

Preparation and Thermal Decomposition of *n*-Alkyl(tri-*n*-butylphosphine)silver(I) Reagents¹

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Abstract: Several primary and secondary alkyl(tri-*n*-butylphosphine)silver(I) compounds have been prepared by reaction between the corresponding organolithium or -magnesium reagents and iodo- or bromo(tri-*n*-butylphosphine)silver(I) in diethyl ether at -78° . The thermal decomposition of these substances occurs rapidly at temperatures between -50 and 0° to yield hydrocarbon products derived from the alkyl group, silver(0), and tri-*n*-butylphosphine. Examination of the hydrocarbon products of the thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)silver(I) (**1**) and comparison of these products with those obtained on photolytic decomposition of **1** and on thermal and photolytic decomposition of **1** in the presence of 2,2,6,6-tetramethylpiperidoxyl radical (TMPO) indicate that thermal decomposition takes place predominantly by a process in which carbon-carbon bond formation, generating octane, is concerted with carbon-silver bond breaking. Intermediate free *n*-butyl radicals and silver(I) hydride are not important intermediates in this decomposition, although radicals are strongly implicated in reactions of **1** in the presence of light or TMPO. The thermal decomposition of *sec*-butyl(tri-*n*-butylphosphine)silver(I) occurs by a different path, possibly involving silver(I) hydride elimination.

This paper describes the preparation and characterization of several *n*-alkyl(tri-*n*-butylphosphine)silver(I) complexes and an investigation of their thermal decomposition. These substances were examined as part of a program exploring the factors that influence the thermal stability of transition metal alkyls⁴ and are of particular interest because the most common pathway for the thermal decompositions of organometallic compounds, the β elimination of metal hydride, is not important in their decomposition (*vide infra*). Studies of the thermal decomposition of substances obtained by reaction between silver salts and organo-magnesium,^{5,6} -boron,⁷ and -lead⁸ reagents have been reported previously;⁹ organosilver(I) compounds have been presumed to be intermediates in these reactions, although they have not been characterized. The results of these studies are not consistent with one another, and their interpretation is complicated by the fact that they involve heterogeneous reaction mixtures. Our efforts have concentrated on phosphine-complexed primary alkylsilver(I) reagents, since these substances can be prepared and convincingly characterized and since their thermal decomposition can be studied in homogeneous solution.

Results and Discussion

The Yields of 1-Butene and *n*-Butane Formed on Thermal Decomposition of *n*-Butyl(tri-*n*-butylphosphine)-

(1) Supported by the National Science Foundation, Grants GP-28586X and GP-14247.

(2) Texaco Predoctoral Fellow, 1971-1973.

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(4) Review: P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973).

(5) M. Tamura and J. Kochi, *J. Amer. Chem. Soc.*, **93**, 1483 (1971); M. Tamura and J. Kochi, *Bull. Chem. Soc. Jap.*, **45**, 1120 (1972).

(6) K. Yamamoto, K. Nakanishi, and K. Kumada, *J. Organometal. Chem.*, **7**, 197 (1967).

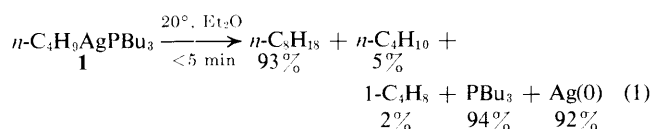
(7) H. C. Brown and C. H. Snyder, *J. Amer. Chem. Soc.*, **83**, 1002 (1961), and references cited therein.

(8) C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, 4162 (1960); C. E. H. Bawn and R. Johnson, *ibid.*, 3923 (1960).

(9) The organometallic chemistry of silver(I) has been reviewed: C. D. M. Beverwijk, G. J. M. Van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev., Sect. A*, **5**, 215 (1970); G. Bahr and P. Burba in "Methoden der Organischen Chemie," Vol. XIII/I, 4th ed, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1970, p 767 ff.

silver(I) (1**) Establish That These Products Are Not Formed Either by an Intermediate Silver(I) Hydride or by Combination and Disproportionation of Free *n*-Butyl Radicals.** Organosilver reagents were prepared by allowing the appropriate alkylsilver(I) or Grignard reagent to react with one stoichiometric equivalent of tetrakis(bromo- or iodo(tri-*n*-butylphosphine)silver(I)) at -78° in diethyl ether; reactions were rapid and quantitative. Solutions of *n*-alkyl(tri-*n*-butylphosphine)silver(I) reagents were colorless when prepared carefully, but they discolored rapidly at temperatures above -50° and on exposure to oxygen. Characterization was accomplished by analysis of their solutions for the constituent components of the organometallic compounds following dioxane precipitation of lithium halide, using techniques described in the Experimental Section: for *n*-butyl(tri-*n*-butylphosphine)silver(I) (**1**), the substance of principal interest in this work, these analyses (normalized to a value of unity for the butane produced on hydrolysis) indicated an empirical composition of $(C_4H_9)_{1.00}Ag_{0.92 \pm 0.1}(P(C_4H_9)_3)_{0.91 \pm 0.1}$, with less than 3.5% lithium ion remaining in solution.

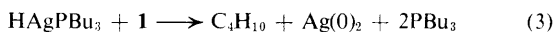
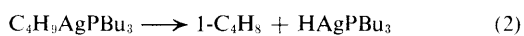
Thermal decomposition of a 0.10 *N* solution of **1** in diethyl ether was complete after 5 min at 20° , yielding octane and small quantities of butane and 1-butene as hydrocarbon products; 2-butene was not detected (eq 1).



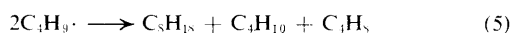
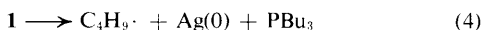
Silver metal and unchanged tributylphosphine could also be isolated. The octane, butane, and butene isolated following thermal decomposition of **1** containing deuterium in the tri-*n*-butylphosphine ligands contained no detectable deuterium; thus, the *n*-butyl groups of the phosphine are not incorporated into the hydrocarbon products. Control experiments outlined in the Experimental Section established that no more than 2-3% of the observed butane, and none of the 1-butene, could be attributed to adventitious hydrolysis of **1**, or to hydro-

carbons in the *n*-butyllithium solution from which **1** was prepared. The product distribution was insensitive to a 40° change in the temperature at which the decomposition was carried out, to the presence of lithium iodide in the solution, or to low levels of ultraviolet and visible light.

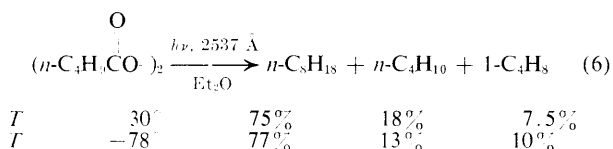
The observation that the yield of butene is much less than that of octane in the decomposition of **1** is sufficient evidence to exclude mechanisms that require the hydrocarbon products to be generated either by elimination and possible subsequent reaction of silver(I) hydride (eq 2 and 3) or by combination and disproportionation



of *n*-butyl radicals (eq 4 and 5). The former mechanism



clearly leads to at least a 50% yield of butene;^{10–12} the latter mechanism can be discounted because it would require that the ratio of the rate constants for disproportionation and combination of *n*-butyl radicals, k_d/k_c , be unreasonable in magnitude. This ratio was established experimentally for *n*-butyl radicals in diethyl ether by examining the hydrocarbon products formed on photolysis of dialkyl peroxide; representative results are summarized for two temperatures in eq 6. These experiments indicate that $k_d/k_c(30^\circ) = 0.20 \pm$



0.01 and $k_d/k_c(-78^\circ) = 0.25 \pm 0.01$, in good agreement with values reported for related systems.^{13–15}

With the two classes of mechanisms represented by eq 1–4 eliminated as major contributors to the thermal decomposition of **1**, two plausible alternatives remain. The first generates octane in a formal four-center transition state by carbon–carbon bond formation between two butyl groups present in a silver cluster (eq 7).^{16–18} This type of reaction has some precedent in

(10) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972), and references cited therein.

