# Organic and Biological Chemistry

## The Thermal Decomposition of Vinylic Copper(I) and Silver(I) Organometallic Compounds[1]

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**Abstract:** The thermal decomposition of *cis-* and *trans-*1-propenylcopper(I) and *cis-* and *trans-*1-propenyl(tri-*n*-butylphosphine)copper(I) yields copper(0) and 2,4-hexadienes with retention of configuration at the olefinic double bonds. This stereochemical result, when interpreted in light of the known rate of inversion of configuration of vinyl radical, is sufficient to establish that free propenyl radicals are not intermediates in these thermal coupling reactions. A comparison of the retention of stereochemistry observed on decomposition of the analogous 2-butenylcopper(I) and -silver(I) compounds with the complete loss of stereochemistry observed on reduction of *cis-* and *trans-*2-bromo-2-butene with tri-*n*-butyltin hydride under free-radical conditions qualitatively supports a similar conclusion. A survey of the yield and stereochemistry of the conversion of *trans-*propenyllithium to 2,4-hexadienes on oxidation with a variety of transition metal salts suggests that free propenyl radicals also are not involved in these couplings.

The reaction of arylmagnesium and -lithium reagents with transition metal halides is widely used synthetically as a method for preparing biaryls.[3–5] These reactions are believed in most instances to involve transition metal aryls as intermediates; the isolated products result from the rapid decomposition of these thermally unstable intermediates under the conditions of the reactions. Although identification of the intermediate organometallic compounds in these reactions and independent demonstration that their thermal decomposition yields coupled product have proved possible in special cases,[5,6] in general the thermal stability of transition metal organometallic compounds has appeared sufficiently low to discourage attempts to examine the mechanisms of this interesting class of coupling reactions in detail.

A number of studies have established copper(I) and silver(I) as among the most useful of the transition metals for the oxidative coupling of aryl and vinylic Grignard reagents.[3,7–11] During these studies several groups have prepared and characterized authentic aromatic and vinylic organometallic compounds of these metals.[8–13] The thermal stability of this class of compounds, although low compared with the stabilities of main group organometallic compounds, appeared to us to be sufficient to make a detailed investigation of their thermal decomposition a practical enterprise. Therefore, in consequence of our interest in the mechanisms and synthetic applications of the Ullman and related coupling reactions,[14–16] as well as in the variety of other organic reactions catalyzed by compounds of copper,[15,17] we have examined the mechanism of thermal decomposition of vinylic copper(I) and silver(I) organometallic compounds to butadienes.

A question of fundamental interest in discussion of these reactions concerns the mechanism of the step in which the carbon–metal bond is broken and the new carbon–carbon bond is formed. This step has been variously suggested to take place by a mechanism in which dimers arise from free radicals generated by homolytic cleavage of the carbon–metal bonds,[9,18] and by a bimolecular or concerted mechanism in which dimer formation occurs within an aggregate of the organometallic compound without the intervention of free radicals.[3,8] In brief, our approach to the question of the intermediacy of free radicals in the dimerization has involved an investigation of the stereochemistry of conversion of 1-propenyl- and 2-butenylcopper(I) and

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(2) National Science Foundation Predoctoral Fellow, 1963–1967.

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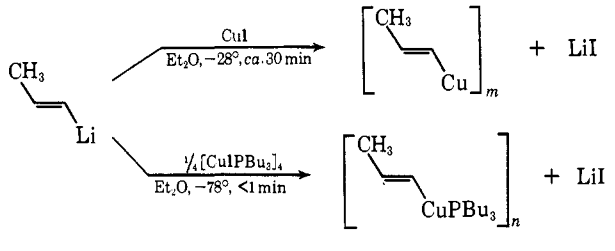
-silver(I) compounds into the corresponding 2,4-hexadienes. Since vinylic radicals have very low configurational stability,[19,20] the observation of extensive isomerization at the double bond in the conversion of, *e.g.*, *trans*-1-propenylcopper(I) into one or more stereoisomeric 2,4-hexadienes would suggest free propenyl radicals as intermediates; conversely, retention of stereochemistry around the double bond would implicate a nonradical mechanism.

In this paper we report the synthesis and characterization of a number of 1-propenyl- and 2-butenylcopper(I) and -silver(I) compounds, and experimental results indicating that their thermal conversion into dienes occurs with complete retention of stereochemistry around the vinylic double bond.[21]

## Results

**Preparation and Characterization.** The vinylic copper(I) and silver(I) organometallic compounds examined in this study were prepared by reaction between the corresponding organolithium reagents and an appropriate copper(I) or silver(I) salt in ether solution at low temperatures. The required isomeric 1-propenyl- and 2-butenyllithium reagents had been prepared previously, and had been demonstrated to be configurationally stable once formed;[22,23] however, the conversion of 1-bromopropene to propenyllithium on reaction with lithium had been reported to be accompanied by a slight loss in stereochemistry.[23] In this work, the isomeric composition of samples of *cis*- and *trans*-1-propenyllithium and 2-butenyllithium was assayed by conversion of these substances to the corresponding vinylic bromides on treatment with 1,2-dibromoethane, followed by glpc analysis of these bromides. Metal–halogen exchange between dibromoethane and alkyllithium reagents apparently takes place, at least in part, by a free-radical mechanism.[24] However, it was possible to establish that conversion of *cis*-propenyllithium to 1-bromopropene occurs essentially stereospecifically with retention of configuration; presumably the conversions of other vinylic organolithium reagents to analogous vinylic bromides follows the same stereochemical course. Thus, careful reaction of 1-bromopropene with lithium, followed by several recrystallizations of the resulting organolithium reagent, afforded a sample of 1-propenyllithium which, on reaction with 1,2-dibromoethane, yielded 1-bromopropene consisting of 99.6 ± 0.2% cis isomer and 0.4 ± 0.2% trans isomer. Similar recrystallization of *trans*-propenyllithium was less satisfactory in its elimination of cis isomer: reaction of recrystallized *trans*-propenyllithium with dibromoethane produced 1-bromopropene consisting of a maximum of 98.8 ± 0.2% trans isomer. Nonetheless, it is clear from the former experiment that a *maximum* of 0.4% isomerization accompanies metal–halogen exchange between *cis*-propenyllithium and 1,2-bromoethane, and we believe that the exchange is in fact stereospecific.[25] Thus, this method provides a reliable method of assaying the stereochemical composition of the organolithium reagents utilized in this study. In practice, the stereochemical purity of the organolithium reagents used as starting materials for the preparation of the copper(I) and silver(I) compounds varied from 97% for *cis*- and *trans*-1-propenyllithium to 93% for *cis*- and *trans*-2-butenyllithium.

Conversion of these vinylic lithium reagents into the corresponding copper(I) and silver(I) compounds was accomplished in high yield either by heterogeneous reaction with solid copper(I) or silver(I) iodide at −28° in diethyl ether or by homogeneous reaction with tetrakis[iodo(tri-*n*-butylphosphine)copper(I)][27] (**1**) or tetrakis[iodo(tri-*n*-butylphosphine)silver(I)][28] (**2**) at −78°. Lithium iodide, produced in the reactions between the organolithium reagents and **1** or **2**, and lithium bromide or chloride present from preparation of the organolithium reagents could be removed by precipitation as ether-insoluble dioxanates on addition of anhydrous dioxane. Addition of dioxane to a solution of the nonphosphine-complexed copper(I) and silver(I) organometallic compounds unfortunately precipitated these compounds together with the lithium halides; however, the presence of lithium halides during the thermal decompositions of either phosphine-complexed or -uncomplexed organocopper(I) and -silver(I) compounds had no influence on either the stereochemistry or yield of the products of these reactions.



Although the presence of the phosphine in the solution increased the thermal stability of the copper and silver compounds slightly, the principal advantage in the preparation of phosphine-complexed reagents over uncomplexed materials was one of convenience: both **1** and **2** are soluble in ether at −78°, and their use as starting materials permitted a rapid homogeneous reaction which avoided the higher temperatures and longer

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(25) The loss of stereochemistry observed on reaction of vinylic bromides with lithium varied erratically over a range of ~2%, with occasional values 6–7% from a nominal "average" value.[28] In at least one instance we have observed reaction of *trans*-1-bromopropene with lithium to yield *trans*-propenyllithium containing <0.1% *cis*-propenyllithium (as determined by reaction with dibromoethane). *Cf.* E. J. Panek, Jr., Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1968, p 140.

(26) For discussions of the mechanism of formation of Grignard and organolithium reagents, see H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **4**, 418 (1965); T. Yoshino, Y. Menabe, and Y. Kikuchi, *J. Amer. Chem. Soc.*, **86**, 4670 (1964); E. Grovenstein and Y.-M. Cheng, *Chem. Commun.*, 101 (1970); M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **91**, 3652 (1969).

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**Table I.** Thermal Decomposition of Vinylic Copper(I) and Silver(I) Compounds[a]

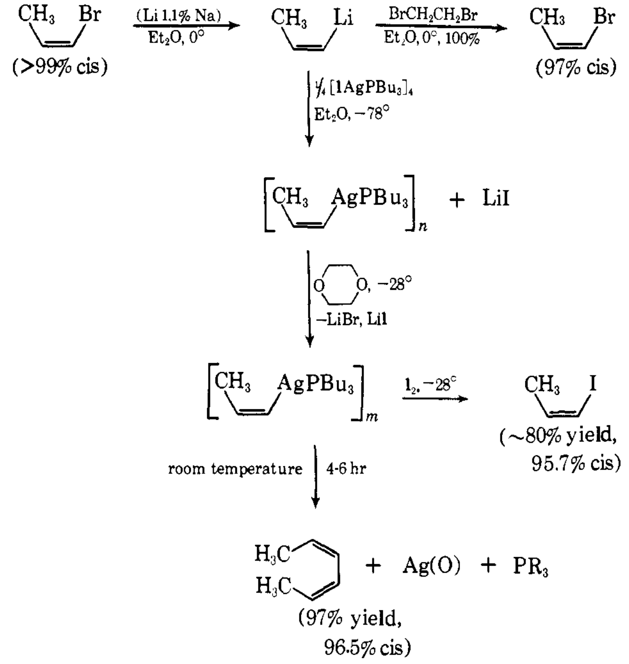
| | Uncomplexed compds | | | Tri-*n*-butylphosphine complexes | | |
|---|---|---|---|---|---|---|
| | Isomeric purity, %[b] | | Yield, %[c] | Isomeric purity, %[b] | | Yield, %[c] |
| Organometallic compd, R–M | RLi[d] | R–R | R–R | RLi[d] | R–R | R–R |
| *trans*-1-Propenylsilver(I) | 97.2 | 98.4 | 90 | 97.2 | 97.2 | 102 |
| *trans*-1-Propenylcopper(I) | 97.2 | 97.7 | 100 | 97.2 | 97.1 | 89 |
| *cis*-1-Propenylsilver(I) | 97.4 | 97.7 | 82 | 97.4 | 97.6 | 103 |
| *cis*-1-Propenylcopper(I)[e] | 97.4 | 98.2 | 84 | 97.4 | 94.7 | 99 |
| *trans*-2-Butenylsilver(I) | 93.1 | 92.2 | 90 | 92.1 | 93.6 | 100 |
| *trans*-2-Butenylcopper(I) | 93.1 | 95.0 | 92 | 92.1 | 93.0 | 99 |
| *cis*-2-Butenylsilver(I) | 93.5 | 95.6 | 74 | 93.5 | 92.7 | 90 |
| *cis*-2-Butenylcopper(I) | 93.5 | 96.2 | 72 | 93.5 | 93.5 | 92 |

