

Radical Intermediates in the Thermal Decomposition of Neophyl(tri-*n*-butylphosphine)copper(I) and Neophyl(tri-*n*-butylphosphine)silver(I)¹

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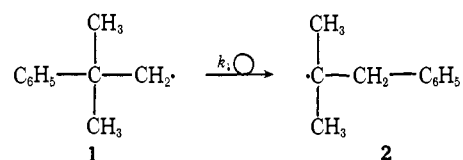
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Abstract: The thermal decomposition of neophyl(tri-*n*-butylphosphine)copper(I) (**3**) in ether solution at temperatures between 30 and 125° takes place in large part by a free-radical mechanism. The initial homolytic scission of the carbon-copper σ bond is followed by competing 1,2-phenyl migration, coupling, and hydrogen abstraction reactions involving the resulting neophyl radicals. The products obtained from thermal decomposition of mixtures of **3** and *tert*-butyl(tri-*n*-butylphosphine)copper(I) under comparable conditions indicate that benzyldimethylcarbinyl(tri-*n*-butylphosphine)copper(I) (**12**) is not an intermediate in the reaction sequence leading to the dimeric products 1,4-diphenyl-2,2,4-trimethylpentane (**10**) and 1,4-diphenyl-2,2,3,3-tetramethylbutane (**11**). Comparison of the product distributions observed from the thermal decomposition of **3** with that from neophyl(tri-*n*-butylphosphine)silver(I) indicates that these two organometallic reagents probably share a common decomposition mechanism.

A previous paper has presented evidence that the thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I) to *n*-butane, 1-butene, copper metal, hydrogen, and tri-*n*-butylphosphine takes place predominantly by a nonradical pathway, involving initial elimination of copper(I) hydride from the *n*-butyl group of one *n*-butylcopper(I) moiety, followed by reduction of the carbon-copper(I) bond of a second by this copper(I) hydride.³ In an effort to establish whether this mechanism provides a pathway for the thermal decomposition of alkylcopper reagents which is uniquely favored energetically, or if it is simply one of several mechanisms with comparable activation energies for the rate-determining step whose relative importance depends on structure or solvent, we have attempted to identify mechanistic alternatives to an initial elimination of copper hydride by exploration of the mechanisms of thermal decomposition of compounds having no C-H bonds β to the C-Cu bond. Decomposition of copper(I) alkyls in which vicinal copper(I) hydride elimination is impossible might *a priori* take place by any of several different types of mechanisms: *viz.*, by nonradical pathways similar to that observed for vinylic copper(I) reagents,⁴ by free-radical mechanisms involving homolytic scission of the carbon-copper σ bonds, or by other, less conventional, routes. However, a small but significant contribution from a free-radical pathway to the overall thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I) has already been suggested,³ and a number of studies have implicated free-radical pathways in the thermal decomposition of the related alkylsilver(I) compounds.⁵ We have

thus concentrated our efforts in this area on attempts to obtain direct evidence for free alkyl radical intermediates in the thermal decomposition of alkylcopper(I) reagents. In this paper we wish to report the preparation of neophyl(tri-*n*-butylphosphine)copper(I) and the examination of the products of its thermal decomposition, both alone in solution, and in solutions containing other alkylcopper(I) reagents. The obvious intent in this study was the detection of intermediate free neophyl radicals (**1**) as evidenced by the isolation of products derived from the rearranged benzyldimethylcarbinyl radical, **2**.



The neophyl moiety has two major attractions as a probe with which to investigate free-radical reactions in this organometallic system. First, neophyllithium, the starting material for preparation of the neophylcopper(I) reagents, is a stable compound and can be obtained in high purity. Neophyllithium does not rearrange to benzyldimethylcarbinyllithium under any conditions we have examined.⁶ Second, the 1,2-aryl migration which characterizes the free neophyl radical is a particularly well-understood radical rearrangement.⁷ In particular, studies of the thermal decomposition of *tert*-butyl 3-methyl-3-phenylperbutyrate⁸ and of the free-radical decarbonylation of 3-methyl-3-phenyl-

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(2) (a) E. B. Hershberg Fellow, 1965-1966; National Institutes of Health Predoctoral Fellow, 1966-1967; (b) National Institutes of Health Predoctoral Fellow, 1967-1970.

