

[Reprinted from the Journal of the American Chemical Society, **88**, 4541 (1966).]
Copyright 1966 by the American Chemical Society and reprinted by permission of the copyright owner.

**The Stereochemistry of the Thermal Decomposition
of Vinylic Copper(I) and Silver(I)
Organometallic Compounds¹**

Sir:

The thermal decomposition of organometallic compounds of copper(I) and silver(I) is important in the oxidative coupling of aryl Grignard reagents by copper(I) and silver(I) halides,² and is probably involved in the Ullman and related reactions.^{3,4} These thermal decomposition reactions have been variously suggested to proceed by a bimolecular or concerted mechanism, in which dimer formation occurs within an aggregate of the organometallic compound,^{3a,4} or by a radical mechanism, in which dimers arise from free radicals generated by homolytic cleavage of the carbon-metal bonds.^{2,5}

We have explored the question of the intermediacy of free radicals in the thermal decomposition of vinylic copper(I) and silver(I) organometallic compounds by

(1) Supported in part by the National Science Foundation under Grant GP-2018.

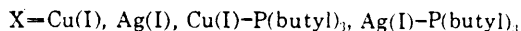
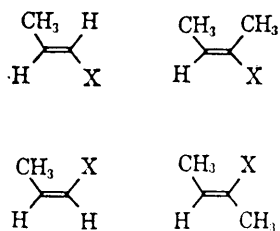
(2) H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891 (1966), and references therein.

(3) (a) A. H. Lewin and T. Cohen, *Tetrahedron Letters*, 4531 (1965); (b) H. C. Brown and C. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1002 (1961).

(4) E. A. Bickley and J. H. Gardner, *J. Org. Chem.*, **5**, 126 (1940).

(5) F. Glockling and D. Kingston, *J. Chem. Soc.*, 3001 (1959); C. E. H. Bawn and F. J. Whitby, *ibid.*, 3923 (1960).

examining the stereochemistry of the diene products obtained on decomposition of 1-propenyl- and 2-butenylcopper(I) and -silver(I) compounds of known stereochemistry.⁶ In each of the decompositions



studied, the result obtained was that, within our limits of detection, the decomposition of the organometallic compound to the corresponding diene took place with complete *retention* of configuration around the carbon-carbon double bond.

In a typical experiment, *cis*-1-propenyl(tri-*n*-butylphosphine)silver(I) (I) was prepared at -78° in ether solution by treating 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)silver(I)]¹⁰ with 1 equiv of 1-propenyl-lithium¹¹ (97% *cis*, as determined by vpc analysis of the propenyl bromides obtained after reaction with 1,2-dibromoethane). After precipitation of lithium halides from the cold reaction mixture with dioxane, addition of iodine to the solution of the organosilver reagent at -28° gave 1-iodopropene having 96% *cis* stereochemistry in 84% yield,¹² indicating that formation of the carbon-silver bond occurred with retention of stereochemistry. Thermal decomposition of either the halogen-free or halogen-containing solutions of I at ambient temperature over 4 hr gave silver(0) (95%), *cis,cis*-2,4-hexadiene (95%), and *cis,trans*-2,4-hexadiene (4.8%), corresponding to 97% *cis*-propenyl groups and 100% stereospecificity in the decomposition, based on 1-propenyllithium.¹³

By an analogous procedure, *trans*-1-propenyllithium (97% *trans*) could be converted quantitatively to a mixture of *trans,trans*- and *cis,trans*-2,4-hexadienes containing 97% *trans*-propenyl groups. Although these organometallic reagents have not yet been characterized as solids, analysis of the products from the thermal decomposition of the halogen-free solutions has established their empirical composition as $[\text{C}_3\text{H}_6]_{1.0}[\text{Ag}]_{0.95 \pm 0.1}[\text{P}(\text{C}_4\text{H}_9)_3]_{1.1 \pm 0.1}$, with less than 0.5% lithium ion remaining in solution.

Tri-*n*-butylphosphine complexes of *cis*- and *trans*-2-butenylsilver(I) and -copper(I) were prepared and characterized using similar procedures. Solutions of

(6) No direct experimental evidence on the extent of aggregation of these compounds is presently available. However, the related compounds phenylethynyl(trimethylphosphine)copper(I),⁷ phenylethynyl(trimethylphosphine)silver(I),⁸ and tetrakis[iodo(tri-*n*-butylphosphine)copper(I)]⁹ are aggregated both in solution and as crystalline solids.