[a] 0.1 *N* solutions in diethyl ether decomposed at ambient temperature, except where noted. Lithium halides were not removed from these solutions. [b] Defined in text. [c] Yield is based on vinylic lithium compound. [d] Determined by 1,2-dibromoethane quench of the starting organolithium reagents. [e] Decomposed at 90° in ether.

reaction times necessary to effect the heterogeneous reactions. We emphasize, however, that the phosphine had no significant influence on the stereochemistry of the thermal decompositions.

The high solubility, thermal instability, and sensitivity to oxygen and water displayed by these reagents are such that we have not yet been successful in isolating them as solids. Consequently, their characterization depends on several kinds of indirect evidence. First, hydrolysis of ethereal solutions containing vinylic copper(I) and silver(I) phosphine complexes from which the lithium halides have been removed yields the corresponding hydrocarbon; thermal decomposition produces high yields of dimers (*vide infra*) and copper or silver metal. These observations establish that reaction of **1** and **2** with vinylic lithium reagents does yield organometallic compounds containing carbon–copper and -silver bonds. Second, the empirical composition of the phosphine complexes can be roughly established by permitting "lithium halide-free" solutions to decompose thermally, and analyzing the resulting mixtures for the ratio of vinylic groups to metal, trialkylphosphine, and lithium ion. Analyses of this type for several typical compounds establish the composition $[R]_{1.0}[M]_{0.9\pm0.1}[PBu_3]_{1.1\pm0.1}$. Third, reaction of the vinylic copper(I) and silver(I) compounds with molecular iodine or bromine yields vinylic halides having the same configuration and stereochemical purity as the starting organolithium reagents. This observation, coupled with the retention of stereochemistry observed in the thermal dimerization, indicates that both formation of the carbon–copper(I) and -silver(I) bonds and their cleavage with halogens proceed with retention of configuration.[29,30] These transformations are summarized for *cis*-1-propenyl(tri-*n*-butylphosphine)silver(I) in Scheme I; taken together, they and similar reaction sequences for others of the organocopper(I) and -silver(I) reagents examined in this work establish that the reaction of 1-propenyl- or 2-butenyllithium with copper(I) iodide, silver(I) iodide, or their tri-*n*-butylphosphine complexes **1** and **2** yields the corresponding copper(I) and silver(I) organometallic compounds with retention of configuration around the double bond.

**Scheme I.** Preparation and Thermal Decomposition of *cis*-1-Propenyl(tri-*n*-butylphosphine)silver(I)

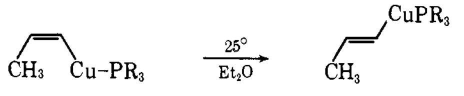


**Thermal Decomposition.** The vinylic copper(I) and silver(I) organometallic compounds decompose thermally over several days at 0°, and within 4 hr at 25°, giving metallic mirrors and high yields of dimers. Table I shows that within experimental error, with the single exception of *cis*-propenyl(tri-*n*-butylphosphine)copper(I), the decompositions to dimers are completely stereospecific. In this table, the isomeric purity of the dimers is defined in terms of the yields of *cis,cis*-, *cis,-trans*-, and *trans,trans*-2,4-hexadienes; *e.g.*

$$\%\ \text{trans isomeric purity} = \frac{2(\text{yield trans,trans dimer}) + (\text{yield cis,trans dimer})}{2(\text{total yield of dimers})} \times 100$$

The yields are calculated on the basis of the starting lithium reagents.

Independent experiments easily established that *cis*-1-propenyl(tri-*n*-butylphosphine)copper(I) was itself configurationally *unstable* under the conditions of the room-temperature thermal decomposition. Quenching one sample of this copper compound with iodine immediately following its preparation produced 1-iodopropene having the same isomeric purity as the starting pro-



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[29] In addition, hydrolysis of *cis*-2-butenylsilver(I) and of the analogous phosphine complex yields *cis*-2-butene.

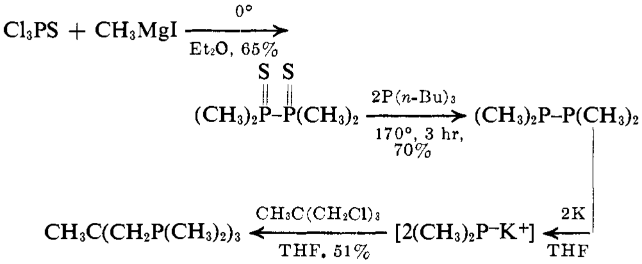
[30] For analogies, see D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, **1**, 138 (1963), and references therein.

penyllithium (92% cis, 8% trans). Quenching the same sample after it had been allowed to stand for 44 hr at 0° produced a mixture of 13% *cis*- and 37% *trans*-1-iodopropene. However, carrying out the thermal decomposition of this compound in a sealed tube at 90° almost completely suppressed the competing configurational isomerization (Table I). This last observation indicates that the isomerization reaction is characterized by a significantly lower enthalpy of activation than the thermal decomposition, and is probably an independent reaction.[31]

No direct experimental evidence concerning the extent of aggregation of the compounds listed in Table I is presently available. However, the related compounds phenylethynyl(trimethylphosphine)copper(I)[32] and -silver,[33] copper(I) diethyldithiocarbamate,[34] tetrakis[iodo(tri-*n*-butylphosphine)copper(I)],[27,35] and $[Cu_8(S_2CC(CN)_2)_6]$[36] are aggregated both in solution and as crystalline solids. We presume by analogy that the vinylic copper(I) and silver(I) compounds examined here are also associated.[13] However, in the absence of firm information concerning their aggregation, in the greater part of what follows we will discuss these organometallic compounds as if they were monomeric.

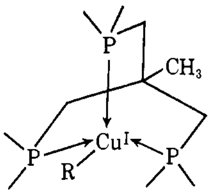
As part of an indirect attempt to investigate the influence of aggregation on the decompositions by changing the degree of aggregation or the structure of the presumed aggregates, the tridentate ligand 1,1,1-tris(dimethylphosphinomethyl)ethane (**3**) was synthesized by the sequence shown in Scheme II. This phosphine is potentially well suited for simultaneous coordination with three of the four possible coordination sites of copper(I).[37] It was our hope that, even without detailed information concerning the structures of the organocopper aggregates in the presence or absence of tri-*n*-butylphosphine, a significant change in the aggregate structure on coordination of the vinylic copper reagents with **3** would be reflected as a change in the yield or stereospecificity of production of dimer in the thermal decomposition reaction. Unfortunately, the results of experiments with **3** were ambiguous. Compound **3** formed a high-melting, insoluble, and probably polymeric 1:1 complex with copper(I) iodide which did not react with lithium reagents in ether at room temperature. Consequently, the effect of **3** on the decomposition of a typical organocopper compound could be investigated only through its addition to a preformed solution of organocopper compound. Addition of *ca.* 1 equiv of **3** to a solution of *trans*-2-butenyl(tri-*n*-butylphosphine)copper(I) did dramatically increase the stability of the copper compound: complete thermal decomposition of the mixture of copper reagent and **3** required heating at 80° for 18 hr. Nonetheless, the stereochemistry of dimers produced in this decomposition indicated that the reaction had taken place with complete retention of stereochemistry. Thus, although the decrease in the rate of decomposition of the organocopper reagent in this experiment indicates that **3** did coordinate with the organocopper reagent, the absence of any change in the stereochemistry of the decomposition leaves unanswered the question of the influence of the extent of aggregation on the stereochemical course of the reaction.[38]

**Scheme II.** Synthesis of 1,1,1-Tris(dimethylphosphinomethyl)ethane



$$\mathrm{Cl_3PS + CH_3MgI} \xrightarrow[\mathrm{Et_2O,\ 65\%}]{0^\circ} \mathrm{(CH_3)_2\overset{\overset{S}{\|}}{P}-\overset{\overset{S}{\|}}{P}(CH_3)_2} \xrightarrow[170^\circ,\ 3\ \mathrm{hr},\ 70\%]{2\mathrm{P}(n\text{-}\mathrm{Bu})_3} \mathrm{(CH_3)_2P-P(CH_3)_2} \xrightarrow[\mathrm{THF}]{2\mathrm{K}} \mathrm{[2(CH_3)_2P^-K^+]} \xrightarrow[\mathrm{THF,\ 51\%}]{\mathrm{CH_3C(CH_2Cl)_3}} \mathrm{CH_3C(CH_2P(CH_3)_2)_3}$$

**3**



## Reactions of *trans*-Propenyllithium with Transition Metal Salts.

Examination of the thermal conversion of vinylic copper(I) and silver(I) organometallic compounds to substituted butadienes established that these reactions are characterized by high yield and stereoselectivity. For comparison, the yield and stereochemistry of the 2,4-hexadienes produced on reaction of *trans*-propenyllithium with a variety of transition metal salts were surveyed (Table II). No effort was made to characterize any intermediate transition metal organometallic compounds in these reactions, to establish optimum stoichiometries for the reactions leading to 2,4-hexadienes, or to determine the fate of the propenyl groups not accounted for in the dimeric products.