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

(4) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *ibid.*, **93**, 1379 (1971).

(5) (a) C. P. Casey, Ph.D. Thesis, Massachusetts Institute of Technology, 1968; (b) K. Yamamoto, K. Nakanishi, and M. Kumada,

J. Organometal. Chem., **7**, 197 (1967); (c) H. C. Brown, N. C. Hébert, and C. H. Snyder, *J. Amer. Chem. Soc.*, **83**, 1001 (1961); (d) C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, 3923 (1960); (e) M. Tamura and J. Kochi, *J. Amer. Chem. Soc.*, **93**, 1483 (1971).

(6) For references to 1,2-aryl migrations in organometallic compounds, see E. Grovenstein, Jr., and G. Wentworth, *ibid.*, **89**, 2348 (1967), and references therein. See also E. Grovenstein, Jr., and Y. Cheng, *Chem. Commun.*, 101 (1970).

(7) Reviews: R. Kh. Freidlina, *Advan. Free Radical Chem.*, **1**, 211 (1965); C. Walling in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Wiley, New York, N. Y., 1963; R. Kh. Freidlina, V. N. Kost, and M. Ya. Khorlina, *Russ. Chem. Rev.*, **31**, 1 (1962).

(8) C. Rüchardt and R. Hecht, *Chem. Ber.*, **98**, 2460, 2471 (1965).

Table I. Product Yields for the Thermal Decomposition of Neophyl Organometallic Compounds

Product	RCu(1)PBu ₃ ^a			RAg(1)PBu ₃ ^a		R ₂ Hg	
	30°, 180 ^d	30°	65°, 15 ^d	125°, <5 ^d	65°, <5 ^d	235°, ^b >10 ³ ^d	235°, ^c >10 ³ ^d
C ₆ H ₅ C(CH ₃) ₃ (5)	59.1	57.5	58.9	45.7	56	29.3	43.2
C ₆ H ₅ CH ₂ CH(CH ₃) ₂ (6)	6.6	6.1	7.0	17.9	17	12.5	39.3
C ₆ H ₅ CH ₂ C(CH ₃)=CH ₂ (7)	4.0	6.0	6.9	14.0	12	12.1	2.5
C ₆ H ₅ CH=C(CH ₃) ₂ (8)	0.3	0.8	1.4	1.7	1.6	8.3	<0.1
R-R' (9)	26.6	26.5	21.2	8.4	7.5	<0.1	<0.1
R-R' (10)	2.2	1.6	2.3	6.5	4.3	<0.1	<0.1
R'-R' (11)	1.0	1.0	2.1	4.6	1.6	21.2	<0.1
Product balance	100	99	100	99	100	83	85
% rearrangement in monomers	16	18	21	42	35	53	49
dimers	7	6	13	40	28	100	

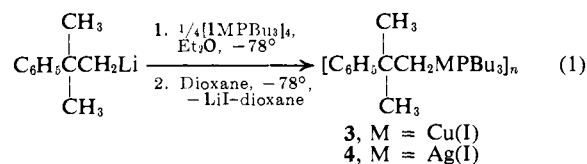
^a 0.1 N in diethyl ether. ^b 0.05 N in *n*-heptane. ^c 0.05 N in *p*-dioxane. ^d Decomposition time (minutes); see text for explanation of this term. ^e R refers to neophyl; R' refers to benzylidimethylcarbinyl.

