nmr spectrum of **11** one of the aryl methyl groups (δ 2.84 d, J = 1.0 Hz) is slightly split by an adjacent aromatic proton (δ 7.45 octet, J = 8.0, 1.0 Hz), while the second aryl methyl (δ 2.73 s), found at nearly identical field but with no adjacent hydrogens, is unsplit. Of the two theoretically possible combinations of units **a** and **b**, that represented in **1** is chosen over the alternative, 1-carbomethoxy-8-formyl-4,5,7-trihydroxyphenazine, on biosynthetic grounds, since we presume lomofungin to arise from oxidative coupling of 2 mol of 4-hydroxyanthranilic acid. In this connection it is significant that a similar substitution pattern is found in the antibiotic griseolutein A.[7]

Synthetic experiments in the lomofungin series will be described in a subsequent report.[8]

Acknowledgment. This work was supported in part by a research grant (No. AI 01278) from the National Institute of Allergy and Infectious Diseases.

(7) S. Nakamura, *J. Antibiot.* (*Tokyo*), **A12**, 55 (1957).

(8) NOTE ADDED IN PROOF. Compound **11** has now been prepared by an unequivocal route.

Craig D. Tipton, Kenneth L. Rinehart, Jr.
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Received October 23, 1969

Mechanism of Thermal Decomposition of *n*-Butyl(tri-*n*-butylphosphine)copper(I)[1]

Sir:

Alkyllithium,[2] -magnesium,[2] and -aluminum[3] reagents react rapidly with transition metal salts, yielding mixtures of hydrocarbons believed to be derived from the thermal decomposition of intermediate transition metal σ-alkyls. Detailed mechanisms for the thermal decomposition of alkyl transition metal compounds have not been established. However, product mixtures from many of the reactions of main group σ-alkyls with transition metal salts contain approximately equal quantities of alkane and alkene. This observation has led to the suggestion that free alkyl radicals, derived from homolytic scission of carbon–metal σ bonds, are involved as reactive intermediates, and that alkane and alkene are derived from disproportionation of these alkyl radicals.[2] Our interest in these reactions and in the general area of mechanisms of thermal decomposition of transition metal organometallic compounds has prompted us to examine in detail the thermal decomposition of authentic *n*-butyl(tri-*n*-butylphosphine)copper(I) (**1**). Here we wish to summarize evidence indicating that the dominant pathway for thermal decomposition of this alkylcopper(I) compound to *n*-butane and 1-butene does *not* involve free *n*-butyl radicals, but rather occurs by a two-step process consisting of initial formation of 1-butene by β elimination of copper(I) hydride from **1**, followed by reduction of a second equivalent of **1** to *n*-butane by this copper(I) hydride.

$$\underset{\mathbf{1}}{\mathrm{CH_3CH_2CH_2CH_2CuP}(n\text{-}\mathrm{Bu})_3} \longrightarrow \mathrm{CH_3CH_2CH{=}CH_2} + \mathrm{HCuP}(n\text{-}\mathrm{Bu})_3 \quad (1)$$

$$\mathrm{CH_3CH_2CH_2CH_2CuP}(n\text{-}\mathrm{Bu})_3 + \mathrm{HCuP}(n\text{-}\mathrm{Bu})_3 \longrightarrow \mathrm{CH_3CH_2CH_2CH_3} + 2\mathrm{Cu}^0 + 2\mathrm{P}(n\text{-}\mathrm{Bu})_3 \quad (2)$$

Typically, **1** was prepared by reaction of 0.25 mmol of $[\mathrm{ICuP}(n\text{-}\mathrm{Bu})_3]_4$ with 1.0 mmol of *n*-butyllithium (15% in hexane) in 10 ml of ether at −78° followed by separation of lithium iodide from the resulting light yellow solution by precipitation with 1.1 mmol of dioxane.[4,5] Compound **1** has not been isolated;[4] however, analysis of its solutions indicates an empirical composition $(\mathrm{C_4H_9})_{0.97\pm0.02}\mathrm{Cu}_{1.00}\mathrm{P}(n\text{-}\mathrm{Bu}_3)_{1.02\pm0.03}$, with 1.7 ± 0.1% Li and <0.5% I based on copper remaining in solution. Thermal decomposition of **1** is complete in 4 hr at 0° in ether solution, yielding copper metal, tri-*n*-butylphosphine, 1-butene (51%) *n*-butane (49%), and hydrogen (10%); less than 0.1% *n*-octane is formed. Hydrolysis of the solution remaining at the conclusion of the thermal decomposition yields an additional 8% hydrogen. Control experiments have demonstrated that the hydrocarbon products are not derived from the tri-*n*-butylphosphine ligands: the thermal decomposition of *n*-butyl(tri-*n*-octylphosphine)copper(I) yields no octane, and that of *n*-butyl-2,2-d_2-(tri-*n*-butylphosphine)copper(I) (**2**) yields no butane-d_1, butane-d_0, or butene-d_0.