Two features of the data in Table II deserve comment. First, copper(I) and (on the basis of work reported in preceding sections) silver(I) appear to be almost unique in their efficiency as coupling agents; only bis(triphenylphosphine)nickel(II) dibromide offers comparable yields. Second, the stereoselectivity observed in conversion of propenyllithium to 2,4-hexadiene is high for most of these metals, even though the yields in most instances are low. Without knowing either the extent to which the presumed propenylmetal intermediates in these reactions themselves isomerize under the reaction conditions, or the relative yields of *cis,cis*-, *cis,trans*-, and *trans,trans*-2,4-hexadienes expected on dimerization of propenyl radicals, it is difficult to interpret the signifi-

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(31) The possibility that an ate complex between propenyllithium and propenylcopper was responsible for the configurational isomerization of *cis*-propenyl(tri-*n*-butylphosphine)copper was eliminated by an independent demonstration of the configurational stability of this ate complex. The concentration of added tri-*n*-butylphosphine or lithium halide also had no effect on the configurational stability of this copper reagent.

(32) P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, 21, 957 (1966).

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

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(35) A. F. Wells, *Z. Kristallogr. Kristallgeometrie, Kristallphys. Kristallchem.*, 94, 447 (1936).

(36) L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, 90, 7357 (1968).

(37) This type of coordination has been established for copper(I) by an X-ray structure determination of the related complex bis(*o*-dimethylarsinophenyl)methylarsinecopper(I)–manganese(I) pentacarbonyl. *Cf.* B. T. Kilbourn, T. L. Blundell, and H. M. Powell, *Chem. Commun.*, 444 (1965). See also A. S. Kasenally, R. S. Nyholm, and M. H. B. Stiddard (*J. Amer. Chem. Soc.*, 86, 1884 (1964)) for the preparation of the monomeric 1,1,1-tris(dimethylarsinomethyl)ethanecopper(I)–manganese(I) pentacarbonyl.

(38) In related experiments a large excess of tri-*n*-butylphosphine was found to increase significantly the resistance of the copper and silver reagents toward thermal decomposition, but not to alter the stereospecificity of their decomposition.

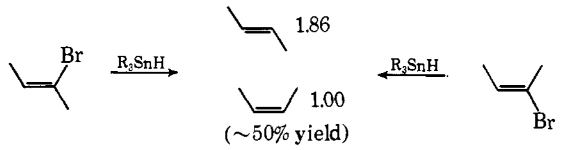
Table II. Isomeric Compositions and Yields of 2,4-Hexadienes Obtained on Reaction of *trans*-Propenyllithium with Transition Metal Halides

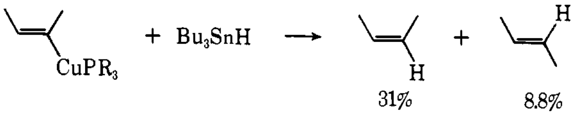
| | | | R–R | |
|---|---|---|---|---|
| $MX_n$ | Condn[a] | $RLi/MX_n$ | Yield, %[b] | % retention[c] |
| $VCl_3$ | | 4.2 | 24 | 99 |
| $CrCl_2$ | *d* | 0.9 | 9 | 99 |
| $CrCl_3$–3THF | *e* | 3.4 | 47 | 95 |
| $MnBr_2$ | | 3.6 | 49 | 90 |
| $FeCl_2$ | *d* | 0.85 | 25 | 99 |
| $FeCl_3$ | | 4.4 | 73 | 87 |
| $CoCl_2$ | | 2.9 | 73 | 99 |
| $(Ph_3P)_2CoCl_2$ | *e* | 2.3 | 98 | 96 |
| $NiCl_2$ | | 0.3 | 44 | 100 |
| $(Ph_3P)_2NiBr_2$ | | 2.6 | 192 | 102 |
| CuI | | 0.7 | 102 | 101 |
| $CuCl_2$ | | 1.1 | 95 | 100 |
| $ZrCl_4$ | *e* | 10.4 | <2 | *f* |
| $MoCl_5$ | *e* | 8.9 | 176 | 100 |
| $PdCl_2$ | | 3.1 | 24 | 98 |
| $TaCl_5$ | *e* | 8.1 | 65 | 90 |
| $(Ph_3P)_3RhCl$ | | 8.9 | 99 | 100 |
| $(Ph_3P)_2PtCl_2$ | | 4.2 | 115 | 98 |

[a] Reactions were carried out by combining the components with stirring in ether solution at −78° and allowing them to stand at 25° for 6–20 hr prior to hydrolysis. The hydrolyzed reaction mixtures were stored at −20° until analyzed by glpc, unless otherwise noted. [b] Typically [RLi] = 0.1–0.2 *N*. For consistency, yield calculations were based on the arbitrary assumption that the metal salts acted only as one-electron oxidants in the reactions leading to 2,4-hexadienes, and yields were calculated on the basis of the limiting reagent. Thus, for experiments involving *a* mmol of RLi and *b* mmol of $MX_n$, and in which $RLi/MX_n < 1$, 100% yield of dimer would correspond to 0.5*a* mmol of dimer; for those in which $RLi/MX_n > 1$, 100% yield would correspond to 0.5*b* mmol of dimer. [c] "% retention" is defined as [(isomeric purity of R–R)/(isomeric purity of RLi)]; see Table I. The accuracy of these numbers is estimated to be ±2%. [d] Not hydrolyzed before analysis. [e] Ether–THF solution. [f] Not determined.

cance of those stereochemical results in the several reactions in which significant isomerization *is* observed; however, those reactions proceeding with high stereoselectivity are probably subject to the same mechanistic constraints as are the thermal decompositions of authentic vinylic copper(I) and silver(I) compounds (*vide infra*).

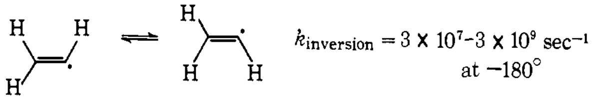
**Reduction of *cis*- and *trans*-2-Bromo-2-butene with Tri-*n*-butyltin Hydride.** For comparison with the stereochemical results obtained on thermal decomposition of 2-butenylmetal compounds, we investigated briefly the configurational stability of 2-butenyl radical under similar conditions by examining the stereochemistry of the 2-butenes obtained on reduction of 2-bromo-2-butene with tri-*n*-butyltin hydride. The same mixture of 65% *trans*- and 35% *cis*-2-butene was obtained in greater than 50% yield from the room temperature reduction of both *cis*- and *trans*-2-bromo-2-butene with either neat tri-*n*-butyltin hydride or with tri-*n*-butyltin hydride in ether solution. Neither the 2-bromo-2-butenes nor *cis*-2-pentene present in the reaction mixture isomerized during the reduction. Hence, under these conditions it appears that the 2-butenyl radical isomerizes much more rapidly than it abstracts a hydrogen atom from trialkyltin hydride.[39] An attempt to generate 2-butenyl radicals in the presence of *cis*-2-butenyl(tri-*n*-butylphosphine)copper(I) by tri-*n*-butyltin hydride reduction of 2-bromo-2-butene was abandoned when it was discovered that the organocopper reagent was reduced to a mixture of butenes more rapidly than was the vinylic bromide.[40]





## Discussion

The rate data which form the basis for our mechanistic interpretation of the stereospecificity of the decomposition of vinylic copper(I) and silver(I) compounds are derived from a number of physical and chemical investigations of the configurational isomerization of vinylic radicals. Epr spectroscopic examinations[19,20,41,42] have established that unsubstituted vinyl radical undergoes inversion of configuration at −180°, with an inversion barrier of *ca.* 2 kcal/mol and a preinversion lifetime of $3 \times 10^{-8}$–$3 \times 10^{-10}$ sec;[19] 1-methylvinyl radical inverts more slowly. The inversion of 1-methyl-substituted vinyl radicals, generated by thermolysis of *tert*-butyl *cis*- and *trans*-α-methyl- and α,β-dimethylpercinnamates, is faster than their hydrogen abstraction from cumene and toluene.[43] Attempts to trap stereoisomeric vinylic radicals using the more reactive scavengers bromotrichloromethane[44] and sodium naphthalide[45] have apparently been partially successful; however, the nature of these scavengers indicates that only materials capable of reacting with vinylic radicals at rates close to diffusion limited can be expected to compete successfully with inversion.



The thermal decomposition of the vinylic copper(I) and silver(I) reagents examined in this work might *a priori* take place by any of several paths. Dimers might be produced by initial homolytic scission of the carbon–metal bond of the organometallic compound R–M to yield vinylic radicals R·, followed by radical–radical

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(39) For a review of the evidence supporting a radical chain mechanism for reductions with tin hydrides, see (a) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); (b) L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964); (c) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

(40) F. J. A. Des Tombe, G. J. M. van der Kerk, H. M. J. C. Creemers, and J. G. Noltes have reported that reaction of dimethylcadium(II) and triphenyltin hydride in dimethoxyethane yields methane and $[(C_6H_5)_3Sn]_2Cd(II) \cdot DME$: *Chem. Commun.*, 914 (1966).

(41) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

(42) F. J. Adrian and M. Karplus, *ibid.*, **41**, 56 (1964).

(43) J. A. Kampmeier and R. M. Fantazier, *J. Amer. Chem. Soc.*, **88**, 1959 (1966); L. A. Singer and N. P. Kong, *ibid.*, **88**, 5213 (1966).

(44) O. Simamura, K. Tokumaru, and H. Yui, *Tetrahedron Lett.*, 5141 (1966).

(45) G. D. Sargent and W. M. Browne, *J. Amer. Chem. Soc.*, **89**, 2788 (1967). The partial retention of stereochemistry observed during decomposition of *trans-tert*-butyl α-chloropercinnamates is *not* due to trapping of a kinetically free α-chloropercinnamyl radical. *Cf.* L. A. Singer and N. P. Kong, *ibid.*, **89**, 5251 (1967). The mechanism of sodium naphthalide reduction of vinylic halides remains uncertain. See, however, S. J. Cristol and R. V. Barbour (*ibid.*, **90**, 2832 (1968)) and J. F. Garst and J. T. Barbas (*ibid.*, **91**, 3385 (1969)) for discussions of the reductions of alkyl halides with sodium naphthalide.

combination in competition with inversion of configuration at the radical center (Scheme III). For the sake of

**Scheme III**

$$[cis\text{-R-M(I)}]_m \longrightarrow cis\text{-R}\cdot + \text{M}(0) + [cis\text{-R-M(I)}]_{m-1}$$

$$cis\text{-R}\cdot \rightleftharpoons trans\text{-R}\cdot \qquad k_{\text{inversion}}$$

$$2cis\text{-R}\cdot \longrightarrow cis,cis\text{-R}_2 \qquad k_c$$

$$cis\text{-R}\cdot + trans\text{-R}\cdot \longrightarrow cis,trans\text{-R}_2 \qquad k_c$$

$$2trans\text{-R}\cdot \longrightarrow trans,trans\text{-R}_2 \qquad k_c$$

simplicity in this scheme we assume that the rate constants $k_{\text{inversion}}$ for the forward and back configurational isomerization reactions are equal, and that the rate constants $k_c$ are the same for each of the possible dimerizations of pairs of *cis*- and *trans*-propenyl radicals. Similarly, an initially produced radical might react directly with intact organometallic compound to yield dimer, again in competition with inversion of configuration (Scheme IV). Alternatively, two radicals might be formed simultaneously in a solvent cage and combine before escaping the cage (Scheme V; a caged geminate radical pair is indicated by a superscript bar). Finally, dimer might be produced by a direct reaction between two molecules of organometallic compounds, without the formation of an intermediate free radical.