butyraldehyde^{9,10} have established that the extensive rearrangement observed in the products of these reactions occurs *after* formation of a discrete classical intermediate neophyl radical; 1,2-phenyl migration in the neophyl system is *not* concerted with formation of the radical. Finally, the neophyl radical rearrangement is a relatively slow process on the time scale of most free-radical reactions. Although the absolute rate constant k_1 for the rearrangement has not been determined directly, phenyl migration in neophyl radical has been demonstrated to occur slightly more rapidly than abstraction of the aldehyde hydrogen of 3-methyl-3-phenylbutyraldehyde by this radical.^{9a,10} The rate constant for this latter reaction is almost certainly smaller than the rate constants for attack of the more reactive *methyl* radical on simple aldehydes, determined by Birrell and Trotman-Dickenson to be approximately 10^6 l. mol⁻¹ sec⁻¹ at 182° in the vapor phase.¹¹ Hence, the rate constant for 1,2-phenyl migration in neophyl radical can be reliably established as $k_1 < 10^6$ sec⁻¹ at 100°; the actual rate is probably several orders of magnitude smaller than this estimate. Regardless of the precise rate of this rearrangement under our conditions, it is clear that the rearrangement of a neophyl radical in solution is much too slow to compete with its diffusion out of the solvent cage in which it is initially formed.¹²

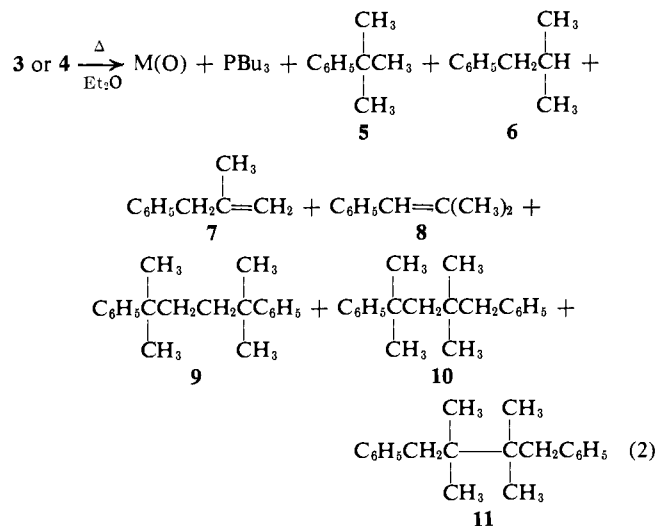
Results and Discussion

Ether solutions of neophyl(tri-*n*-butylphosphine)copper(I) (3) were prepared by the reaction of 1 equiv of neophyllithium with 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] at -78°. For comparison of thermal decomposition products, neophyl(tri-*n*-butylphosphine)silver(I) (4) was prepared in a similar manner from tetrakis[iodo(tri-*n*-butylphosphine)silver(I)].¹³ Treatment of solutions of these organometallic compounds with 1.2 equiv of dioxane/equiv of neophyllithium at -78° removed the lithium iodide formed in the preparations as an insoluble dioxanate. "Lithium

halide-free" solutions of *tert*-butyl(tri-*n*-butylphosphine)copper(I) were prepared using analogous procedures.¹⁴



Both 3 and 4 are appreciably more stable thermally than *n*-butyl(tri-*n*-butylphosphine)copper(I)³ or -silver(I). Decomposition of *ca.* 0.1 N ethereal solutions of 3 and 4 at temperatures above 30° proceeded at convenient rates and in high yields to mixtures of hydrocarbon products containing both neophyl and benzylidimethylcarbinyl fragments (eq 2). Representative yields of these products are given in Table I for decompositions carried out at several temperatures. For comparison, the products of the high-temperature thermal decomposition of dineophylmercury are also



listed in this table. Approximate measures of the relative rates of these thermal decompositions are given by the "decomposition times" listed in Table I. These numbers represent an estimate of the length of time required for the reaction mixture to stop the deposition of metal (see Experimental Section). The product yields in these reactions were reasonably reproducible. These yields in experiments run under apparently

(9) (a) C. Ruchardt, *Chem. Ber.* **94**, 2599, 2609 (1961); (b) C. Ruchardt and H. Trautwein, *ibid.*, **96**, 160 (1963); (c) C. Ruchardt and S. Eichler, *ibid.*, **95**, 1921 (1962).