(7) P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, **16**, A-71 (1963).

(8) P. W. R. Corfield and H. M. M. Shearer, *ibid.*, **20**, 502 (1966).

(9) A. F. Wells, *Z. Krist.*, **94**, 447 (1936); F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).

(10) F. G. Mann, A. F. Wells, and D. Purdie, *ibid.*, 1828 (1937).

(11) D. Seyferth and L. G. Vaughan, *J. Am. Chem. Soc.*, **86**, 883 (1964).

(12) We are indebted to Dr. R. C. Neuman, Jr., for an authentic sample of 1-iodopropene: R. C. Neuman, Jr., *J. Org. Chem.*, **31**, 1852 (1966).

(13) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

copper(I) and silver(I) compounds which contained no tri-*n*-butylphosphine could be prepared in ether at -28° by heterogeneous reaction between the corresponding vinylic lithium reagents and copper(I) or silver(I) iodide. Decomposition of these reagents was complete after 1 hr at ambient temperature. In each case, dimeric products were produced in 70–90% yields, with greater than 99% retention of configuration.

These stereochemical results strongly suggest that free propenyl radicals are not intermediates in these reactions. Making the reasonable assumption that the rate of inversion of configuration of 1-propenyl radical is approximately the same as that established by epr spectroscopy for vinyl radical ($k_{\text{inversion}} = 10^8\text{--}10^{10} \text{ sec}^{-1}$),¹⁴ the rate of conversion of an intermediate propenyl radical into dimer must be at least 10^2 faster than the rate of its inversion of configuration in order to be consistent with the observed stereochemical results. Under the reaction conditions used, the undecomposed organometallic compound is the most concentrated solution component potentially capable of reaction with propenyl radicals to form dimers. Therefore

$$k_{\text{coupling}}[\text{R}\cdot][\text{RM}] \geq 10^2 k_{\text{inversion}}[\text{R}\cdot]$$

In these reactions, $[\text{RM}] \leq 0.1 \text{ M}$; hence, k_{coupling} must be greater than $10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ to compete with inversion. The possibility that a reaction is taking place in solution whose rate constant is of this magnitude can clearly be excluded by consideration of the maximum rates attained by other fast reactions.¹⁵

These results do not rigorously exclude the occurrence of solvent-caged radicals as intermediates; however, we feel that a cage mechanism is improbable because the yield of dimeric products observed in the decomposition of I would require that the efficiency of cage combination approach 100%. An alternative path for the decomposition, in which vinylic radicals are formed but remain π bonded to the metal atoms of an aggregate, cannot be excluded.

Although the rate of inversion of 2-butenyl radical is probably slower than that of vinyl radical,¹⁴ recent studies have indicated that this inversion is also rapid on the time scale of most reactions.¹⁶ The retention of stereochemistry observed in decomposition of the 2-butenyl organometallic compounds lends qualitative support to the proposal that long-lived free radicals are not intermediates in the decomposition of vinylic copper(I) and silver(I) compounds. However, in the absence of a reliable quantitative value for the rate of inversion of configuration of 2-butenyl radical, it is not possible to define a lower limit for the lifetime of any radical intermediates in the decomposition of these compounds.

These proposals cannot be extended without modification to include the thermal decomposition of *ali-*

(14) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(15) For example, the absolute rate constant for combination of methyl radicals is approximately $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$: A. F. Trotman-Dickenson, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **55**, 36 (1958).

(16) J. A. Kampmeier and R. M. Fantazier, *J. Am. Chem. Soc.*, **88**, 1959 (1966); L. A. Singer and N. P. Kong, *Tetrahedron Letters*, 2089 (1966). In related experiments, we have observed that tri-*n*-butyllithium hydride reduction¹⁷ at ambient temperatures of either *cis*- or *trans*-2-bromo-2-butene yields the same mixture of 65% *trans*- and 35% *cis*-2-butene.

(17) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964).

phatic copper(I) compounds, since these reactions give fundamentally different types of products. For example, thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I) at room temperature in ether gives butane (50%) and 1-butene (50%), but no detectable octane. Details of these reactions will be discussed in later papers.

George M. Whitesides, Charles P. Casey

*Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139*

Received July 14, 1966