**Scheme IV**

$$cis\text{-R}\cdot \rightleftharpoons trans\text{-R}\cdot \qquad k_{\text{inversion}}$$

$$cis\text{-R}\cdot + cis\text{-R-M(I)} \longrightarrow cis,cis\text{-R}_2 + \text{M}(0) \qquad k_c'$$

$$trans\text{-R}\cdot + cis\text{-R-M(I)} \longrightarrow cis,trans\text{-R}_2 + \text{M}(0) \qquad k_c'$$

**Scheme V**

$$[cis\text{-R-M(I)}]_m \longrightarrow \overline{cis\text{-R}\cdot\ cis\text{-R}\cdot} + \text{M}(0)_2 + [cis\text{-R-M(I)}]_{m-2}$$

$$\overline{cis\text{-R}\cdot\ cis\text{-R}\cdot} \rightleftharpoons \overline{cis\text{-R}\cdot\ trans\ \text{R}\cdot} \qquad k_{\text{inversion}}$$

$$\overline{cis\text{-R}\cdot\ cis\ \text{R}\cdot} \longrightarrow cis,cis\text{-R}_2 \qquad k_c''$$

etc.

**Scheme VI**

$$[cis\text{-R-M(I)}]_m \longrightarrow cis,cis\text{-R}_2 + \text{M}(0)_2 + [cis\text{-R-M(I)}]_{m-2}$$

Our interpretation of the stereospecificity of the thermal decomposition of 1-propenylcopper(I) and -silver(I) compounds in terms of these alternatives rests on 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: $k_{\text{inversion}}(-180°) \geq 3 \times 10^7\ \text{sec}^{-1}$.[19] Assuming a classical frequency factor of $10^{13}$ and extrapolating the rate to 25°, the estimated magnitude of $k_{\text{inversion}}$ for 1-propenyl radical under the conditions used for the organocopper and -silver thermal decompositions is *ca.* $10^9\ \text{sec}^{-1}$.[46] To be consistent with the complete retention of stereochemistry observed in the thermal decompositions, the rate of dimerization of any intermediate propenyl radicals must be at least $10^2$ faster than the rate of their inversion of configuration: *e.g.*, for Scheme IV

$$k_c'(\text{R}\cdot)(\text{R-M}) \geq 10^2 k_{\text{inversion}}(\text{R}\cdot) \qquad (1)$$

For all the reactions summarized in Table I the initial concentration of the organometallic compound (RM) was *ca.* 0.1 *M*. Thus, in order for coupling to take place to the exclusion of inversion, the bimolecular rate constant $k_c'$ in Scheme IV must necessarily be greater than $10^{12}\ M^{-1}\ \text{sec}^{-1}$. This magnitude is greater than that of a diffusion-controlled reaction under the conditions of the organometallic decompositions by *ca.* $10^2$.[47] On the basis that any reaction pathway requiring a bimolecular rate constant of this magnitude is physically unreasonable, we exclude the mechanism of Scheme IV, and by a similar argument that of Scheme III, as possible descriptions of the thermal decomposition of propenylcopper(I) and -silver(I).[51]

The stereochemical results of Table I cannot be used rigorously to exclude a cage mechanism of the type outlined in Scheme V for the production of 2,4-hexadiene from the 1-propenyl organometallic compounds. The lifetime of a caged geminate radical pair has been estimated to be on the order of $10^{-11}$ sec.[52] Even a lifetime as short as this would be expected to result in some interconversion of *cis*- and *trans*-propenyl radicals; unfortunately, without knowing the rate constant for primary recombination for these radicals, it is difficult to decide if the maximum 1% isomerization which would have gone undetected in our experiments would be compatible with cage recombination.[53] However, in order for Scheme V to provide a correct description of the mechanism of these reactions, the primary cage recombination must not only proceed without loss of stereochemistry in the propenyl moieties, but must also proceed with an overall efficiency approaching 100% for each of these compounds in Table I for which the dimer yield approaches 100%. The requirement of primary cage combination of this efficiency is physically unreasonable, and provides sufficient grounds to discard Scheme V as a possible mechanistic description.[54]

The elimination of mechanisms based on Schemes III, IV, and V leaves the direct conversion of organometallic compound into dimer (Scheme VI), without intermediate free propenyl radicals, as the only plausible description of the decomposition.[55] However, it is worth pointing out that Scheme VI covers a variety of

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(46) This value is probably a minimum value: see footnote 50 of ref 19.

(47) Typical values for absolute rate constants ($M^{-1}\ \text{sec}^{-1}$) for radical–radical reactions in solution are: $1.0 \pm 0.3 \times 10^9$ ($n\text{-C}_5\text{H}_{11}\cdot$, benzene solution, 25°);[48] $4.1 \pm 1.2 \times 10^9$ (benzyl$\cdot$, benzene 25°);[48] $1.7 \pm 0.4 \times 10^8$ ($\text{C}_2\text{H}_5\cdot$, ethane, −177°);[19,49] $4.7 \times 10^9$ ($\text{C}_2\text{H}_5\cdot$, isoctane, 25°).[50] Although an absolute rate constant for the dimerization of propenyl radicals has not been measured, the rate of dimerization of vinyl radicals is *ca.* 2.2 times that of dimerization of ethyl radicals at −160° in liquid ethane–ethylene.[19]

(48) R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).

(49) R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).

(50) R. K. Lyon, *J. Amer. Chem. Soc.*, **86**, 1907 (1964).

(51) Using this argument, at least 10% isomerization would be expected in any reaction involving a kinetically free (*i.e.*, nonsolvent caged) 1-propenyl radical in a solution of normal viscosity, even in the presence of a 1 *M* concentration of a radical trapping reagent reacting at a diffusion-controlled rate. In consequence, configurational isomerization of the 1-propenyl grouping provides a very sensitive probe for a free-radical intermediate.

(52) R. M. Noyes, *Progr. Reaction Kinet.*, **1**, 129 (1961).

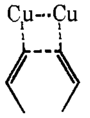
(53) In a number of experiments which have detected cage combination of radicals using various stereochemical tests, the reaction stereospecificities have been relatively low: H. M. Walborsky and C. Chen, *J. Amer. Chem. Soc.*, **89**, 5499 (1967); E. I. Heiba and R. M. Dessau, *ibid.*, **89**, 2238 (1967); K. B. Wiberg and G. Foster, *ibid.*, **83**, 423 (1961); R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965); C. G. Overberger, N. Weinshenker, and J. P. Anselme, *ibid.*, **86**, 5364 (1964); F. D. Greene, M. A. Berwick, and J. C. Stowell, *ibid.*, **92**, 867 (1970), and references therein.

(54) See, for example, H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964).

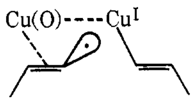
(55) In light of this conclusion it seems best to reformulate the "radical" reaction proposed[11,56] to account for the reaction of 2-methyl-1-propenylsilver(I) and ethanol-*O-d* to yield 2-methyl-1-propene-1-*d* as deuterolysis of the carbon–metal bond.

(56) F. Glockling, *J. Chem. Soc.*, 716 (1955); 3640 (1956).

quite different mechanisms between which we cannot presently distinguish. For example, mechanisms which would involve a four-center transition state (**4**), "$\sigma$–$\pi$" interconversion to an intermediate containing a 1-propenyl radical $\pi$ bonded to a copper atom cluster **5**, or



**4**



**5**

disproportionation of two molecules of copper(I) organometallic reagent to a copper(0) atom and a copper(II) organometallic intermediate would all be compatible with our present knowledge of this reaction.

The observation of stereospecific dimer formation in the decomposition of 2-butenylcopper(I) and silver(I) 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. Although these decompositions almost certainly proceed by the same mechanism as do those of 1-propenylcopper(I) and -silver(I), in the absence of a reliable quantitative value for the rate constant describing the inversion of configuration of 2-butenyl radical, it is difficult to define a lower limit for the lifetime of any radical intermediates in the butenyl organometallic decompositions. A very rough estimate for this rate constant can be obtained from the observation that tri-*n*-butyltin hydride is not a sufficiently active hydride donor under the conditions used in our experiments to trap the stereoisomeric 2-butenyl radicals before interconversion.[57] We assume that the rate constant for reaction of tri-*n*-butyltin hydride with 2-butenyl radical is greater than or equal to that for reaction with *tert*-butyl radical; *viz.*, $k_{\text{reduction}} \geq 3 \times 10^5\ M^{-1}$ sec.[58,59] With this assumption, and the additional assumption of a bimolecular rate law for reaction of 2-butenyl radical with tri-*n*-butyltin hydride, the relative rates of inversion and reduction for 2-butenyl radical are given by eq 2. Hence,

$$k_{\text{inversion}}[\text{R}\cdot] > 10^2 k_{\text{reduction}}[\text{R}\cdot][\text{R}_3\text{SnH}] \qquad (2)$$

for $[\text{R}_3\text{SnH}] = 1\ M$, $k_{\text{inversion}} > 3 \times 10^7\ M^{-1}$ sec. Using this value in eq 1 and proceeding through an argument analogous to that given previously for 1-propenyl radical, a value of $k_c > 10^{10}$ would be required to rationalize the complete retention of configuration observed in the decomposition of the 2-butenyl organometallic compounds on the basis of a mechanism involving a free intermediate 2-butenyl radical. Although this argument is quantitatively less convincing than that for 1-propenylcopper(I) and -silver(I), it leads to the same qualitative conclusion: free vinylic radicals are not involved as intermediates in these thermal decomposition reactions.