(10) F. H. Seubold, Jr., *J. Amer. Chem. Soc.*, **75**, 2532 (1953); S. Winstein and F. H. Seubold, Jr., *ibid.*, **69**, 2916 (1947).

(11) R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 2059 (1960).

(12) R. M. Noyes, *Prog. React. Kinet.*, **1**, 129 (1961).

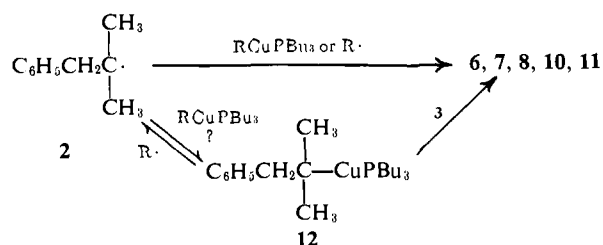
(13) F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1828 (1937).

(14) H. O. House, W. L. Respass, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

identical conditions fluctuated by up to 10%, perhaps due to accidental hydrolysis of the starting organometallic reagents, variations in the thermal history of their solutions, or other, unexplored, effects. Consequently, the trends in product yields on varying conditions in Table I and succeeding tables are more significant than the absolute yields from any given experiment.

The observation that a significant fraction of the products from the thermal decomposition of **3** and **4** contain the benzyldimethylcarbinyl moiety indicates that these reactions take place, at least in part, by a mechanism involving initial homolytic scission of the carbon-metal bond, partial rearrangement of the resulting neophyl radicals to benzyldimethylcarbinyl radicals, and subsequent reaction of these radicals.

Exclusion of Benzyldimethylcarbinylcopper(I) (12) as an Intermediate in the Formation of 10 and 11 during the Thermal Decomposition of 3. Although the data of Table I indicate that the benzyldimethylcarbinyl radical is a precursor of products **6**, **7**, **8**, **10**, and **11**, they do not demonstrate that this radical is the *immediate* precursor of these products. At least two plausible and distinct reaction sequences could be invoked to rationalize the conversion of the rearranged radical **2** to products. In one, the benzyldimethylcarbinyl radical would be converted to product directly, either by reaction with solvent, with other radicals present in solution, or with undecomposed organometallic reagents. In a second, the radical would first be converted to benzyldimethylcarbinylcopper(I) (**12**) by alkyl group displacement on **3**,¹⁵ by addition to a copper(0) atom in solution, or by some other route, and the subsequent reaction of **12** would lead to the observed products.



It is possible to establish that **12** is *not* an intermediate in the formation of the dimeric hydrocarbons **10** and **11** by examining the products observed on decomposition of mixtures of *tert*-butyl(tri-*n*-butylphosphine)copper(I) and **3**. The decision to study *tert*-butyl(tri-*n*-butylphosphine)copper(I) as a model for **12**, rather than to examine **12** directly, was made for two reasons. First, *tert*-butyllithium is much more readily obtained than benzyldimethylcarbinyllithium. Second, the use of *tert*-butyl(tri-*n*-butylphosphine)copper(I) as a model for **12** permits a clear identification of the origin of each of the products in the decomposition of mixtures with **3**; interpretation of the product yields observed on decomposition of mixtures of **3** and **12** would necessarily be ambiguous, since both **3** and **12** would give rise to products containing the benzyldimethylcarbinyl moiety.

Table II lists the products of thermal decomposition of solutions of pure neophyl- and *tert*-butyl(tri-*n*-butylphosphine)copper(I), and of mixtures of these two re-

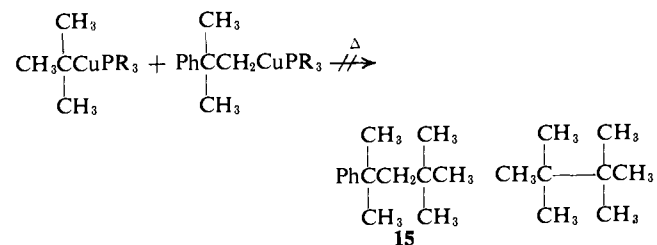
Table II. Yields (Per Cent) of Products Obtained on the Thermal Decomposition of Mixtures of *tert*-Butyl- and Neophyl(tri-*n*-butylphosphine)copper(I) in Ether at 30°^a