(11) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 1426 (1970).

(12) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968); R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968); C. A. Tolman and J. P. Jesson, *Science*, **181**, 501 (1973).

(13) W. E. Morganroth and J. G. Calvert, *J. Amer. Chem. Soc.*, **88**, 5387 (1966); P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 2551 (1963).

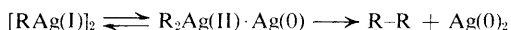
(14) A. P. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968).

(15) R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 4395 (1970).

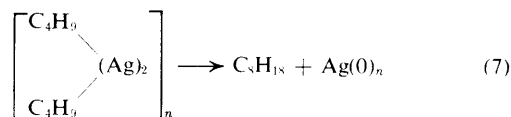
(16) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

(17) A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968); **93**, 247 (1971); A. Cairncross, H. Omura, and W. A. Sheppard, *ibid.*, **93**, 248 (1971).

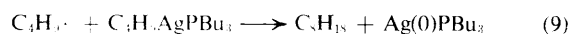
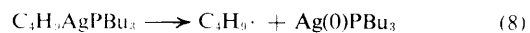
(18) This reaction could reasonably occur by migration of alkyl groups across the surface of an alkylsilver aggregate or by a disproportionation reaction. Little is known about the details of the struc-



tures of organosilver compounds in solution; aggregation is, however, common in the solid: cf. B. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, **20**, 502 (1966); F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1828 (1937).

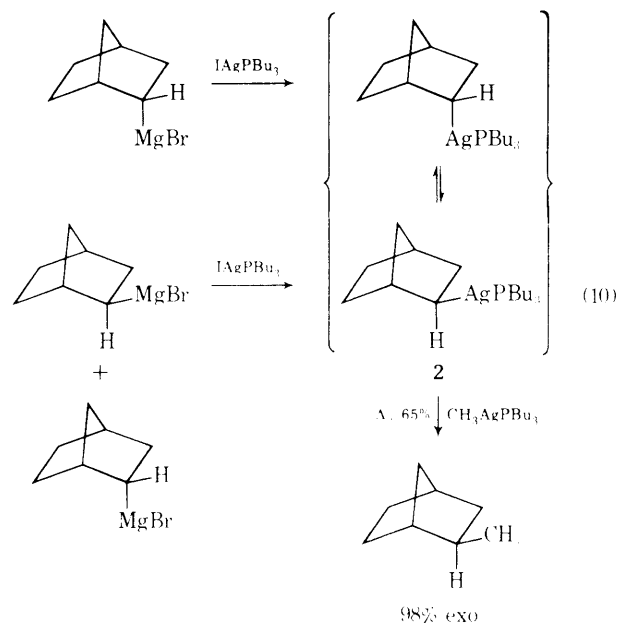


the thermal decomposition of vinylic and aromatic copper(I) compounds.^{16,17} The second would involve initial homolytic scission of a carbon–silver bond with formation of an *n*-butyl radical, followed by reaction of this radical with undecomposed silver compound to yield octane (eq 8 and 9). The low yield of butane pro-



duced in the thermal decomposition of **1** places an important limitation on the reactions represented by eq 9, viz., that the rate of reaction between the butylsilver moiety and the butyl radical must be very fast, in order for this reaction to dominate the rapid abstraction of a hydrogen atom from diethyl ether by the butyl radical.¹⁹ Thus, the central mechanistic distinction to be made concerning the thermal decomposition of **1** revolves on the question of the intermediacy of free *n*-butyl radicals, viz., does the conversion of **1** to octane take place by a mechanism in which carbon–carbon bond formation is synchronous with carbon–silver bond breaking (eq 7), or does it occur by a (necessarily very rapid) reaction between an initially formed *n*-butyl radical and an undecomposed butylsilver moiety (eq 8 and 9)?

Stereochemical Tests and Free Radical Scavengers Are Not Useful in Attempts to Detect Free Alkyl Radicals in the Thermal Decomposition of Alkyl(tri-*n*-butylphosphine)silver(I) Reagents. Attempts to detect a free radical intermediate in the conversion of alkylsilver reagents into coupled hydrocarbon by examining the stereochemical course of the cross dimerization between *endo*-2-norbornyl(tri-*n*-butylphosphine)silver(I) (*endo*-**2**) and methyl(tri-*n*-butylphosphine)silver(I) were frustrated by the observation that **2** epimerized at a



rate competitive with its thermal decomposition. Similarly, attempts to detect radicals through the

(19) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966; C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967); A. L. Williams, E. A. Obberight, and J. W. Brooks, *J. Amer. Chem. Soc.*, **78**, 1190 (1956).

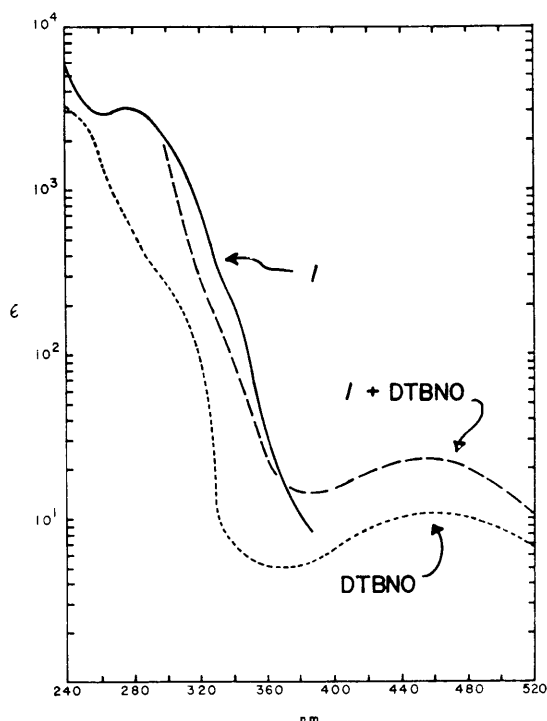
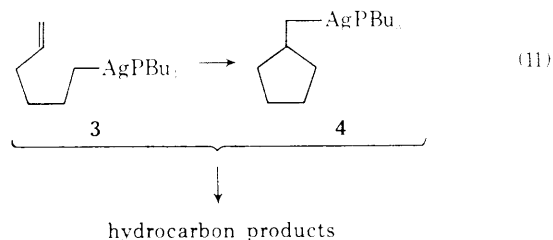


Figure 1. Spectra of **1** (—), DTBNO (···), and a mixture of **1** and DTBNO (---) in diethyl ether solution at ca. -70° . The nominal concentration of **1** and of DTBNO in each spectrum was 10^{-4} M. However, loss of organosilver reagent in handling at these dilutions is such that this concentration estimate is only qualitative.

characteristic^{15, 20} cyclization of 5-hexenyl radical to cyclopentylcarbonyl radical failed when it was established that 5-hexenyl(tri-*n*-butylphosphine)silver(I) (**3**) cyclized to cyclopentylcarbonyl(tri-*n*-butylphosphine)silver(I) (**4**) at a rate competitive with its conversion to hydrocarbon products (eq 11).²¹



Efforts to scavenge free *n*-butyl radicals from the thermal decomposition of **1** directly also failed in their primary objective. Chemically reactive scavengers (iodine, oxygen, mercaptans, tin hydrides, and phenols) react directly with the organosilver reagents. Chemically reactive hydrocarbons (styrene and butadiene) may be capable of influencing the reactivity of the organosilver compounds by coordination or of inducing radical behavior.²²

(20) J. F. Garst and F. E. Barton, *Tetrahedron Lett.*, 587 (1969); C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, **94**, 6059 (1972).