The question of how far these results can be generalized to include the thermal decomposition of other organometallic compounds is an interesting one. Other studies in these laboratories have established that completely different mechanisms describe the thermal decomposition of aliphatic copper(I) and silver(I) compounds;[61] however, it does seem probable that a nonradical pathway describes the decomposition of the very similar arylcopper(I) and -silver(I) reagents, particularly since neither these reactions nor the Ullman reaction show evidence of the products which would be expected from attack on solvent in a reaction characterized by extensive involvement of free radicals.[62] Further, the high stereoselectivity observed on conversion of *trans*-propenyllithium to 2,4-hexadiene during reaction with a variety of transition metal salts (Table II) suggests that free propenyl radicals are also not intermediates in these reactions.

## Experimental Section[63]

**General Methods.** All reactions involving organometallic compounds were carried out under inert atmospheres using standard techniques.[64] Helium was used without further drying or deoxygenation; prepurified nitrogen was passed through two drying tubes containing calcium sulfate before use. Ether and tetrahydrofuran were distilled from lithium aluminum hydride under a nitrogen atmosphere immediately before use and were transferred under an inert atmosphere using hypodermic syringes or cannulas. Pentane and dioxane were purified by distillation from a dark purple solution of sodium benzophenone dianion.

Analytical glpc analyses were performed on F & M Model 810 instruments equipped with flame ionization detectors and Disc integrators, using the following columns: column A, 8-ft 20% SE-30 on Chromosorb P; column B, 4-ft 20% SE-30 on Chromosorb P; column C, 12-ft 15% 1,2,3-tris(2-cyanoethoxy)propane (TCEOP) on Chromosorb W; column D, 8-ft 15% Carbowax 20 M on Chromosorb W. Absolute yields were calculated from peak areas using internal standard techniques, utilizing response factors obtained with authentic samples.

**Vinylic Halides.** ***trans*-1-Chloro-1-propene** (bp 39°) and ***cis*-1-bromo-1-propene** (bp 57°) were obtained in >99% purity (glpc, column A) by careful distillation of commercial material (Columbia Organics, Inc.) from powdered sodium bicarbonate using a Nester–Faust Teflon annular spinning band column. The bromide was collected over sodium bicarbonate and stored at −10° to inhibit its facile thermal and acid-catalyzed isomerization. (The higher boiling trans isomer could not be obtained in pure form in this distillation due to thermal isomerization to the cis isomer in the distillation column.) ***cis*-2-Bromo-2-butene** was prepared by dehydrohalogenation of *meso*-2,3-dibromobutane[65] using the procedure of Dreiding and Pratt.[23] The product of dehydrohalogenation (97% cis isomer, 3% trans by glpc, column B) isomerized on attempted purification by distillation, and was used directly after drying ($MgSO_4$). ***trans*-2-Bromo-2-butene** was prepared by a similar procedure[23] from *dl*-2,3-dibromobutane.[65] Distillation using a Nester–Faust Teflon spinning band column

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(57) Kuivila has reported partial retention of configuration on reduction of 2-bromo-2-butene with tri-*n*-butyltin hydride at −75°.[39c]

(58) D. C. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 1055 (1968).

(59) There are no data pertinent to the question of the relative reactivities of these two radicals. Phenyl radicals show approximately the same reactivity as methyl radicals.[60] A vinylic radical might be expected to be comparable to a phenyl radical in its reactivity, and hence *more* reactive than a *tert*-butyl radical.

(60) R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

(61) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *ibid.*, **91**, 1426 (1970); C. P. Casey, J. San Filippo, Jr., P. E. Kendall, E. R. Stedronsky, E. J. Panek, and G. M. Whitesides, unpublished.

(62) A similar conclusion has been reached by A. Cairncross and W. A. Sheppard.[13]

(63) Melting points were determined using a Thomas Hoover capillary melting point apparatus, and are uncorrected. Boiling points are uncorrected. Nmr spectra were run on a Varian A-60 spectrometer. Infrared spectra were taken in sodium chloride cells using a Perkin-Elmer Model 237B or 337 grating spectrophotometer. Ultraviolet spectra were determined on a Cary 14 spectrophotometer. Mass spectra were determined on a Hitachi-Perkin-Elmer RMU-6D mass spectrometer. Lithium analyses were carried out using a Baird-Atomic flame photometer, using standard solutions of lithium nitrate to calibrate the galvanometer. Microanalyses were performed by Dr. S. M. Nagy and associates at M.I.T.

(64) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, Chapter 7.

(65) F. G. Bordwell and P. S. Landis, *J. Amer. Chem. Soc.*, **79**, 1593 (1957).

yielded material having bp 44° (160 mm) [lit.[23] bp 82–83° (740 mm)], which consisted of 99% trans isomer (glpc, column C).

**Analysis of Lithium Reagents.** The concentration of lithium reagents was determined by a modification of Gilman's double titration method.[66] A 1-ml hypodermic syringe with 0.01-ml graduations was used to transfer 1 ml of the lithium reagent to *ca.* 10 ml of water in a 50-ml erlenmeyer flask. The aqueous solution was titrated with 0.1 *N* hydrochloric acid using phenophthalein as an indicator to determine the total amount of base in the solution.

About 5 ml of 1,2-dibromoethane was passed through a short column of alumina into a 50-ml Erlenmeyer flash which had been dried at 110° in an oven. The flask was capped with a serum stopper and flushed with nitrogen. Lithium reagent (1 ml) was injected through the stopper into the 1,2-dibromoethane. The solution was swirled and ~10 ml of water was added. The aqueous solution was titrated with 0.1 *N* hydrochloric acid using phenolphthalein as indicator. The concentration of residual base in the 1,2-dibromoethane quench of the lithium reagent was subtracted from the concentration of total base to obtain the true concentration of the lithium reagent.

The cis–trans ratio of the vinylic lithium reagents was determined by glpc analysis (columns C or D) of the isomeric vinylic bromides produced by quenching *ca.* 0.5 ml of lithium reagent with *ca.* 0.5 ml of 1,2-dibromoethane under nitrogen.

***trans*-1-Propenyllithium.** Following a procedure similar to that of Seyferth and Vaughan,[22] 100 ml of ether and 2.0 g (0.29 g-atom) of lithium (1.1% sodium) cut into small pieces were added to a 200-ml Morton flask equipped with a dropping funnel and high-speed stirrer and protected by a helium atmosphere. The flask was cooled in an ice-water bath, and *trans*-1-chloro-1-propene (2.0 g, 0.026 mol, 99% trans) in 10 ml of ethyl ether was added dropwise over 0.5 hr. After 1.5 hr of additional stirring, analysis of a hydrolyzed aliquot by glpc showed 1% unreacted 1-chloro-1-propene and a similar amount of *trans,trans*-2,4-hexadiene. (In several preparations, incomplete reaction of *trans*-1-chloro-1-propene was observed, even after 6 hr of high speed stirring. These cases all involved attempts to prepare more concentrated (>0.3 *N*) solutions of the lithium reagent.) Solid lithium chloride and sodium chloride were allowed to settle before this lithium reagent was decanted for storage. Double titration showed the solution to be 0.154 *N* in lithium reagent and 0.008 *N* in residual base. Reaction of the lithium reagent with 1,2-dibromoethane gave 97.2% *trans*-1-bromo-1-propene and 2.8% *cis*-1-bromo-1-propene, in addition to 2% *trans,trans*-2,4-hexadiene present in the lithium reagent.

***cis*-1-Propenyllithium.** Following a similar procedure,[22] *cis*-1-bromo-1-propene (5.7 g, 0.047 mol, >99% cis) in *ca.* 20 ml of ethyl ether was added to lithium metal (2 g, 0.29 g-atom) in 100 ml of ethyl ether at −28° (carbon tetrachloride-Dry Ice slush) with high speed stirring over 40 min. After 20 min of additional stirring, analysis of a hydrolyzed aliquot by glpc showed no remaining *cis*-1-bromo-1-propene and no 2,4-hexadienes. Double titration indicated that the solution was 0.32 *N* in lithium reagent and 0.028 *N* in residual base. Reaction of the lithium reagent with 1,2-dibromoethane gave 97.4% *cis*-1-bromo-1-propene and 2.6% *trans*-1-bromo-1-propene (glpc, column C, in >95% yield).

***trans*-2-Butenyllithium.**[22] *trans*-2-Bromo-2-butene (6.1 g, 0.045 mol, >99% pure) in *ca.* 20 ml of ethyl ether was added to lithium metal (1.6 g, 0.237 g-atom) in 80 ml of ethyl ether at −28° with high-speed stirring over 0.75 hr. After 1 hr of additional high-speed stirring, analysis of a hydrolyzed aliquot showed no remaining *trans*-2-bromo-2-butene and no dimers. The resulting solution was 0.347 *N* in lithium reagent and 0.01 *N* in residual base as shown by double titration. Reaction of an aliquot of the lithium reagent with 1,2-dibromoethane gave 93.1% *trans*- and 6.9% *cis*-2-bromo-2-butene (glpc, column D).

***cis*-2-Butenyllithium.**[23] *cis*-2-Bromo-2-butene (5.1 g, 0.038 mol, 96.5% cis, 3.5% trans, containing *ca.* 4% by weight 2-butyne) was added to lithium metal (1.5 g, 0.22 g-atom) in ether at −28° with high-speed stirring over 0.5 hr and stirred an additional 1.5 hr. Analysis of a hydrolyzed aliquot showed no remaining 2-bromo-2-butene and no dimers. Double titration showed that the solution was 0.22 *N* in lithium reagent and 0.028 *N* in residual base. Reaction of the lithium reagent with 1,2-dibromoethane gave 93.5% *cis*- and 6.5% *trans*-2-bromo-2-butene (glpc, column D).

**Determination of the Stereochemistry of Reaction of Propenyllithium Reagents with 1,2-Dibromoethane.** Samples of *cis*- and *trans*-propenyllithium used in these experiments were prepared as described above, except that commercial lithium dispersion (Foote Mineral Co., 50% by weight in hexane, 1% sodium) was used in place of lithium wire and a magnetic stirrer, rather than a high-speed stirrer, was used. Yields and purities of propenyllithium reagents prepared using lithium dispersion were higher than those prepared using wire; however, these reagents could not be analyzed accurately using the double titration procedure, because of difficulties in separating the lithium dispersion from the solution. Instead, solutions were analyzed by quenching with 1,2-dibromoethane, followed by glpc analysis of the resulting propenyl bromides.