Product	—Neophyl: <i>tert</i> -butyl ratio ^a —			
	1:0	1:1	1:7	0:1
C ₆ H ₅ C(CH ₃) ₃ (5)	57.5	67.8	59.1	
C ₆ H ₅ CH ₂ CH(CH ₃) ₂ (6)	6.1	7.2	8.9	
C ₆ H ₅ CH ₂ C(CH ₃)=CH ₂ (7)	6.0	5.4	7.1	
C ₆ H ₅ CH=C(CH ₃) ₂ (8)	0.8	0.9	1.2	
R-R ^b (9)	26.5	12.5	15.2	
R-R' ^b (10)	1.6	4.2	2.1	
R'-R' ^b (11)	1.0	0.1	1.0	
(CH ₃) ₃ CH		52	56	55
(CH ₃) ₂ C=CH ₂		42	45	43
(CH ₃) ₃ CC(CH ₃) ₃	<0.1	<0.1	<0.1	
C ₆ H ₅ C(CH ₃) ₂ CH ₂ C(CH ₃) ₃ (15)	<0.1	<0.1		
Product balance (based on 3)	99	98	95	
% rearrangement in monomers	18	17	23	
dimers	15	17	11	
Product balance (based on <i>tert</i> -butylcopper(I))		94	101	98

^a The total concentration of alkylcopper(I) compounds in solution was 0.10 *N*. ^b R refers to neophyl; R' refers to benzyldimethylcarbinyl.

agents. The thermal stabilities of these two copper alkyls are sufficiently disparate that if their rates of decomposition in the mixed solutions are in the same ratio as are those in solutions in which each is the only organometallic component, the decomposition of the *tert*-butylcopper(I) compound should be complete before that of the neophylcopper(I) compound has progressed appreciably.

The data of Table II contain two significant pieces of information. First, the decompositions of the two organocopper reagents in solutions of their mixtures appear to proceed independently. In particular, the yields of isobutylene and isobutane obtained from *tert*-butyl(tri-*n*-butylphosphine)copper(I) are clearly independent of the concentration of **3**. The apparent variation in the yield of **9** on decreasing the starting ratio of neophyl to *tert*-butyl groups is undoubtedly real, but may reflect changes in the concentration of **3** or of tri-*n*-butylphosphine rather than interaction between **3** and the *tert*-butylcopper(I) reagent. Second, none of the "mixed" dimer 2-phenyl-2,4,4-trimethylpentane (**15**) is formed in the decomposition of the mixtures of the neophyl- and *tert*-butylcopper reagents, even under circumstances in which an appreciable yield of the dimer **10** is formed. Similarly, no hexamethylethane is formed in the decomposition of *tert*-butyl(tri-*n*-butylphosphine)copper(I)



under conditions in which an easily detectable quantity of dimer **11** is formed.¹⁶ The absence of **15** and of

(15) (a) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969); (b) A. G. Davies and B. P. Roberts, *J. Organometal. Chem.*, **19**, 17 (1969); (c) A. Ricker, *Angew. Chem.*, **76**, 601 (1964).

(16) An authentic sample of another possible mixed dimer from these reactions, 1-phenyl-2,2,3,3-tetramethylbutane, was not available during these studies. However, no unidentified peak of appreciable area having a retention time of the magnitude expected for this compound was observed during the glpc analyses of these reaction mixtures.

hexamethylethane establishes that *tert*-butyl(tri-*n*-butylphosphine)copper(I) does not couple either with **3** or with itself under the conditions of these reactions.