(21) The extent of isomerization could be followed by quenching solutions containing **3** and **4** with iodine. Interestingly, the distribution of hydrocarbon products produced in the thermal decomposition of **3** is very sensitive to the presence of magnesium salts, particularly magnesium iodide; lithium salts have little influence on the reaction course. This phenomenon, which has been evident in several of our studies of copper(I) and silver(I) organometallic compounds, may underlie some of the variation in products reported by different research groups working (ostensibly) with the same reagents. Details of these experiments may be found in the Ph.D. thesis of P. E. Kendall, Massachusetts Institute of Technology, 1973.

(22) Tamura and Kochi have presented data suggesting that styrene is capable of intercepting alkyl radicals without reacting with organosilver compounds.⁵

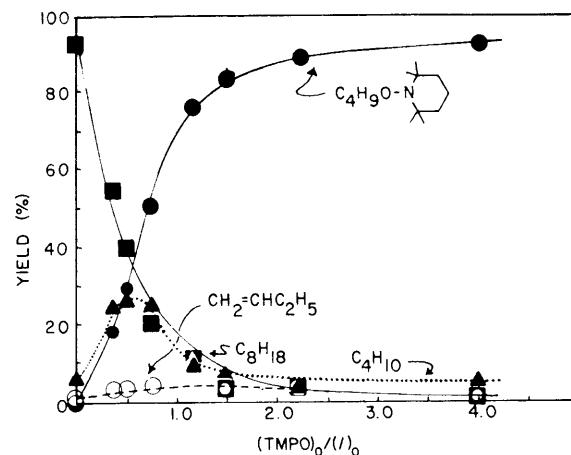
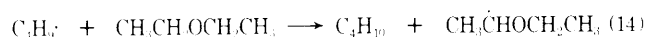
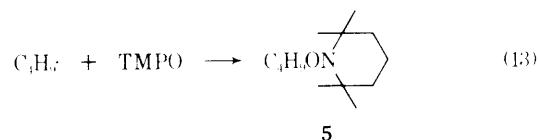
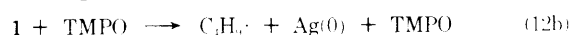
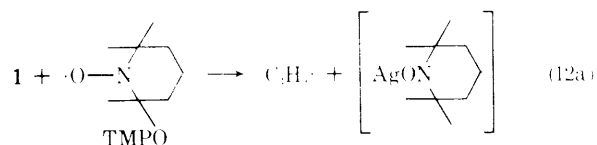


Figure 2. The products of reaction of **1** and TMPO in diethyl ether solution establish *n*-butyl radicals as intermediates.

The Products of Reactions of Nitroxyl Radicals with **1 Provide Evidence That Free *n*-Butyl Radicals Are Not Intermediates in Its Thermal Decomposition.** The stable nitroxyl radicals 2,2,6,6-tetramethylpiperidine-1-oxyl (TMPO) and di-*tert*-butylnitroxyl (DTBNO) were tested for possible use as a scavenger for alkyl radicals in the presence of organosilver reagents. DTBNO did not react with **1** at -78° for extended periods.²³ Moreover, within fairly broad experimental error, the optical spectrum of mixtures of **1** and DTBNO gave no indication of a deviation from the sum of the individual components (Figure 1). However, when **1** was allowed to decompose thermally in an ether solution containing TMPO, relatively high yields of butane and 1-butene were observed among the products (Figure 2). The variation in the yields of these products, particularly butane, with changes in the ratio $[\text{TMPO}]_0/[\mathbf{1}]_0$ provides convincing evidence that the reaction of **1** with nitroxyl radicals generates free *n*-butyl radicals (eq 12–14)²⁵ and,



by inference, that the thermal decomposition of **1** in the absence of nitroxyl radicals does *not* generate free *n*-butyl radicals.

(23) Carbon–silver bonds could be assayed in mixtures of DTBNO and **1** by bromination (see the Experimental Section). This assay does not preclude reversible complex formation.²⁴

(24) B. M. Hoffman and T. B. Eames, *J. Amer. Chem. Soc.*, **91**, 5168 (1969); A. H. Cohen and B. M. Hoffman, *ibid.*, **95**, 2061 (1973); W. Beck, K. Schmidtner, and H. J. Keller, *Chem. Ber.*, **100**, 503 (1967); W. Beck and K. Schmidtner, *ibid.*, **100**, 3363 (1967).

(25) Aryloxyl radicals have been shown to react with alkyl organometallics to give products derived from alkyl radicals: cf A. Rieker, *Angew. Chem., Int. Ed. Engl.*, **3**, 654 (1964); A. Rieker, E. Müller, and W. Beckert, *Z. Naturforsch. B*, **17**, 718 (1962). Diphenyl nitroxide reacts with Grignard reagents in a similar fashion: cf K. Maruyama, *Bull. Chem. Soc. Jap.*, **37**, 1013 (1964); see also K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley, New York, N. Y., 1971.

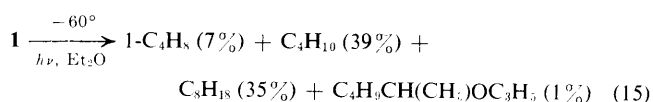
The high yield of butane observed at $[\text{TMPO}]_0/[\mathbf{1}]_0 \simeq 0.5$ can plausibly be explained by attack of *n*-butyl radicals on diethyl ether or possibly on tri-*n*-butylphosphine; butane is not generated by disproportionation of *n*-butyl radicals or by attack of butyl radicals on $\mathbf{1}$, since the yield of butene is always less than 5%. Butyl radicals must, in turn, be produced by reaction between $\mathbf{1}$ and TMPO. Whether this reaction involves radical displacement at silver and generation of a transitory silver(I) tetramethylpiperidoxide (eq 12a) or direct catalysis of the homolysis of the carbon–silver bond of $\mathbf{1}$ by TMPO in some unspecified fashion (eq 12b) is not evident from the available data. However, if eq 12a is followed, the silver tetramethylpiperidoxide must regenerate TMPO by decomposition at a rate comparable to the rate of conversion of $\mathbf{1}$ to products, since the yield of $\mathbf{5}$ is *ca.* 65% for $[\text{TMPO}]_0/[\mathbf{1}]_0 = 1$.^{26, 27}

Thus, it appears that free butyl radicals are formed by reaction of $\mathbf{1}$ and TMPO. At high concentrations of TMPO, these radicals are scavenged with high efficiency and appear as $\mathbf{5}$; at low concentrations of TMPO, some appear as $\mathbf{5}$ and some as butane. The inference that butyl radicals present in an ether solution of $\mathbf{1}$ can abstract hydrogen from some solution component other than $\mathbf{1}$ is sufficient evidence to exclude a mechanism of the type represented by eq 8 and 9 for thermal decomposition of $\mathbf{1}$ in the absence of TMPO. Any mechanism for this thermal decomposition that involves intermediate free butyl radicals can be reconciled with the observation that butane is a minor product of the decomposition only by postulating that $\mathbf{1}$ is itself so reactive toward these radicals that they never have the opportunity to attack solvent. The data of Figure 2 establish that this hypothesis is untenable. Hence eq 8 and 9 can be discarded as a description of the thermal decomposition of $\mathbf{1}$, and the remaining of the two mechanisms, that represented by eq 7 or some equivalent process in which the carbon–carbon bond of octane is formed without a radical intermediate, must describe the decomposition.