Recrystallization of *cis*-1-propenyllithium was accomplished by cooling a solution in ether (0.13 *N*, <0.00006 *M* in bromopropene) to −110° for 3 hr. Approximately one-half of the supernatant solution over the resulting white crystals was discarded and the solution was allowed to warm until homogeneous and then cooled again to −110°. This process was repeated three times. Glpc analysis of the mixture obtained by reaction of the 1-propenyllithium remaining in the final solution with 1,2-dibromoethane indicated that it contained *cis*- and *trans*-1-bromopropene in 99.6:0.4 relative yields. The overall recovery of propenyllithium from these crystallizations was ~4%.

Recrystallization of *trans*-propenyllithium was accomplished by a different procedure. A solution of *trans*-1-propenyllithium in ether (20 ml, 0.21 *N*) was reduced in volume to ~3 ml under vacuum, and the supernatant solution over the resulting white mass was discarded. Pentane (25 ml) was added to the flask containing the organolithium reagent. Cooling an aliquot (10 ml) of the resulting saturated solution to −78° for 10 hr resulted in precipitation of propenyllithium. The supernatant solution was again discarded, and the residue was taken up in ether and quenched with 1,2-dibromoethane. Glpc analysis of this solution indicated the presence of *cis*- and *trans*-1-bromopropene in 1.4:98.6 relative yields. Repeated recrystallization did not appear to improve the purity of this lithium reagent appreciably.

**Tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] (1).** In a modification of the method of Mann, Purdie, and Wells,[27] copper(I) iodide (95 g, 0.50 mol) was dissolved in 600 ml of saturated aqueous potassium iodide solution and stirred with tri-*n*-butylphosphine (95 g, 0.47 mol) in 400 ml of ether for 1 hr. The layers were separated and the ether layer was washed with saturated potassium iodide solution and with water. The ether layer was concentrated to give 170 g (92% yield) of $(CuIPBu_3)_4$ as a white waxy solid. The solid was dissolved in 250 ml of 90% acetone–10% methanol at room temperature. Cooling to −10° gave 100 g of $(CuIPBu_3)_4$, mp 75–75.5° (lit.[27] mp 75°); further cooling to −78° gave an additional 40 g (76% total yield) of $(CuIPBu_3)_4$, mp 75°. This compound was stored in the refrigerator. Storage at room temperature resulted in decomposition to a green solid after a variable period of time.

**Tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] (2).** Following the procedure of Mann, Wells, and Purdie,[28] silver(I) iodide (39.6 g, 0.168 mol) was dissolved in 150 ml of saturated aqueous potassium iodide solution. The solution was filtered and shaken with tri-*n*-butylphosphine (30.3 g, 0.15 mol) for 2 hr in a separatory funnel. The product separated as an oily upper layer and was washed with 25 ml of saturated potassium iodide solution. The oily product was dissolved in boiling ethanol. Upon cooling to room temperature, a viscous oil separated from the ethanol solution. The oil became a crystalline mass when cooled to −15°. A saturated solution of this solid in ethanol at room temperature was cooled to −15° to give white crystalline $(AgIPBu_3)_4$ (31.5 g, 48% yield) which was dried at 10-mm pressure at room temperature, mp 44° (lit.[28] mp 43°).

**Tri-*n*-butylphosphine Complexes of Vinylic Copper(I) and Silver(I) Compounds.** All of the tri-*n*-butylphosphine complexes of *cis*- and *trans*-2-butenyl- and -1-propenylcopper(I) and -silver(I) were

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(66) H. Gilman, F. K. Cartledge, and S. Y. Sim, *J. Organometal. Chem.*, **1**, 8 (1963). See also R. A. Finnegan and H. W. Kutta, *J. Org. Chem.*, 30, 4138 (1965). A number of alternative methods have been proposed for analysis of organolithium reagent solutions. (For examples, see S. C. Watson and J. F. Eastham, *Anal. Chem.*, **39**, 171 (1967), R. L. Eppley and J. A. Dixon, *J. Organometal. Chem.*, **8**, 176 (1967), and J. R. Urwin and P. J. Reed, *ibid.*, **15**, 1 (1968), and references therein.) However, in our hands the Gilman procedure has proved to be simple to use and quite reproducible *provided that acidic impurities have been removed from the 1,2-dibromoethane by filtration through alumina immediately before use.* The yield of the vinylic bromides formed in the 1,2-dibromoethane quench was shown in a number of instances to be between 95 and 100% of the amount calculated on the basis of the double titration method by glpc analysis: this agreement provides a practical check on the accuracy of this method of analysis.

prepared in solution using similar procedures, exemplified here for *trans*-1-propenyl(tri-*n*-butylphosphine)copper(I). To a flame-dried 12-ml centrifuge tube capped with a serum stopper was added 190 mg (0.483 mequiv) of $(CuIPBu_3)_4$, and the tube was flushed with nitrogen. Ether (*ca.* 2 ml) was transferred into the flask from a storage vessel using a stainless steel cannula.

*trans*-Propenyllithium (*ca.* 30 ml) was transferred by cannula from a storage bottle to a 40-ml graduated centrifuge tube sealed with a serum stopper. *n*-Decane (an internal glpc standard) was injected into the lithium reagent with a 1-ml hypodermic syringe and the increase in weight measured with an accuracy of ±0.1 mg. The weight of *n*-decane per mole of lithium reagent was calculated from these data. The concentration of the solution was recalculated to take into account the dilution of the lithium reagent by internal standard.

A portion of this lithium reagent solution was transferred to a 12-ml graduated centrifuge tube whose volume could be read with an accuracy of ±0.1 ml. One equivalent (4.0 ± 0.1 ml = ±3%) of the lithium reagent was transferred by cannula to the cold (−78°) solution of the phosphine complex. Mixing the reagents produced either a yellow solution of the tri-*n*-butylphosphine complex of the vinylic copper(I) compound or a pink solution of the tri-*n*-butylphosphine complex of the vinylic silver(I) compound. Ethyl ether was then added by cannula to give a solution of the desired concentration.

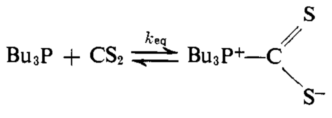
**Dioxane Precipitation of Lithium Halides from Tri-*n*-butylphosphine Complexes of Vinylic Copper(I) and Silver(I) Compounds.** Solutions of the tri-*n*-butylphosphine complexes of the organocopper(I) and -silver(I) compounds were prepared at −78° in 12-ml graduated centrifuge tubes as described above, except that *n*-decane was not present in the lithium reagent. The solution was warmed to −28° (carbon tetrachloride slush) and 2.4–3.0 equiv of anhydrous dioxane/equiv of copper or silver compound was added to the solution using a 50-μl Hamilton syringe. The white precipitate which formed was shaken several times at −28° over 30 min and then centrifuged in a precooled centrifuge bucket at ∼−50° for 0.5–1.0 min to compact the precipitate. The supernatant solution was transferred through a cannula to another centrifuge tube at −28°. A known amount of *n*-decane (internal glpc standard) was added with a 50-μl syringe. Flame photometric analysis of these solutions after decomposition typically showed that 0.1–0.005 equiv of $Li^+$/equiv of organocopper reagent was left in the solution by this procedure.

**Composition of the Tri-*n*-butylphosphine Complexes of Vinylic Copper(I) and Silver(I) Compounds.** These organometallic compounds were too unstable thermally for traditional isolation and combustion analysis to be practical. Instead, approximate determinations of their empirical compositions were carried out by allowing their solutions from which lithium ion had been removed to decompose thermally (*vide infra*) and by subsequently analyzing the resulting mixtures for metal, phosphine, lithium ion, and vinylic groups.

Metallic copper formed in the decomposition of organocopper compounds was transferred to a sintered glass crucible, washed with ether and water, and oxidized to copper(II) with *ca.* 15 ml of 50% nitric acid. The resulting solution was filtered and analyzed using the Kuehnel–Hagen volumetric procedure.[67]

Silver metal formed from organosilver reagents was transferred to a sintered glass crucible, washed with ether and water, and oxidized to silver(I) with *ca.* 15 ml of 50% nitric acid. The resulting solution was filtered through the sintered glass crucible and the crucible was washed with water. Silver was determined by addition of saturated aqueous sodium bromide solution and gravimetric determination of the resulting silver bromide.

Tri-*n*-butylphosphine was determined by spectrophotometric analysis of its adduct with carbon disulfide. The red adduct of tri-*n*-butylphosphine with carbon disulfide has $\lambda_{max}$ 362 mμ with a weaker absorption at 498 mμ. Since the adduct does not obey Beer's law in ethanol solution, tri-*n*-butylphosphine and carbon disulfide are probably in equilibrium with their adduct.



$$Bu_3P + CS_2 \underset{}{\overset{k_{eq}}{\rightleftharpoons}} Bu_3P^+{-}C(=S)S^-$$

$$K_{eq} = [Bu_3PCS_2]/[Bu_3P][CS_2]$$

Hence

$$OD = \epsilon[Bu_3PCS_2] =$$

$$\epsilon\left(\frac{K_{eq}[CS_2]}{1 + K_{eq}[CS_2]}\right)([PBu_3] + [Bu_3PCS_2])$$

Thus, the apparent observed extinction coefficient for a solution containing tri-*n*-butylphosphine in equilibrium with its carbon disulfide adduct will be

$$\epsilon_{obsd} = \epsilon\left(\frac{K_{eq}[CS_2]}{1 + K_{eq}[CS_2]}\right)$$

and will be constant if $[CS_2]$ is constant. When a $3.4 \times 10^{-2}$ *M* solution of carbon disulfide in ethanol (OD = 1.58 at 315 mμ; OD = 0.00 at 362 mμ) was used for all dilutions of tri-*n*-butylphosphine, an apparent extinction coefficient of $\epsilon_{obsd} = 5.7 \times 10^3$ $M^{-1}$ $cm^{-1}$ was determined at 362 mμ. This value did not vary with the concentration of tri-*n*-butylphosphine.

In a typical analysis for tri-*n*-butylphosphine in the thermal decomposition of vinylic copper(I) and silver(I) compounds, *ca.* 5 μl of the decomposition solution was added to 10 ml of the stock solution of carbon disulfide in ethanol. The optical density of the solution at 362 mμ was determined on a Zeiss spectrophotometer and the concentration of tri-*n*-butylphosphine was calculated.

Lithium ion was determined in the organometallic solutions by extraction of a 1-ml aliquot of the solution with 5 ml of water, followed by flame photometric analysis. The limit of detection in these analyses was *ca.* 1 ppm lithium ion with an accuracy of ±20%.

