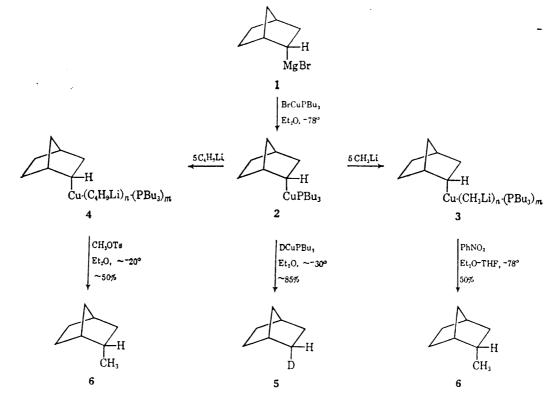
(2) For reviews of representative reactions, see R. Heck, *Advan. Organometal. Chem.*, **4**, 243 (1966); L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience Publishers, New York, N. Y., 1966, Chapter IV; R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

(3) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, New York, N. Y., 1956, Chapter 4; T. G. Traylor, *Chem. Ind.* (London), 1223 (1959).

(4) D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, **91**, 719 (1969); L. I. Zakharkin and I. M. Khorlina, *Zh. Obshch. Khim.*, **32**, 2783 (1962).

(5) This procedure is based on that developed by Wiberg and Henle,[6] but yields CuH of higher purity than that obtained using LiAlH₄ as a reducing agent.[7] The results of our examination of the material produced by the Wiberg–Henle procedure are in general agreement with those reported by Shriver;[7] in particular, we concur that this material *is* CuH, howbeit extensively contaminated.

(6) E. Wiberg and W. Henle, *Z. Naturforsch.*, **7b**, 250 (1952).

(7) J. A. Dilts and D. F. Shriver, *J. Amer. Chem. Soc.*, **90**, 5769 (1968); **91**, 4088 (1969).

(8) See also ref 7.

Scheme I

bons in high yield under very mild conditions.[9] We have explored the intermediacy 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) 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, HCuPBu₃ does not reduce norbornene or 1- or 2-butene.

Typically, 2 was prepared by reaction of *endo*-2-norbornylmagnesium bromide (1)[10] with bromo(tri-*n*-butylphosphine)copper(I) in ether at −78° (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 methyllithium, followed by oxidative coupling by reaction with nitrobenzene at −78° to yield 2-methylnorbornane (98% *endo*, 2% *exo*).[11] The same stereochemical result was obtained on nucleophilic coupling of methyl tosylate with the ate complex 4 formed on addition of 3–5 equiv of *n*-butyllithium to 1 equiv of 2.[12] Control reactions carried out using equilibrium mixtures (55–60% *endo*)[10] of epimeric 2-norbornyl Grignard reagents yielded mixtures of 2-methylnorbornanes containing ~60% of the *endo* isomer. Taken together, these results establish

that conversions of 1 to 2, and of 3 and 4 to 6, take place 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)[13] in ether at −30° yielded norbornane-2-*d₁* (98 ± 5% *endo*).[14] Reduction of a mixture of *endo*- and *exo*-2-norbornyl-(tri-*n*-butylphosphine)copper(I) (60% *endo*) under similar conditions produced norbornane-2-*d₁* (~60% *endo*). Thus, reduction of 2 to 5 takes place with *retention* of stereochemistry. Since the intermediacy 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 DCuPBu₃ must take place by a nonradical pathway.[16]

The conclusion that free organic radicals are not intermediates in the reduction of organocopper(I) compounds by HCuPBu₃ is supported by two related observations: first, reduction of either *cis*- or *trans*-2-butenyl(tri-*n*-butylphosphine)copper(I) in ether at −30° yields the corresponding 2-butene with >97% retention

(9) Copper(I) hydride and its derivatives also act as reducing agents toward a number of other organic and organometallic substrates. For example, hydrido(tri-*n*-butylphosphine)copper(I) reduces iodobenzene to benzene (80%), and benzoyl chloride to benzaldehyde (50%) in 2 hr at 25° in ether, and diphenylmercury(II) to benzene quantitatively at −50°.

(10) F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966).

(11) G. M. Whitesides, J. San Fillippo, Jr., C. P. Casey, and E. J. Panek, *ibid.*, **89**, 5302 (1967).

(12) E. J. Corey and G. H. Posner, *ibid.*, **90**, 5615 (1968); G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *ibid.*, **91**, 4871 (1969), and references therein.

(13) Copper(I) deuteride was prepared using diisobutylaluminum deuteride synthesized by a procedure described for the preparation of diethylaluminum deuteride: G. Wilke and H. Muller, *Ann.*, **629**, 222 (1960). Isotopic purity of the CuD was established by analysis of the mixture of H₂ (3.5%), HD (95.1%), and D₂ (1.3%) obtained on protonolysis at −30° with methanolic HCl.

(14) The epimeric compositions of the norbornane-2-*d₁* from the reaction mixtures were determined by comparison of their ir spectra with spectra of mixtures of *endo*- and *exo*-norbornane-2-*d₁* of known epimeric composition. The presence of norbornane-*d₀* among the reaction products made it impossible to use the fingerprint region[15] for these analyses, and the relative insensitivity of the C–D stretching region to changes in the ratio of *endo*- to *exo*-norbornane-2-*d₁* limited the accuracy of ir analysis to ~±5% in samples containing >90 mole % *endo* epimer.

(15) A. Nickon and J. H. Hammons, *J. Amer. Chem. Soc.*, **86**, 3322 (1964).

(16) The results of Scheme I also exclude free norbornyl radicals as intermediates in the oxidative or nucleophilic coupling reactions of the copper(I) ate complexes 3 and 4. By contrast with the conversion of 2 to 5, reduction of either *exo*- or *endo*-2-chloronorbornane with tri-*n*-butyltin deuteride under radical conditions (AIBN, *hν*, 20°) yields mixtures of the epimers of norbornane-2-*d₁* containing 84 ± 5% *exo* isomer.

of configuration;[17] and second, reduction of neophyl-(tri-*n*-butylphosphine)copper(I) under similar conditions leads to *t*-butylbenzene, with no observable rearrangement 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 mechanism of this and related reactions, and of the role of copper hydride in the thermal decomposition of alkylcopper(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, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

(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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