In an effort to clarify the process in which $\mathbf{1}$ reacts with TMPO, the kinetics of thermal decomposition of $\mathbf{1}$ were briefly examined, both alone and in solutions containing TMPO. These kinetics suggested that decomposition in the presence of TMPO occurred slightly faster than in its absence. However, both reactions yielded complex kinetic data that suggested that distinct reactions might dominant at different times during the decompositions, and these kinetic preliminaries were not pursued further.²⁸

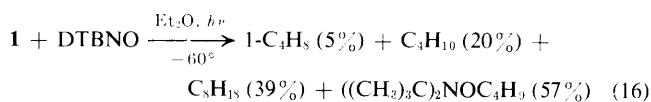
Photolysis of $\mathbf{1}$ Generates Free *n*-Butyl Radicals. To test the conclusion that the reactivity of $\mathbf{1}$ toward butyl radicals is not sufficient to suppress their reaction with ether, we wished to generate butyl radicals from $\mathbf{1}$ by some route other than thermal reaction between $\mathbf{1}$ and TMPO. For this purpose we turned to the photolysis of $\mathbf{1}$.²⁹ Decomposition of an ethereal solution originally

0.1 *N* in $\mathbf{1}$ occurs rapidly at -60° on irradiation with a 500-W medium-pressure Hanovia lamp (eq 15). This



product distribution again qualitatively implicates *n*-butyl radicals as intermediates. The high yield of *n*-butane produced, the observation that the yield of 1-butene generated is far short of that required to account for this yield of butane by disproportionation, and the generation of 2-ethoxyhexane all point to *n*-butyl radicals as intermediates. The significance of this implication for the mechanism of the thermal decomposition of $\mathbf{1}$ is the same as that reached in considering the products of the thermal reaction of $\mathbf{1}$ and TMPO; *viz.*, the photolysis of $\mathbf{1}$ appears to generate butyl radicals, and these butyl radicals are not scavenged by $\mathbf{1}$.

In an effort to confirm the intermediacy of alkyl radicals during photolysis of organosilver compounds, $\mathbf{3}$ was irradiated in diethyl ether at -78° . Iodine quenches at partial photolysis indicated that rearrangement of $\mathbf{3}$ to $\mathbf{4}$ occurred faster than the photolysis of $\mathbf{3}$ to hydrocarbon products. The photolysis of $\mathbf{1}$ in the presence of 2 equiv of DTBNO was carried out in an additional attempt to examine the behavior of butyl radicals during photolysis of $\mathbf{1}$; the product solution was shown to contain significant amounts of *O*-*n*-butyl-*N,N*-di-*tert*-butylhydroxylamine (eq 16). In order



to determine whether DTBNO was inducing radical production from $\mathbf{1}$ under these conditions, the influence of DTBNO concentration on the rate of photolysis was examined. The rate data outlined in Figure 3 establish qualitatively that the presence of DTBNO in solutions of $\mathbf{1}$ significantly increases the rate of photolysis of this substance. The observation of *O*-*n*-butyl-*N,N*-di-*tert*-butylhydroxylamine as a product in these reactions is again compatible with the conclusion reached previously, *viz.*, that butyl radicals are produced on irradiation of $\mathbf{1}$ but that both ether and DTBNO compete effectively with undecomposed $\mathbf{1}$ in reaction with these radicals.

Thermal Decomposition of *sec*-Butyl(tri-*n*-butylphosphine)silver(I) ($\mathbf{6}$) Follows a Different Mechanism Than Does Decomposition of $\mathbf{1}$. The thermal decomposition of $\mathbf{6}$, a representative *sec*-alkylsilver(I) reagent, was examined briefly for comparison with $\mathbf{1}$. The thermal stability of $\mathbf{6}$ is qualitatively lower than that of $\mathbf{1}$. The hydrocarbon products of its decomposition, and the course of the reaction, differ qualitatively from those of $\mathbf{1}$ in several respects. First, unlike those of $\mathbf{1}$, the results of thermal decomposition of $\mathbf{6}$ proved very difficult to reproduce; the products always contained 1-butene, *cis*- and *trans*-2-butene, and 3,4-dimethylhexane, but the yields of these materials varied substantially in experiments carried out using apparently identical procedures. Equation 17 summarizes products and

established method of generating organic free radicals: J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1967; A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, pp 462–471.

(26) An alternative although less likely possibility is that reductive elimination of $\mathbf{5}$ might occur from an organosilver cluster containing both silver tetramethylpiperidoxide and $\mathbf{1}$.

(27) Thermal decomposition of certain copper(I) alkoxides under conditions similar to those encountered in the reaction of $\mathbf{1}$ with TMPO generates free alkoxyl radicals in good yield: G. M. Whitesides, J. S. Sadowski, and J. Lilburn, *J. Amer. Chem. Soc.*, **96**, 2829 (1974).

(28) Kinetic studies of thermal decomposition of organocopper(I) compounds also reveal complex behavior: *cf.* K. Wada, M. Tamura, and J. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970).

(29) Irradiation of organometallic compounds provides a well-

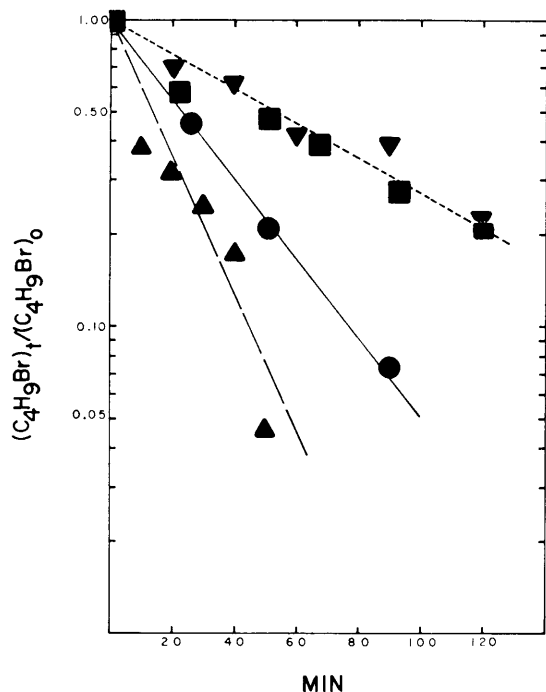
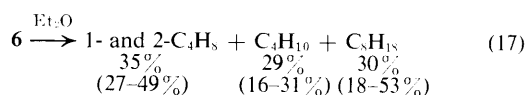


Figure 3. The rate of photolysis of **1** in ether solution is increased by the presence of DTBNO: ▼ and ■, $[1]_0 \cong 0.020\text{ N}$; ●, $[1]_0 \cong 0.02\text{ N}$, DTBNO $\cong 0.024\text{ N}$; ▲, $[1]_0 \cong 0.02\text{ N}$, DTBNO $\cong 0.044\text{ N}$.



yields obtained in a single experiment; the data in parentheses in this equation are the ranges covered by these yields over several experiments. Second, and again in contrast with results obtained with **1**, 15–20% more butenes than butane were always observed in the products.