In interpreting these experiments, we make the plausible assumption that the thermal stability, reactivity, and mode of thermal decomposition of *tert*-butyl(tri-*n*-butylphosphine)copper(I) and of **12** are sufficiently similar that the former is a satisfactory model for the latter. Then, if the dimer **10** were produced in the thermal decomposition of neophylcopper by a pathway involving the initial conversion of **3** to **12**, followed by subsequent reaction of **12** with **3** to yield **10**, analogous reactions taking place during the thermal decomposition of *tert*-butyl(tri-*n*-butylphosphine)copper(I) in the presence of **3** should lead to the mixed dimer **15**. Since **15** is not observed as a product, we conclude that the rearranged copper(I) compound **12** is *not* a significant intermediate in the reactions leading to the dimeric products containing the rearranged neophyl skeleton, and in consequence that the most probable precursor to these products is in fact the benzyldimethylcarbonyl radical **2**. This conclusion cannot be extended automatically to exclude the intermediacy of **12** in the formation of the monomeric products **6**, **7**, and **8**, and we have no convincing evidence establishing the structure of the immediate precursor of these hydrocarbons. However, the neophyl radical is again clearly implicated at some stage of the reaction sequence leading to their formation by the fact that all three contain the benzyldimethylcarbonyl moiety.

Relative Reactivities of Alkylcopper(I) Reagents toward Copper(I) Hydride. Observations on the Thermal Decomposition of *tert*-Butyl(tri-*n*-butylphosphine)copper(I). The observation that the formation of isobutane and isobutylene from *tert*-butyl(tri-*n*-butylphosphine)copper(I) present in a solution containing neophyl(tri-*n*-butylphosphine)copper(I) proceeds by a reaction sequence which is independent of the concentration of the neophylcopper deserves comment. If the thermal decomposition of *tert*-butyl(tri-*n*-butylphosphine)copper(I) is assumed to take place predominantly by a copper hydride elimination-reduction process analogous to that established for *n*-butyl(tri-*n*-butylphosphine)copper(I),³ it is not obvious *a priori* that the neophylcopper reagent should not be capable of competing with the *tert*-butylcopper for the copper hydride assumed to be present as an intermediate during the decomposition of the latter. To establish the relative reactivity of typical alkylcopper(I) reagents toward copper hydride, pairs of copper reagents were allowed to decompose thermally in solutions containing limiting quantities of deuterido(tri-*n*-butylphosphine)copper(I), and the quantity of deuterium incorporated into each alkyl group of the reduced products was determined mass spectrometrically. The relative reactivities inferred from these competition experiments are listed in Table III. These data demonstrate that the relative reactivity of alkylcopper reagents toward copper deuteride varies only slightly with structure. Thus, the observation that the thermal decompositions of mixtures of **3** and *tert*-butyl(tri-*n*-butylphosphine)copper(I) proceed independently must reflect some feature of these mixtures other than the relative reactivity of their constituent alkyl moieties toward copper hydride. It is possible that this independence reflects in some way the

Table III. Relative Reactivities of Organocopper(I) Reagents [RCuP(*n*-Bu)₃]_n toward Deuterido(tri-*n*-butylphosphine)copper(I)

R	Rel reactivity ^a
CD ₃ CH ₂ CH ₂ CH ₂ ^b	1.0
CH ₃ CH ₂ CH(CH ₃)	1.3
C ₆ H ₅ C(CH ₃) ₂ CH ₂	3.0 ^c
(CH ₃) ₃ C	3.3

^a Relative reactivities between pairs of organocopper(I) reagents were determined in diethyl ether at ~0°, unless otherwise noted; the starting concentration of each organocopper(I) reagent was 0.05 *N*, and that of DCuPBu₃ was 0.01 *N*. ^b The deuterium label in this alkyl moiety was included to facilitate mass spectroscopic analysis (see the Experimental Section). ^c This datum was determined in ether-pentane (50:50, v/v).

composition, structure, or extent of aggregation of the organometallic compounds in solution;^{17,18} however, it is also possible that the mechanism of thermal decomposition of *tert*-butyl(tri-*n*-butylphosphine)copper(I) differs from that of *n*-butyl(tri-*n*-butylphosphine)copper(I).¹⁹ A mechanism involving *tert*-butyl free radicals as intermediates cannot be excluded at this time, although the low yield of hexamethylethane observed as a product of reaction effectively precludes bimolecular disproportionation and combination between *tert*-butyl radicals as the source of the hydrocarbon products.²⁰