The absence of octane among the products of decomposition of **1** is sufficient to establish that butane and 1-butene are not formed by disproportionation of *n*-butyl radicals, since the ratio of rate constants for the disproportionation and combination of these radicals falls in the range 0.1–0.2.[6] In addition, the ratio of the yields of *n*-butane and 1-butene formed on thermal decomposition of **1** is invariant to the hydrogen-donor ability of the solvent: almost identical ratios are observed in ether, *n*-hexane, and 9:1 v/v *n*-hexane–cumene solutions. Moreover, thermal decomposition of the related copper(I) reagent hex-5-enyl(tri-*n*-butylphosphine)copper(I) in ether yields 44% 1-hexene, 52% 1,5-hexadiene, and only 3.5% cyclized hydrocarbons.[7] Taken together, these data effectively preclude the important involvement of *n*-alkyl radicals derived from homolytic scission of the carbon–copper(I) σ bonds of **1** during its thermal decomposition.

Both the detection of hydrogen among the products of thermal decomposition of **1** and the formation of additional hydrogen on acidification of the solution remaining after complete decomposition implicate a copper hydride[8] as an intermediate in the reaction. The formation of significant quantities of "CuH" during decomposition of **1** was confirmed using isotopic dilution techniques. Partial decomposition (10 min, 0°,

---

(1) Supported by the National Science Foundation, Grants 7266 and 14247, and by the International Copper Research Association, Inc.

(2) H. Gilman, R. G. Jones, and L. A. Wood, *J. Amer. Chem. Soc.*, **76**, 3615 (1954); M. H. Abraham and M. J. Hogarth, *J. Organometal. Chem.*, **12**, 1 (1968); W. B. Smith, *J. Org. Chem.*, **26**, 4206 (1961); F. W. Frey, Jr., *ibid.*, **26**, 5187 (1961); M. S. Kharasch, *et al.*, *ibid.*, **21**, 322 (1956).

(3) M. I. Prince and K. Weiss, *J. Organometal. Chem.*, **2**, 166 (1964).

(4) For experimental procedures, see G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J Amer. Chem. Soc.*, **91**, 4871 (1969), and references therein.

(5) Although the degree of association of **1** is not known, it is assumed to be aggregated; see L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *ibid.*, **90**, 7357 (1968), for references to relevant structures. The reactions represented by eq 1 and 2 probably take place within the confines of common copper atom clusters.

(6) N. E. Morganrath and J. G. Calvert, *ibid.*, **88**, 5387 (1966); A. P. Stefani, *ibid.*, **90**, 1694 (1968), and references in each.

(7) Cyclization of the 5-hexenyl radical is more rapid than hydrogen atom abstraction from ether solvents: *cf.* C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 5361 (1966); J. F. Garst and F. E. Barton, *Tetrahedron Lett.*, 587 (1969).

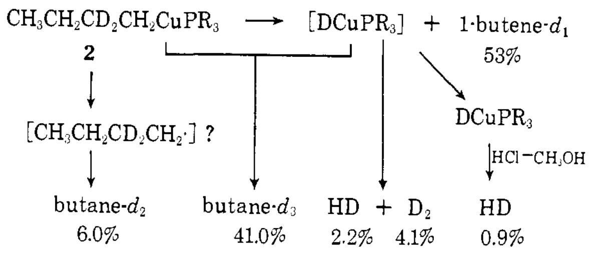
(8) (a) G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969); (b) J. A. Dilts and D. F. Shriver, *ibid.*, **90**, 5769 (1968); **91**, 4088 (1969).

ether) of **2** in the presence of 1 equiv of $HCuP(n\text{-}Bu)_3$,[8] followed by quenching of the reaction mixture with methanolic HCl, yielded, in addition to H_2, 29.7% of HD, the product expected from protonolysis of $DCuP(n\text{-}Bu)_3$.[8] The ability of copper(I) hydride to reduce **1** to butane under the conditions used for the thermal decomposition reactions was established by the isolation of butane-d_1 (24%) together with butane-d_0 (34%) and 1-butene-d_0 (42%) from thermolysis of **1** in the presence of 1.4 equiv of $DCuP(n\text{-}Bu)_3$.[9] Thus, copper(I) hydride *is* formed in the thermal decomposition of **1**; moreover, copper hydride *does* reduce **1**, in a reaction whose rate appears to be competitive with the rate of its formation from **1**. These data are those expected on the basis of the mechanism represented by eq 1 and 2. The absence of HD among the products from thermolysis of **1** in the presence of added D_2 effectively excludes a possible alternative to eq 2 involving thermolysis of the CuH intermediate to yield H_2 and subsequent hydrogenolysis of **1** to form *n*-butane and to regenerate CuH.