These product distributions are particularly interesting in their suggestion that silver(I) hydride elimination³⁰ may play a part in the decomposition of **6**. The yield of butenes relative to butane is such that a quantity of hydrogen equal approximately to 0.1 equiv of hydrogen per equivalent of **6** is not accounted for in the hydrocarbon products. Attempts to detect molecular hydrogen among the products of the decomposition were unsuccessful, although small amounts of hydrogen could be detected after treatment of fully decomposed solutions with acid. Regardless of present uncertainties concerning the path of the decomposition of **6**, it is evident that this decomposition follows a significantly different course than does that of **1**.

Discussion

The evidence outlined in this paper indicates that the thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)silver(I) (**1**) takes place predominantly by conversion to *n*-octane, silver(0), and tri-*n*-butylphosphine by a process involving a concerted carbon–silver bond cleavage and carbon–carbon bond formation, without production of intermediate *n*-butyl radicals. The principal arguments leading to this conclusion are the following. First,

(30) Silver hydride has been detected in the vapor phase and inferred in solution: B. Siegel, *J. Chem. Educ.*, **38**, 496 (1961); J. Halpern, *Advan. Catal. Relat. Subj.*, **11**, 301 (1959); J. Halpern, C. Czapski, J. Jortner, and G. Stein, *Nature (London)*, **186**, 629 (1960).

the predominance of octane among the products, and the very low yield of butene, exclude silver(I) hydride elimination as an important reaction (eq 2 and 3). Second, the high ratio of octane to 1-butene is incompatible with product formation by bimolecular reaction of butyl radicals (eq 4 and 5). Third, the distribution of products observed in the thermal decomposition of **1** in the presence of TMPO, and in the photochemical decomposition of **1**, both alone and in the presence of DTBNO, all indicate that these reactions *do* produce significant quantities of *n*-butyl radicals. The response of the yield of butane to the ratio $[\text{TMPO}]_0/[1]_0$ (Figure 2) establishes that **1** is not a particularly effective scavenger for butyl radicals, if, in fact, it is a scavenger at all. Since very rapid reaction of butyl radicals with **1**, to the virtual exclusion of reaction with ether, would be required to rationalize the low yield of butane produced on thermal decomposition of **1** on the basis of schemes represented by eq 8 and 9, mechanisms based on radical–organosilver reactions may be discarded. The most plausible remaining mechanism is the concerted one (eq 7). This conclusion is in accord with that reached by Tamura and Kochi in a closely related study.³¹

This mechanistic conclusion cannot be generalized to other organosilver(I) reagents. 1-Propenyl- and 2-butenylsilver(I) and their tri-*n*-butylphosphine complexes also decomposed by a concerted mechanism.¹⁶ However, neophyl(tri-*n*-butylphosphine)silver(I)³² and probably trimethylsilylmethylsilver(I)⁶ generate free radicals on decomposition, and 2-butyl(tri-*n*-butylphosphine)silver(I) decomposes by yet another pathway, possibly involving silver(I) hydride elimination. The factors that determine whether concerted, radical, or metal hydride elimination mechanisms dominant remain undefined.

Experimental Section³³

Tetrakis(iodo(tri-*n*-butylphosphine)silver(I)) having mp 44° (lit.¹⁸ mp 43°) was prepared in 48% yield by the procedure of Mann, Purdie, and Wells.¹⁸

(31) The significance of CIDNP and spin trapping experiments reported by Janzen suggesting free alkyl radical intermediates in the reaction of silver nitrate with tetraethyllead is obscure. Our work does not exclude small contributions from radical mechanisms in the decomposition of **1**. Alternatively, Janzen's reactions may generate silver reagents that differ significantly in their decomposition from **1**: cf. E. G. Janzen, *Accounts Chem. Res.*, **4**, 39 (1971); Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, February 1970, ORGN 20. Our efforts to detect CIDNP signals during thermal decomposition of **1** were unsuccessful, except in one instance in which improper closure of the nmr tube allowed oxygen to leak into the sample during the thermolysis.

(32) G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 232 (1972).

(33) All melting points and boiling points are uncorrected. Infrared spectra were taken in sodium chloride cells on a Perkin-Elmer, Model 237, grating spectrophotometer. Nmr spectra were determined on a Varian T-60 nmr spectrometer. Chemical shifts are reported in parts per million relative to internal tetramethylsilane and coupling constants are in hertz. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-60 mass spectrometer. Optical spectra were determined on a Cary Model 14 spectrophotometer. Analytical analyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind. Samples for elemental and spectral analyses were purified on a Hewlett-Packard, Model 700, thermal conductivity gas chromatograph. Analytical glpc analyses were performed on F and M Model 810 flame ionization instruments, using a 4% Apiezon N on alumina column for C₄ hydrocarbons and UC-W98 or squalane on Chromosorb for higher molecular weight materials. Absolute yields of products were calculated from peak areas using internal standard techniques, with response factors obtained from authentic samples. Diethyl ether and tetrahydrofuran (THF) were distilled from lithium aluminum hydride under an inert

Table I. Products Observed in the Thermal Decomposition of Mixtures of **1** and **2**

1:7	Product yield ^a						
	Propene	Propane	1-Butene	<i>n</i> -Butane	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane
7:93			0.0	2.5			98.4
7:93			1.0	2.6			91.4
50:50	1.6	1.5	1.4	4.5	32.6	62.7	31.2

^a Yields of propane, propene, and *n*-hexane are given in percentages based on the amount of *n*-propyllithium used in the preparation. Yields of *n*-butane, 1-butene, *n*-heptane, and *n*-octane are given in percentages based on the amount of *n*-butyllithium used in the preparation. A blank in the table indicates that the quantity was not measured.

Bromo(tri-*n*-butylphosphine)silver(I). Silver bromide (20.7 g, 0.110 mol) was dissolved in 800 ml of a saturated aqueous solution of potassium bromide. Tri-*n*-butylphosphine (15.8 g, 0.077 mol) was dissolved in 15 ml of diethyl ether, and the ether solution was stirred over the aqueous silver bromide solution for 24 hr. The organic phase was separated, washed with 20 ml of a saturated aqueous solution of potassium bromide, and dried. The ether was removed at 0.01 Torr, leaving the silver bromide complex as a viscous oil. Ethanol (10 ml) was added to this oil and was stirred over the insoluble silver complex for 5 min. The ethanol was then removed by decantation. The resulting silver complex was dried overnight at 0.01 Torr to give a clear, water-white, viscous oil which was stored at 20° under a nitrogen atmosphere.