Estimation of the Relative Importance of Radical and Nonradical Mechanisms in the Thermal Decomposition of **3 and **4**.** Having established that neophyl and benzyldimethylcarbonyl radicals are precursors to an appreciable fraction of the products observed in the thermal decomposition of **3**, the question remains as to whether the free-radical mechanism producing these species is the *only* important process involved in the decomposition, or whether there are other nonradical processes which make significant contributions to the decomposition process. This problem is difficult to resolve with high precision. Although the experimental observation of the variety of products expected from the reaction and rearrangement of neophyl radicals in a particular reaction of interest provides an excellent *qualitative* test for a free-radical mechanism, quantitative estimation of the importance of nonradical contributions to a reaction proceeding predominantly through a radical pathway is more difficult. Nonetheless, inspecting the products of decomposition of **3** at 125° in ether (Table I), it is clear that **11** must have come exclusively through a radical reaction, since it is derived entirely from benzyldimethylcarbonyl radical. Ben-

(17) The influence of the extent of aggregation of the alkylcopper(I) reagents on their reactivity is largely unknown. See ref 3 for a discussion of this point.

(18) It has proved possible to demonstrate that organocopper reagents generated initially in different clusters *are* capable of reaction with one another under conditions similar to those employed during this work. Thus, thermal decomposition of 1:1 mixtures of methyl- and *tert*-butyl(tri-*n*-butylphosphine)copper(I) in ether at 0° yields isobutane (36%) and neopentane (64%), with less than 0.1% isobutylene. Although the mechanism responsible for production of these products is presently obscure, the detection of high yields of neopentane demonstrates that interaction between alkylcopper reagents of different structure and thermal stability can occur, and provides some further support for the contention that rearrangement of **3** to **12** in the thermal decomposition of mixtures of **3** and *tert*-butylcopper reagents would have resulted in detectable yields of **15**.

(19) Evidence of M. Tamura and J. Kochi points to a similar conclusion: *J. Amer. Chem. Soc.*, **93**, 1485 (1971).

(20) The ratio of rate constants for the disproportionation and combination of *tert*-butyl radicals is ~4.6; cf. W. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 317.

zylidimethylcarbonyl radical must be a precursor for 6, 7, and 8 at some point. It is difficult to rationalize the production of *tert*-butylbenzene in this reaction from routes other than attack by radical 1 on solvent, disproportionation between 1 and 2 (or 12), and hydrolysis.²¹ Dineophyl (9) might be derived in part from a nonradical reaction; however, coupling between two neophyl radicals or attack of neophyl radical on 3 would seem more consistent with the clearly radical nature of the decomposition. Hence, we conclude that nonradical contributions to the thermal decomposition of 3 are probably of minor importance.

The close similarity between the observed product distributions from the thermal decomposition of 3 at 125° and 4 at 65° strongly suggests that these reagents decompose by similar mechanisms. The difference in the temperature at which these experiments were conducted probably reflects primarily a difference in the activation energy for homolytic scission of carbon-copper(I) and carbon-silver(I) bonds. The data in Table I indicate that increasing the temperature at which the thermal decomposition of a neophyl organometallic compound is carried out increases the amount of rearrangement observed in the products. However, as is clear from earlier work,⁸⁻¹⁰ those factors which influence the lifetime of the radical intermediates at any particular temperature also influence the distribution of reaction products.²² Hence, the observation that similar product distributions are obtained from decomposition of 3 and 4 only at different temperatures probably reflects a complex balancing of the rates of radical-radical and radical-solvent reactions, rather than differences in the activation energies for corresponding reactions of the intermediate free radicals in these two decompositions. This supposition is consistent with the observation that the overall rates of decomposition of 3 at 125° and of 4 at 65° are approximately equal.