Since previous examination of the products of the thermal decomposition of these vinylic copper and silver reagents had established that their conversion to the corresponding butadienes was essentially quantitative (Table I), the above analyses were referenced to the yields of dienes determined by glpc analysis. Typical analyses are shown in Table III.

**Table III.** Normalized Empirical Compositions of Vinylic Copper(I) and Silver(I) Compounds[a]

| $RMPBu_3$ | R[b] | M | $PBu_3$ | Li |
|---|---|---|---|---|
| *cis*-Propenylcopper(I)·$PBu_3$ | 1.00 | 0.91 | 1.2 | 0.005 |
| *cis*-Propenylsilver(I)·$PBu_3$ | 1.00 | 0.94 | 1.1 | 0.004 |
| *trans*-Butenylcopper(I)·$PBu_3$ | 1.00 | 0.84 | 1.2 | 0.06 |
| *trans*-Butenylsilver(I)·$PBu_3$ | 1.00 | 0.86 | 1.1 | 0.11 |

[a] Data are for 0.1 *N* ether solutions. [b] Assumed.

**Thermal Decomposition of Tri-*n*-butylphosphine Complexes of Vinylic Copper(I) and Silver(I) Compounds.** *Ca.* 0.1 *N* solutions of the tri-*n*-butylphosphine complexes of the vinylic copper(I) and silver(I) compounds were thermally decomposed to metallic mirrors and dimers at ambient temperature within 4–6 hr. (The *cis*-propenyl(tri-*n*-butylphosphine)copper(I) was decomposed in a sealed tube on a steam bath at approximately 90° to minimize isomerization of copper compound prior to decomposition.) At 0°, the compounds decomposed over several days. Although no quantitative rates were measured, it was noted that the copper compounds were more stable than the silver compounds, and that the butenyl compounds were more stable than the propenyl compounds. The solutions were analyzed for hydrocarbon products by glpc (column C).

**Reaction of *cis*-1-Propenyl(tri-*n*-butylphosphine)copper(I) with Iodine.** A lithium halide free solution of *cis*-1-propenyl(tri-*n*-butylphosphine)copper(I) at −28° (2.4 ml, 0.12 *N*, 0.29 mmol, 90.5% cis) was transferred through a cannula into a centrifuge tube containing a cold solution of iodine in ether (2.0 ml, 0.20 *N*; 0.40 mmol). The ether solution became clear immediately and a white solid (possibly a product of the reaction of iodine with tri-*n*-butylphosphine) precipitated.

The solution was analyzed by glpc (column C, 40°). The products obtained were *cis,trans*-2,4-hexadiene (2%), *cis,cis*-2,4-hexadiene (8%), *cis*-1-iodo-1-propene (81.6%), and *trans*-1-iodo-1-propene (7.4%). The iodopropenes were identified by comparison of

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(67) M. Dozinel, "Modern Methods of Analysis of Copper and its Alloys," S. L. Man, translator, Elsevier, Amsterdam, 1963, p 88.

glpc retention times and ir spectra with an authentic sample[68] and with *cis*-1-iodo-1-propene (98.7% cis) prepared by reaction of *cis*-1-propenyllithium (97.9% cis) with iodine.

**Decomposition of *cis*-2-Butenyl(tri-*n*-butylphosphine)silver(I) in the Presence of 1,2-Dibromoethane.** When a solution of *cis*-2-butenyl(tri-*n*-butylphosphine)silver(I) containing 1.3 equiv of [AgI·PBu$_3$] and approximately 2 equiv of dibromoethane was decomposed at room temperature, the products obtained were *cis,cis*- and *cis,trans*-3,4-dimethyl-2,4-hexadiene in a ratio of 92:8 and a combined yield of 65%. No 2-bromo-2-butene could be detected.

**Tetramethyldiphosphine** was prepared according to the procedure of Maier.[69] Tri-*n*-butylphosphine (50 g, 0.247 mol) and tetramethyldiphosphine disulfide[70] (20 g, 0.118 mol) were heated together under a nitrogen atmosphere at 170° for 3 hr. The product was distilled from the reaction mixture using a bath temperature of 240° at 100–140° (760 mm), and at 40–50° (25 mm). A total of 10 g (70%) of extremely pyrophoric liquid was obtained, whose nmr spectrum agreed with that reported.[71]

**1,1,1-Tris(dimethylphosphinomethyl)ethane.** Approximately 350 ml of anhydrous tetrahydrofuran was added to a 1-l. three-necked flask which had been flamed out in a stream of nitrogen. Tetramethyldiphosphine (41.5 g, 0.34 mol) was added by cannula. Potassium metal (27 g, 0.69 g-atom) was added in small pieces and the mixture was stirred for 20 hr to give a red solution of potassium dimethylphosphide. The solution was decanted from the excess potassium metal into a 500-ml three-necked flask and cooled in an ice–methanol bath. 1,1,1-Tris(chloromethyl)ethane[72] (34.5 g, 0.194 mol) was added slowly to the cold solution, and the reaction mixture was refluxed for 1 hr. Water was added to destroy any remaining organometallic species, and the reaction mixture was poured into 700 ml of water in a separatory funnel under a nitrogen atmosphere. The tetrahydrofuran layer was separated and protected from atmospheric oxygen. The aqueous layer was saturated with sodium chloride and extracted with two 100-ml portions of hexane. The combined organic layers were washed with saturated aqueous sodium chloride solution, dried (MgSO$_4$), and concentrated. Distillation through a platinum spinning band column at reduced pressure gave a colorless air-sensitive liquid, 1,1,1-tris(dimethylphosphinomethyl)ethane (22.5 g, 51%), bp 93° (0.6 mm). This compound was characterized by its nmr spectrum (benzene), which had peaks at $\delta$ 1.68 (d, 6, P-C$H_2$, $J$ = 3.3 Hz), 1.10 (s, 3, C$H_3$), and 0.93 (d, 18, P-C$H_3$, $J$ = 3.4 Hz).

**Reaction of CuI with CH$_3$C[CH$_2$P(CH$_3$)$_2$]$_3$.** A suspension of copper(I) iodide (3.17 g, 16.6 mmol) was stirred overnight with 1,1,1-tris(dimethylphosphinomethyl)ethane (4.25 g, 16.8 mmol) in 50 ml of ether. The white solid which formed was washed with ether and dried in a vacuum oven. The solid was insoluble in water, methylene chloride, benzene, and acetone. It began decomposing at 220° and became liquid at 310°. The solid did not react with *n*-butyllithium at room temperature.[73]

*Anal.* Calcd for C$_{11}$H$_{27}$PCuI: C, 29.83; H, 6.15. Found: C, 30.88; H, 6.55.

**Decomposition of *trans*-2-Butenylcopper(I) in the Presence of 1,1,1-Tris(dimethylphosphinomethyl)ethane.** A 0.11 *N* solution of *trans*-2-butenyl(tri-*n*-butylphosphine)copper(I) in ether was prepared at −78° from [CuIPBu$_3$]$_4$ (0.444 g, 1.13 mequiv) and *trans*-2-butenyllithium (1.20 ml, 0.94 *N*, 1.13 mequiv, 90.6% trans). Lithium salts were precipitated by the addition of 225 $\mu$l of dioxane. A portion of the supernatant solution (2.5 ml, 0.28 mmol) was decanted into an 8-mm test tube. Addition of 1,1,1-tris(dimethylphosphinomethyl)ethane (70 mg, 0.28 mmol) gave a solution containing a gummy oil. The tridentate ligand greatly stabilized the copper compound: decomposition required heating the sample for 18 hr at 80° in a sealed tube. Glpc analysis showed 50.5% *trans,trans*- and 11.9% *cis,trans*-3,4-dimethyl-2,4-hexadiene (90.4% trans groups). The gummy oil was rich in organocopper compound since the solution decanted from the oil gave only an 18% yield of dimer.

**Uncomplexed Vinylic Copper(I) and Silver(I) Compounds.** The cis and trans isomers of 2-butenyl- and -1-propenylcopper(I) and -silver(I) were prepared by the following procedure. Silver(I) iodide (Bader Reagent) or copper(I) iodide (Fischer Reagent) was added to a 40-ml centrifuge tube containing a stirring bar. The metal iodides were dried by flaming the tube under a nitrogen atmosphere. (The metal iodides decompose if heated excessively.) Several milliliters of anhydrous ethyl ether were added and the tube was cooled to −78°. The appropriate lithium reagent (normally, less than 1 equiv/equiv of copper or silver) was added by cannula. The solution was diluted to *ca.* 0.1 *N* with ethyl ether. No reaction occurred at −78°. However, when the mixture was stirred at −28° for approximately 30 min, reaction occurred accompanied by dissolution of the metal iodide. The color of the resulting solutions was not reproducible and ranged from light yellow through blue-green, to dark red. *cis*-1-Propenylsilver(I) was exceptional in that an orange to tan solid was produced in addition to dissolved *cis*-propenylsilver(I).

Thermal decomposition and analysis of these compounds were carried out as described for the corresponding phosphine complexes.

**Identification of Isomeric 2,4-Hexadienes.** Unsubstituted *cis,-cis*-, *cis,trans*-, and *trans,trans*-2,4-hexadiene produced in the thermal decompositions were characterized by collection from glpc and comparison of ir spectra and relative glpc retention times with those reported by Bartlett;[74] the ir spectra and retention times of these materials also agreed with compounds isolated from a mixture of isomers available from Columbia Organics, Inc.

**3,4-Dimethyl-3,4-hexanediol.** A solution of mercuric chloride (21 g, 0.08 mol) in 2-butanone (126 g, 1.75 mol) was added slowly to magnesium turnings (20 g, 0.83 g-atom) in 200 ml of benzene until the reaction mixture began to reflux spontaneously. The remainder of the solution of mercuric chloride in 2-butanone was added over a 45-min period at such rate that a vigorous reflux was maintained. After the reaction mixture had been refluxed for an additional 1.5 hr, 40 ml of water was added and the mixture was heated to reflux for 30 min. The gray solid which formed upon addition of water was separated from the benzene solution by filtration and returned to the reaction flask, together with 175 ml of fresh benzene. This mixture was refluxed and filtered. The benzene filtrates were combined, concentrated, and distilled under reduced pressure to give 34.7 g (31.7%) of 3,4-dimethyl-3,4-hexanediol, bp 108–109° (19 mm) [lit.[75] 98–106° (6 mm)].