Anal. Calcd for C₁₂H₂₇PAgBr: C, 36.92; H, 6.93. Found: C, 36.96; H, 7.14.

Analysis of Solutions of Butyllithium for C₃ and C₄ Hydrocarbons. One-milliliter aliquots of *n*-butyllithium were quenched with bromine and water, respectively, and *n*-pentane and *n*-nonane were added to each solution as internal glpc standards. The bromine quench was analyzed for *n*-butane, and the water quench was analyzed for 1-butene and *n*-octane. Typically, 1 ml of lithium reagent contained 1.60 mmol of *n*-butyllithium, 0.08 mmol of *n*-butane, 0.03 mmol of 1-butene, and 0.013 mmol of *n*-octane.

***n*-Butyl(tri-*n*-butylphosphine)silver(I) (1).** A 12-ml centrifuge tube capped with a serum stopper was flame dried under a nitrogen atmosphere and tetrakis(iodo(tri-*n*-butylphosphine)silver(I)) (0.436 g, 1.0 mmol of IAgPBu₃) was added. The tube was flushed with nitrogen for 5 min, and *n*-pentane and *n*-nonane were weighed in as internal standards. The tetrakis(iodo(tri-*n*-butylphosphine)silver(I)) was dissolved in 8 ml of diethyl ether, and the solution was cooled in a Dry Ice–2-propanol bath under nitrogen. A solution of *n*-butyllithium in hexane (1.60 *N*, 0.625 ml, 1.0 mmol) was added by syringe. The solution was shaken well, and then a solution of dioxane in diethyl ether (1.1 *N*, 1.0 ml, 1.10 mmol) was added by syringe to precipitate the lithium iodide. The precipitate was compacted by centrifugation at –78° for 2 min, and the supernatant solution of **1** was transferred through a stainless steel cannula to a dry, oxygen-free centrifuge tube at –78°.

Larger samples used in decomposition condition studies were made in the same manner in 40-ml centrifuge tubes. After centrifugation, liquids were transferred into dry, oxygen-free, 12-ml centrifuge tubes.

Estimation of the concentration of lithium ion in these samples was accomplished by allowing the solution to decompose, extracting a 0.5-ml aliquot with 5 ml of water, and analyzing by atomic absorption. Silver metal in the decomposed mixture was estimated by filtering the reaction solution through a glass frit and washing the silver on the filter and on the walls of the tube successively with two 1-ml portions of a saturated solution of potassium iodide, two 1-ml portions of distilled water, 1 ml of acetone, and 1 ml of diethyl ether. The remaining solids in the reaction tube and

glass frit were dissolved in concentrated nitric acid. The resulting solution was diluted with distilled water, treated with excess sodium chloride, and then boiled to coagulate the precipitated silver chloride. Silver chloride precipitate was filtered from solution on to a predried and preweighed glass-fritted filter, washed with two 1-ml portions of water, and dried in an oven. The filter was weighed and silver chloride determined by difference.

Thermal Decomposition of 1. Thermal decomposition of **1** was accomplished by removing the tube containing the solution of **1** from the isopropyl alcohol–Dry Ice bath and allowing it to warm to room temperature under ambient lighting. Decomposition was accompanied by formation of a silver mirror on the wall of the tube and was complete after 5 min at room temperature. Similar product distributions were obtained when the decomposition was carried out in the dark, at 0°, at 45°, or under illumination from a Mineralight UVSL025 uv lamp (365 nm). If the dioxane precipitation of lithium iodide was omitted, the product distribution was unchanged. Hydrocarbon products were analyzed by glpc.

Analysis for Tri-*n*-butylphosphine in the Thermal Decomposition Products of 1. A solution containing 0.585 g of **1** was prepared using deuterium-labeled tetrakis(iodo(tri-*n*-butylphosphine)silver(I)) (prepared from deuterated tri-*n*-butylphosphine having isotopic composition 60.5% *d*₁, 11.5% *d*₂, 16.8% *d*₃, and 11.2% *d*₄) and was allowed to decompose thermally. Tri-*n*-butylphosphine (0.0800 g, 0.396 mmol) was added to the product mixture, and the solution was concentrated to an oily sludge on a rotary evaporator. A mass spectrum (15 eV) of tri-*n*-butylphosphine distilled from this sludge in the mass spectrometer indicated that at least 0.549 mmol of the deuterium-labeled phosphine (94%) had been present in the reaction mixture at the conclusion of the thermal decomposition.

Demonstration that *n*-Butyl Moieties Do Not Exchange between the Phosphine Ligand and the Silver(I). A solution containing 0.826 mmol of **1** was prepared using deuterium-labeled tetrakis(iodo(tri-*n*-butylphosphine)silver(I)) and was allowed to decompose thermally. The 1-butene, *n*-butane, and octane were purified by glpc³⁶ and analyzed at low ionizing voltage by mass spectroscopy, none showed evidence of deuterium incorporation.

Control experiments to establish the influence of adventitious hydrolysis on the yield of butane in the decomposition of 1 were carried out by preparing a small quantity of *n*-propyl(tri-*n*-butylphosphine)silver(I) (**7**) in the flask in which the sample of **1** was to be decomposed and allowing the **7** to scavenge materials that might have reacted with **1**. Typically, a solution of tetrakis(iodo(tri-*n*-butylphosphine)silver(I)) in ether was prepared, as described in the preparation of **1**. A solution of *n*-propyllithium in decane (0.06 ml, 0.07 mmol) was added *via* syringe. The solution was shaken well and cooled to –78°. A solution of *n*-butyllithium in decane (1.96 *N*, 0.48 ml, 0.93 mmol) was added by syringe. Thermal decompositions were carried out immediately without removal of the lithium iodide. Representative results of these experiments, given in Table I, indicate that the yield of RH from RAgPBu₃ may fall below 3%.

Divaleryl Peroxide. Divaleryl peroxide was prepared from valeryl chloride and hydrogen peroxide according to the procedure of Sheldon and Kochi.¹⁵ The diacyl peroxide was not isolated but was used as an ether solution. Titration with sodium iodide as described by Hart and Chloupek³⁷ showed the ether solution to be 0.35 *M* in peroxide.

Photolysis of Divaleryl Peroxide. A known amount of the 0.35 *M* peroxide solution described above was added to a quartz tube containing 20 ml of distilled diethyl ether. A Dewar condenser

atmosphere before use. Olefins were removed from hydrocarbon solvents by treatment with sulfuric acid, and the olefin-free hydrocarbons were purified by distillation from a suspension of sodium benzophenone ketyl before use. Dimethoxyethane (DME) was distilled from a solution of sodium benzophenone dianion before use. Methyl-, cyclopentyl- and *n*-butyllithium reagents were supplied by Foote Mineral Corp.; *sec*-butyllithium was supplied by Alfa Inorganics, Inc. Grignard reagent solutions were analyzed by titration for total base, and lithium reagents were analyzed by the Gilman double titration method.^{16,34} All reactions involving organometallic reagents were carried out under prepurified nitrogen, using standard inert atmosphere techniques.³⁵

(34) H. Gilman, F. K. Cartledge, and S.-Y. Sim, *J. Organometal. Chem.*, **1**, 8 (1963).

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

(36) Experimental techniques used for these analyses are described in the Ph.D. Thesis of E. R. Stedronsky, Massachusetts Institute of Technology, Cambridge, Mass., 1971.