To establish the site of elimination of hydrogen from **1**, the alkene products of thermal decomposition of *n*-butyl-1,1-d_2-(tri-*n*-butylphosphine)copper(I) (**3**) and **2** were compared. Decomposition of **3** yields 1-butene-d_2 uncontaminated by -d_1 or -d_0 species, while decomposition of **2** yields 1-butene-d_1. These observations are consistent only with β-hydride elimination occurring without prior scrambling of the deuterium label between α and β positions.

The complete products of decomposition of **2**, together with a schematic rationalization of the paths by which they are formed, are outlined in Scheme I. It is not presently clear whether the small amounts of butane-d_2 and HD formed in this reaction are the result of radical side reactions involving **2** and $DCuP(n\text{-}Bu)_3$, respectively, or whether they reflect an unidentified reaction generating copper *hydride*.[10,11] Regardless, this product distribution is clearly consistent with the proposed mechanism.

Scheme I



A mechanism for thermal decomposition of **1** involving copper hydride elimination has good precedent in related studies of rhodium,[12] platinum,[13] and lithium[14] alkyls. However, this study provides the first easily interpretable example in which subsequent reaction of a metal hydride and its parent metal alkyl is important in determining the products of a thermal decomposition. Similar mechanisms may be involved in the variety of thermal reactions of other transition metal alkyls which yield approximately equal quantities of alkene and alkane.

---

[9] Previously reported studies have established that reaction of copper(I) hydride and copper(I) alkyls takes place by a nonradical mechanism.[8a]

[10] Oxidative addition of a carbon–hydrogen bond of solvent or of tri-*n*-butylphosphine to d^{10} copper(0) might provide a method of introducing hydrogen into Scheme I. For relevant oxidative additions to d^8 metals, see F. Piacenti, *et al.*, *J. Amer. Chem. Soc.*, 90, 6847 (1968); S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968); G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, **91**, 4990 (1969).

[11] Adventitious hydrolysis of **2** is not responsible for the formation of *n*-butane-d_2: thermal decomposition of **2** (1.00 mmol) prepared from a solution of $[ICuPBu_3]_4$ (0.27 mmol) which was previously treated with methyllithium (0.08 mmol) to remove impurities capable of protonolyzing organocopper reagents produced *n*-butane-d_3 (41%), *n*-butane-d_2 (8%), and 1-butene-d_1 (51%).

[12] R. Cramer, *Accounts Chem. Res.*, 1, 186 (1968).

[13] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc., A*, 190 (1968), and references therein.

[14] R. A. Finnegan and H. W. Kutta, *J. Org. Chem.*, 30, 4138 (1965).

[15] (a) National Institutes of Health Predoctoral Fellow, 1967–1970; (b) National Science Foundation Predoctoral Fellow, 1963–1967; (c) National Institutes of Health Predoctoral Fellow, 1966–1969.

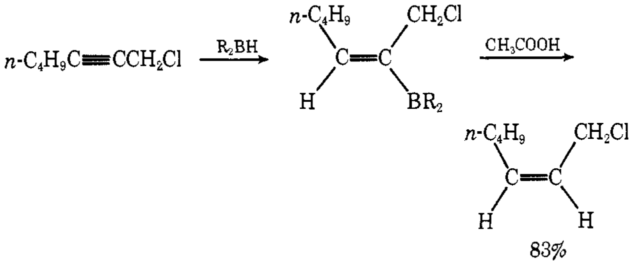
George M. Whitesides, Erwin R. Stedronsky[15a]
Charles P. Casey,[15b] **Joseph San Filippo, Jr.**[15c]
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received December 8, 1969

The Hydroboration of Substituted Propargyl Chlorides. A Convenient Synthesis of Terminal Allenes[1]

Sir:

In the course of exploring the chemistry of organoboranes derived from functionally substituted alkynes we have investigated the unsaturated chloroorganoboranes derived from the reactions of dialkylboranes with 1-chloro-2-alkynes. We now wish to report that these organoboranes afford, after treatment with aqueous sodium hydroxide, good yields of the corresponding allenes which are free from by-products.

A study of the stoichiometry of hydroboration of 1-chloro-2-heptyne with disiamylborane in tetrahydrofuran solvent at 0° revealed that the reaction proceeds readily to the monohydroboration stage. The intermediate organoborane is stable in tetrahydrofuran solution, as evidenced by its conversion to isomerically pure *cis*-1-chloro-2-heptene on protonolysis with glacial acetic acid.[2]



In order to determine the position of the boron in the monohydroboration product, 1-chloro-2-heptyne was allowed to react with 1 equiv of the disiamylborane (R_2BD) derived from 2-methyl-2-butene and deuterioborane. The resultant organoborane was protonolyzed with acetic acid, and the *cis*-1-chloro-2-heptene obtained was treated with ozone in cyclohexane. The ozonide was diluted with ether and then reduced with lithium aluminum hydride.[3] Nmr examination of the 1-pen-

---

[1] This research was supported by the National Science Foundation through Grant No. GP-9398.

[2] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 3834 (1961).

[3] J. A. Sousa and A. Bluhm, *J. Org. Chem.*, **25**, 108 (1960).