***cis,cis*-3,4-Dimethyl-2,4-hexadiene** prepared from 3,4-dimethyl-3,4-hexanediol by the method of Macallum and Whitby[76] had bp 136°, $n^{23}$D 1.4740 (lit.[77] bp 134–135°), and was >99% pure by glpc. The nmr spectrum (CCl$_4$) of this isomer consisted of peaks at $\delta$ 5.21 (q, 2, $J$ = 6.5 Hz), 1.68 (s, 6), and 1.42 (d, 6, $J$ = 6.5 Hz); each of these peaks was further split ($J \sim$ 1 Hz) into *ca.* four lines. The ir spectrum of this and the other 3,4-dimethyl-2,4-hexadiene isomers all have absorption above 3000 cm$^{-1}$ for vinyl C–H stretching vibrations, but are most readily distinguishable in the region between 1100 and 800 cm$^{-1}$. The cis,cis isomer had absorptions (CS$_2$) at 795, 815, 835, 875, 890, 995, 1020, 1050, and 1650 cm$^{-1}$. The uv spectrum of this material has $\lambda_{max}$ (ethanol) 234 m$\mu$ ($\epsilon$ 17,000).

***cis,trans*-3,4-Dimethyl-2,4-hexadiene** was isolated from the dehydration of 3,4-dimethyl-3,4-hexanediol by collecting a fraction from glpc. A boiling point of 113° was obtained using a micro boiling point apparatus (lit.[77] bp 113–114°). This isomer had nmr (CCl$_4$) which appeared to be approximately a superposition

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[68] We are indebted to Professor R. C. Neuman, Jr. (University of California at Riverside), for providing an authentic sample of *cis*- and *trans*-1-iodo-propene: R. C. Neuman, Jr., *J. Org. Chem.*, **31**, 1852 (1966).

[69] L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 275 (1962).

[70] H. Niebergall and B. Langenfeld, *Chem. Ber.*, **95**, 64 (1962).

[71] E. G. Finer and R. K. Harris, *Mol. Phys.*, **12**, 457; **13**, 65 (1967); R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).

[72] W. H. Urry and J. R. Eiszner, *J. Amer. Chem. Soc.*, 74, 5822 (1952).

[73] A different complex was formed when a suspension of copper(I) iodide (0.184 g, 0.97 mmol) in 10 ml of ether was stirred with 1,1,1-tris(dimethylphosphinomethyl)ethane (0.21 g, 0.92 mmol) for only 1 hr. The mixture was filtered to give a white solid, mp 149–151°, which was soluble in ethanol, acetone, and benzene. This lower melting complex is thought to be monomeric while the higher melting complex is thought to be polymeric.

[74] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

[75] I. V. Gostunskaya, E. A. Krasnyanska, and B. A. Kazansky, *Zh. Obshch. Khim.*, **25**, 1488 (1955).

[76] A. D. Macallum and G. S. Whitby, *Trans. Roy. Soc. Can.*, **22**, 39 (1928); *Chem. Abstr.*, **22**, 2080 (1928).

[77] R. Criegee and K. Noll, *Justus Liebigs Ann. Chem.*, **627**, 1 (1959). The current *Chemical Abstracts* name for this compound is (*E*,*E*)-3,4-dimethyl-2,4-hexadiene,[78] and not the cis,cis designation used by Criegee and repeated here. We have used Criegee's nomenclature, since it emphasizes the retention of stereochemistry in the preparation of *cis,cis*-3,4-dimethyl-2,4-hexadiene from *cis*-2-butenyllithium.

[78] J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, 90, 509 (1968).

of the spectra of the two symmetrical isomers with peaks at $\delta$ 5.12 (q, 2, $J \sim 7$ Hz with further fine splitting), 1.42–1.75 (m, 12); ir ($CS_2$) 815, 835, 875, 945, 1000, 1030, 1040, 1055, and 1085 cm$^{-1}$; the uv spectrum showed only end absorption $\lambda$ (ethanol) 230 m$\mu$ ($\epsilon$ 2900).

*trans,trans*-**3,4-Dimethyl-2,4-hexadiene** was prepared by thermal decomposition of 2-butenylsilver(I) and purified by glpc (column C).[79] Its structure was assigned on the basis of spectra and analysis, and by elimination of the cis,trans and cis,cis isomers as possible structures: nmr ($CCl_4$) $\delta$ 5.48 (q, 2, $J = 6.5$ Hz), 1.72 (s, 6), and 1.67 (d, 6, $J = 6.5$ Hz); ir ($CS_2$) 810, 1020, 1070 cm$^{-1}$; uv, end absorption $\lambda$ (ethanol) 230 m$\mu$ ($\epsilon$ 1200).

*Anal.* Calcd for $C_8H_{14}$: C, 87.19; H, 12.81. Found: C, 87.07; H, 12.82.

**Reactions of *trans*-Propenyllithium with Transition Metal Halides.** The same general procedure was used for each reaction. Anhydrous transition metal halide (50–100 mg) was transferred into a tared flame-dried 12-ml stoppered centrifuge tube in a nitrogen-filled glove bag, the tube was removed from the bag, and the weight of the salt determined by weighing the tube. The tube was flushed with nitrogen, the salt suspended in ether or THF ($\sim$2–10 ml, sufficient to result in a solution $\sim$0.1 *M* in metal ion), and the suspension cooled to −78°. A measured volume of an ether solution of *trans*-propenyllithium ($\sim$0.1–0.2 *N*) containing *n*- decaneas internal glpc standard was transferred by forced siphon through a cannula into the suspension of transition metal salt. The centrifuge tube containing the reaction mixture was shaken or stirred at −78° for 5–15 min, then allowed to stand at room temperature for 6–18 hr. The reaction mixtures were usually hydrolyzed with 0.2 ml of water before analysis by glpc on column C.

**Reduction of 2-Bromo-2-butene with Tri-*n*-butyltin Hydride.** *cis*-2-Bromo-2-butene (0.883 g, 6.54 mmol, 91% cis), *cis*-2-pentene (Phillips Petroleum, 0.170 g, 95% cis), and *n*-heptane (0.212 g, glpc internal standard) were placed in a 5-ml flask. Samples could be taken by inserting a syringe needle through a serum stopper and a stopcock connected to the flask. Tri-*n*-butyltin hydride[80] (2.247 g, 7.72 mmol) was added to the *cis*-2-bromo-2-butene by syringe. No effort was made to flush air from the system whose dead volume was *ca.* 4 ml.

Samples were withdrawn at intervals and analyzed on either column C at 65° or on a 6-ft 10% benzylnitrile–silver nitrate column[81] at −15°. After 1 hr, the cis–trans ratio of 2-butenes formed was 33.5:66.5. After 17 hr, 48% of *cis*-2-bromo-2-butene had been converted to 2-butene with a 33.5:66.5 cis–trans ratio, and 45% of the *cis*-2-bromo-2-butene (86% cis) had not reacted. After 2-hr reaction, the cis–trans ratio of 2-pentene was still 95:5.

Similarly, *trans*-2-butene (1.077 g, 7.98 mmol, >99% trans) was reduced with tri-*n*-butyltin hydride (2.255 g, 7.75 mmol) at room temperature in the presence of *cis*-2-pentene (0.109 g, 95% cis) and *n*-heptane (0.155 g, glpc internal standard). After 1 day, 28% of the *trans*-2-bromo-2-butene had been converted to a 36:64 mixture of *cis*- and *trans*-2-butene, while 69% of the *trans*-2-bromo-2-butene had not reacted. Neither *trans*-2-bromo-2-butene nor *cis*-2-pentene were isomerized under the reaction conditions after 1 day.

**Reaction of Tri-*n*-butyltin Hydride with *cis*-2-Butenyl(tri-*n*-butylphosphine)copper(I).** A 0.15 *N* solution of *cis*-2-butenyl(tri-*n*-phosphine)copper(I) (0.96 mmol) from which lithium halide had been removed as a dioxane precipitate was cooled to −78° and tri-*n*-butyltin hydride (200 $\mu$l; 0.756 mmol) was added to give a deep red solution. Upon warming to room temperature, the solution became black. *n*-Heptane and *n*-decane were added to the decomposed solution for use as glpc standards. The solution was analyzed by glpc on column C and on a 6-ft 10% benzylnitrile–silver nitrate column. The products were 2-butene (0.38 mmol, 40% yield, 78% cis) and *cis,cis*-2,4-hexadiene (0.05 mmol, 11% yield).

In a similar reaction, *cis*-2-butenyl(tri-*n*-butylphosphine)copper(I) (0.84 mmol), tri-*n*-butyltin hydride (0.76 mmol), and *trans*-2-bromo-2-butene (0.96 mmol) were mixed at −78° and warmed to room temperature for several hours. Analysis showed that the solution contained 2-butene (0.40 mmol, 47% yield, 66% cis), 3,4-dimethyl-2,4-hexadienes (0.05 mmol, 12% yield, 85% cis isomeric purity), and *trans*-2-bromo-2-butene (0.83 mmol).

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[79] The glpc retention times of the three isomeric 3,4-dimethyl-2,4-hexadienes on this column at 30° under comparable conditions were: trans,trans, 8.6 min; cis,trans, 12.2 min; cis,cis, 27.0 min.

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# Reactions of Iodine with Olefins. I. Kinetics and Mechanism of Iodine Addition to Pentene Isomers[1]

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**Abstract:** The kinetics of the addition of iodine to 1-pentene, *cis*- and *trans*-2-pentenes, 2-methyl-1-butene, and 2-methyl-2-butene have been studied using $^{131}$I-labeled iodine. The data support the view that the stereospecific addition is the result of an attack of an iodine atom or molecule on a charge-transfer complex between the olefin and the corresponding iodine molecule or atom. For 1-pentene at 25° it was found that the charge-transfer equilibrium constant $K_c$ is $1.0 \times 10^{-1}$ mol$^{-1}$ l. The rate constant, $k_1$, for the reaction of the iodine atom or molecule with the complex was found to be $2.38 \times 10^{-1}$ min$^{-1}$ mol$^{-1/2}$ l.$^{1/2}$. It was also found that the vicinal diiodides, the products of the addition, were reasonably stable in the dark, if care was taken to remove all excess iodine.

Sumrell, *et al.*,[2] and Skell and Pavlis[3] have reported that, contrary to information commonly found in the literature,[4–7] iodine readily adds to 1-pentene and $C_4$ alkenes, respectively. They reported that in the liquid phase and ordinary room illumination the reac-

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