(37) H. Hart and F. J. Chloupek, *J. Amer. Chem. Soc.*, **85**, 1155 (1963).

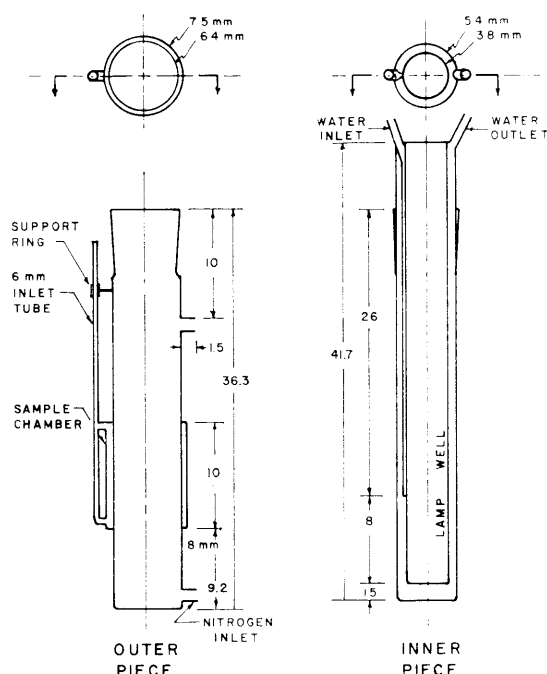


Figure 4. The single-chamber photolysis apparatus. All unlabeled dimensions are centimeters. All tubing dimensions are given as millimeters in outside diameter.

Table II. Products from the Photolysis of Divaleryl Peroxide

Temp, °C	Yield, %			k_d/k_c	Extent of decomp, %
	Butane	1-Butene	Octane		
30	0 ^a	0 ^a	0 ^a		
30	18	7.5	75	0.20	96
30	<i>b</i>	<i>b</i>	1.0 ^b	0.195	<i>c</i>
-78	0 ^a	0 ^a	0 ^a		
-78	0.35 ^b	0.25 ^b	1.0 ^b	0.25	<i>c</i>
-78	13	10	77	0.26	100

^a A quench of the divaleryl peroxide with tri-*n*-butylphosphine at the indicated temperature gave no detectable product by glpc.

^b Only the relative amounts of butane, 1-butene, and octane were determined. ^c This value was not determined.

containing Dry Ice-2-propanol and a Dry Ice-2-propanol trap were connected to the photolysis tube to trap any volatile products. The photolysis was carried out for 2 hr at 30° or for 6-8 hr at -78°. In the latter case, the photolysis apparatus was immersed in a quartz bath containing Dry Ice-2-propanol. The sample was irradiated with 2537-Å light in a Rayonet photoreactor and analyzed by glpc following destruction of any unphotolyzed peroxide by reaction with tri-*n*-butylphosphine. Data from these experiments are summarized in Table II.

O-*n*-Butyl-2,2,6,6-tetramethylpiperidylloxyl (**5**) was prepared following a reported procedure³⁸ from *n*-butylmercuric bromide, NaBH₄, and TMPO.³⁹

Qualitative Rate Studies of the Thermolysis of 1. Preliminary studies, using solutions of **1** prepared as described above, showed that taking aliquots during the decomposition of **1** gave unreliable results, presumably because of thermal decomposition of **1** in the handling procedures. Consequently, a solution of **1** prepared at -78° was transferred to a series of centrifuge tubes at -78° by forced siphon with a cannula. Samples that had been transferred without any visible decomposition were used in the rate studies. This series of centrifuge tubes was then placed in a -40° Dry Ice-dichloroethylene bath and samples were quenched at various times

with the addition of 0.1 ml of bromine. The extent of decomposition was monitored by glpc by measuring the amount of *n*-butyl bromide.

Thermolysis of Mixtures of Methyl- and 2-Norbornyl(tri-*n*-butylphosphine)silver(I). Bromo(tri-*n*-butylphosphine)silver(I) (0.4160 g, 1.07 mmol) and *n*-octane (0.0679 g, 0.829 mmol) were dissolved in 8 ml of diethyl ether, and the solution was cooled to -78°. Norbornyl Grignard reagent⁴⁰ (1.13 N, 63% *endo*, 0.468 ml, 0.53 mmol) or pure *endo*-epimer,⁴³ and methyllithium (1.45 N, 0.340 ml, 0.53 mmol) were added by syringe, and the solution was shaken at -78°. The resulting mixture of alkylsilver(I) reagents was allowed to decompose thermally by warming the solution to room temperature. Analysis followed techniques described previously.⁴²

Epimerization of 2. Solutions containing **2** or mixtures of **2** and methyl(tri-*n*-butylphosphine)silver(I) were allowed to stand for a known period of time at a known temperature then quenched at -78° with anhydrous DCl. The resulting deuterated norbornane was purified by glpc and the stereochemistry of the C-D bond established by comparing the ratio of the 2185- and 2170-cm⁻¹ bands with a calibrated curve obtained from mixtures of *endo*- and *exo*-norbornane-2-*d*₁ of known composition.⁴⁴ Results of representative experiments are stereochemistry (% *endo*) of the 2-norbornylmagnesium bromide used to prepare **2**, stereochemistry (% *endo*) of **2** inferred from the DCl quenching experiments, temperature, and time (minutes) that the solution was allowed to stand before quenching: 70, 71, -78°, 5: 96, 94, -78°, 5: 93, 86, -78°, 30; 96, 67, quenched at room temperature shortly after decomposition had begun.

5-Hexenyl(tri-*n*-butylphosphine)silver(I) (3**)** was prepared from 5-hexylmagnesium bromide (typically contaminated with 5% of cyclopentylcarbinylmagnesium bromide) and thermally decomposed using procedures analogous to that described for **1**. Its isomerization to **4** was followed by quenching samples with iodine and analyzing the resulting solutions for 1-iodo-5-hexene and iodo-methylcyclopentane. The yield of the latter compound increased from 1.5% (based on **3** and corrected for **4** present originally before thermal decomposition had begun) to 12% after 8 min at 20°.

Photolysis of 1. Two photochemical reactors were designed for the low-temperature irradiation of air- and water-sensitive solutions carried out as a part of these studies. The first (Figure 4) was used for experiments in which only one solution was irradiated at a time; the second (Figure 5) was used for kinetics experiments requiring simultaneous irradiation of several samples. Both were constructed of Pyrex and were designed for use with a 550-W Hanovia medium-pressure mercury arc lamp; with this lamp, the sample cells are positioned in the region of maximum luminosity. A total thickness of 6 mm of Pyrex lies between the lamp and the sample solutions. The lamp well is cooled by a water jacket. The sample chambers are cooled on the outside surface by the cold bath in which the apparatus is immersed and on the inside surface by a stream of cold nitrogen.

