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

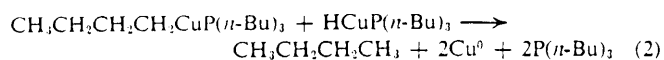
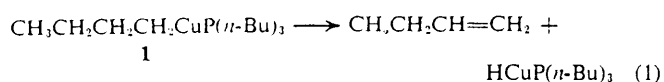


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Mechanism of Thermal Decomposition of *n*-Butyl(tri-*n*-butylphosphine)copper(I)¹

Sir:

Alkyl lithium,² -magnesium,³ and -aluminum³ 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.



Typically, **1** was prepared by reaction of 0.25 mmol of $[\text{ICuP}(\textit{n}\text{-Bu})_3]_2$ 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 $(\text{C}_4\text{H}_9)_{0.97 \pm 0.02}\text{Cu}_{1.00}\text{P}(\textit{n}\text{-Bu})_{3.10 \pm 0.05}$, with $1.7 \pm 0.1\%$ Li and $<0.5\%$ I based on copper remaining in solution.

(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).

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*₆, or butene-*d*₆.

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 hydride⁸ 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° ,

(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. Ponnaras, 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).