The appropriate apparatus was dried immediately prior to use by washing the sample chamber(s) with methyllithium and rinsing with dry diethyl ether. The apparatus was then placed in a large dewar that also held the cooling coil for the nitrogen stream (4 ft of 0.25 in. copper tubing). The apparatus was held in position by styrofoam blocks positioned between the dewar wall and the apparatus. The dewar was filled with an 2-propanol-Dry Ice bath. Cold nitrogen gas was passed through the apparatus at a rate of ca. 1.4 l./min. The apparatus required 15 min of precooling before silver reagents could be placed in the chambers. A copper-constantin thermocouple immersed in the sample during photolysis showed that a temperature below -55° was maintained. The apparatus was removed from the cold bath immediately on completion of the irradiation and allowed to warm to 20°. The samples were

(40) 2-Norbornyl Grignard reagent was prepared from 2-bromonorbornane⁴¹ using unexceptional procedures. Its stereochemistry was assayed by conversion to 2-methylnorbornane.⁴²

(41) J. D. Roberts, E. R. Trumbell, Jr., W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72**, 3116 (1950).

(42) G. M. Whitesides and P. E. Kendall, *J. Org. Chem.*, **37**, 3718 (1972).

(43) *endo*-2-Norbornylmagnesium bromide was prepared by the method of F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966). Reference 42 describes details of this procedure.

(44) A. Nikon and J. H. Hammons, *J. Amer. Chem. Soc.*, **86**, 3322 (1964); G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970). An independent method of analysis based on ir techniques has been developed by Professor J. K. Stille; we thank Professors Nikon and Stille for providing us with details of their work.

(38) C. L. Hill and C. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 870 (1974).

(39) T. Toda, E. Mori, and K. Mukayama, *Bull. Chem. Soc. Jap.*, 1904 (1972).

transferred to storage vessels, and the sample chambers were washed in succession with water, concentrated nitric acid, water, a saturated aqueous solution of potassium iodide, water, acetone, and ether in order to remove silver metal and silver salts from the system.

Photolyses of 1. A solution of **1** (1 mmol), containing internal glpc standards, was prepared and transferred to the precooled single-chamber photolysis apparatus. In certain experiments, an ether solution containing a weighed quantity of di-*tert*-butyl nitroxide was then transferred into the apparatus. The remaining volume of the sample chamber was filled by diluting the solution of **1** with cold diethyl ether. The resulting solution of **1** was irradiated for 4 hr, and the product solution was analyzed.

Ethyl 2-hexyl ether was prepared in 25% yield by reaction of iodoethane and sodium 2-hexoxide in diethyl ether: bp 131–134° (lit.⁴⁵ bp 124–126° (747 Torr)), and nmr (CCl₄) δ 3.0–3.6 (m, 3), 0.8–1.5 (m, 15).

Optical spectra at –70° were run on a Cary 14 spectrophotometer whose sample chamber was swept with a rapid stream of cold nitrogen; the temperature of the chamber was regulated by controlling the rate of the nitrogen stream. A copper–constantin thermocouple, taped to the cell holder directly over the sample cell, was used with a Digitec Digital thermometer to indicate the sample chamber temperature. The chamber could be cooled to temperatures as low as –100°; temperature variation within the chamber, after equilibration, was *ca.* $\pm 2^\circ$. Spectra of organosilver solutions were run at –70°. Troublesome frost formation on the lamp lens was observed at this temperature after several hours of operation. It proved helpful to use a beam attenuator in the reference optical trains to compensate for frost in the sample beam. Frost formation on the sample cell was not observed.

Samples of organosilver reagents were prepared by volumetric dilutions of a stock solution at –78°. A solution of **1** was prepared in a 12-ml graduated centrifuge tube, and its concentration was calculated. One milliliter of this solution was transferred into a 12-ml graduated centrifuge tube containing 7 ml of diethyl ether at –78°. Similar dilutions were continued until a sample which was calculated to be *ca.* 1×10^4 *N* was obtained. The quartz sample cell, fitted with a serum cap, was then purged with nitrogen and placed in a diethyl ether–Dry Ice bath. The sample was transferred into the quartz cell through a cannula, and the cell was rapidly placed in the cold sample chamber of the spectrophotometer.

Rate Studies for the Photolysis of 1. In preliminary experiments, the five sample chambers of the multichamber photolysis apparatus were calibrated by comparing the rates of photolysis of a solution of azoisopropane⁴⁶ in each. Five solutions of **1** (1 mmol, ~ 0.1 *N*), each containing internal glpc standard, were prepared independently and transferred to the sample chambers of the precooled multichamber photolysis apparatus. The remaining volume of each of the sample chambers was filled by diluting the solution of **1** with cold diethyl ether. Irradiation was begun, and at intervals the total content of a sample chamber was transferred to a clean, dry, 40-ml centrifuge tube and was quenched with 0.1 ml of bromine. Each of the five quenched solutions obtained was analyzed for octane and 1-bromobutane by glpc.

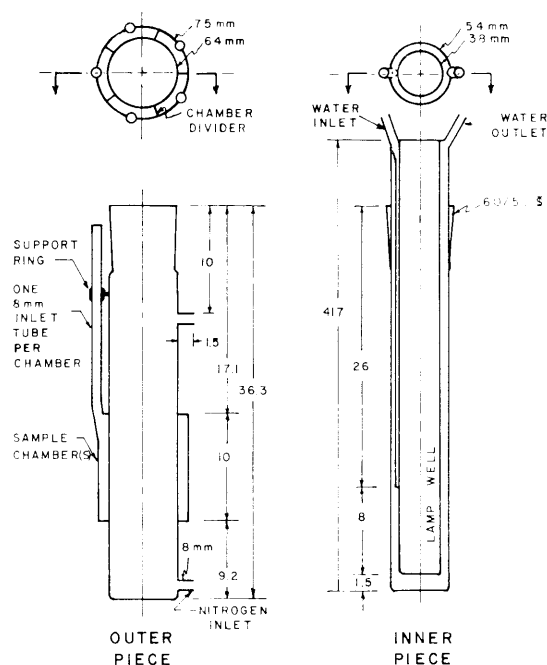


Figure 5. The multichamber photolysis apparatus. All unlabeled dimensions are centimeters. All tubing dimensions are given as millimeters for outside diameter.

sec-Butyl(tri-*n*-butylphosphine)silver(I) was prepared from *sec*-butyllithium using procedures analogous to those described for **1**. Glpc analyses for 3,4-dimethylhexane were carried out on an 8-ft, 20% UC-W98 column at 110°, using nonane as internal standard.

Analysis for Hydrogen. Analysis for hydrogen was carried out by glpc, on a 1/8-in., 23-ft, 4% Apiezon N on alumina column at room temperature, using methane as the internal standard. A thermal conductivity detector was used, with nitrogen as the carrier gas. The response factor of hydrogen relative to methane was measured by injecting known volumes of each gas into a 12-ml centrifuge tube containing 6 ml of diethyl ether. The observed molar response factor of 0.276 was a function of the relative volumes of liquid and vapor phases and is not considered to be more accurate than $\pm 50\%$.

Acknowledgment. A number of the techniques described in this study for the synthesis and examination of alkylsilver reagents were developed by Dr. C. P. Casey; we wish to thank him for his contributions to this work. Dr. Erwin Stedronsky provided deuterated compounds used in preparing deuterated tri-*n*-butylphosphine. Compound **5** was first prepared in our laboratories by Dr. Terry Newirth.

(45) M. F. Shostakovskii and M. R. Kulibekov, *Zh. Obshch. Khim.*, **28**, 578 (1958); *Chem. Abstr.*, **52**, 18285 f (1958).

(46) R. Renaud and L. C. Litch, *Can. J. Chem.*, **32**, 545 (1954).