In conclusion, the work described in this paper establishes that the thermal decomposition of 3, an aliphatic copper(I) reagent in which the β elimination of CuH is impossible, proceeds in major part by a free-radical mechanism. This result bears contrast with the previous demonstration⁴ that the thermal decomposition of vinylic (and presumably aromatic)²³ copper(I) and silver(I) reagents takes place by a nonradical mechanism.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under prepurified nitrogen or grade A helium using the usual techniques for handling air- and water-sensitive compounds.²⁴ Dioxane was purified by distillation under nitrogen from a dark purple solution of sodium benzophenone dianion. Ether and tetrahydrofuran were distilled from lithium aluminum hydride under a nitrogen atmosphere immediately before use. Hydrocarbon solvents were scrubbed with concentrated sulfuric acid to remove olefinic impurities and distilled from a suspension of sodium benzophenone ketyl under a nitrogen atmosphere im-

mediately before use. Melting points were obtained using a Thomas Hoover Capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Nmr spectra were run as carbon tetrachloride solutions on a Varian A-60 spectrometer; chemical shifts are reported in parts per million downfield from tetramethylsilane and coupling constants are in hertz. Infrared spectra were taken in sodium chloride cells using Perkin-Elmer Models 237, 237B, or 337 grating spectrophotometers. Mass spectra were determined on a Hitachi-Perkin-Elmer Model RMU-6D mass spectrophotometer; spectra used for isotopic analysis were obtained using low ionizing voltages. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

Analytical glpc analyses were performed on F and M Model 810 instruments equipped with flame ionization detectors using response factors obtained with authentic samples. All components derived from 3 in a reaction mixture could be analyzed using a 6 ft \times 1/4 in. 5% diethylene glycol succinate on 80-100 mesh Chromosorb W column, temperature programmed from 60 to 210°. In addition, an 8 ft \times 1/4 in. 20% UC-W98 on 80-100 mesh Chromosorb W column could be used at 110° for analyses of the monomeric hydrocarbon products more accurately than those obtained with the diethylene glycol succinate column. Neophyl dimers were on occasion analyzed separately using a 6 ft \times 1/4 in. 13% SE-52 on 80-100 mesh Chromosorb W column. The yields of *tert*-butylbenzene formed in reactions of neophyllithium were corrected for the amount of *tert*-butylbenzene present before preparation of 3, as determined by 1,2-dibromoethane quench. Low molecular weight products derived from reactions of *tert*-butyl(tri-*n*-butylphosphine)copper(I) were analyzed using an 8 ft \times 1/4 in. 20% UC-W98 on 80-100 mesh Chromosorb W column.

Concentrations of organolithium reagent solutions were determined by the Gilman double titration method using 1,2-dibromoethane.^{3,25} Solutions of methylolithium (prepared from methyl chloride) in ether and *n*-butyllithium in hexane were purchased from Foote Mineral Co.; *tert*-butyllithium in pentane was purchased from Alpha Inorganics, Inc.

Neophyl chloride, prepared by the alkylation of benzene with 3-chloro-2-methylpropene using sulfuric acid as a catalyst,²⁶ had bp 110-111° (13 mm); n_D^{20} 1.5250.

Neophylmagnesium Chloride. A 2.0 M solution of neophylmagnesium chloride was prepared by allowing 33.0 g (0.20 mol) of neophyl chloride and 5.0 g (0.21 g-atom) of magnesium turnings activated with 1,2-dibromoethane to react in 100 ml of ether. The magnesium turnings were covered with approximately 50 ml of ether. The reaction mixture was refluxed overnight to ensure complete reaction. THF solutions of neophylmagnesium chloride were prepared in a similar fashion.

Neophyl bromide was prepared by the reaction of neophylmagnesium chloride with bromine in ether at 0°: ^{27a} bp 85-86° (3 mm), n_D^{20} 1.5450 (lit.^{27a} bp 110° (4.5 mm), n_D^{20} 1.5433; lit.^{27b} bp 91.3-91.5° (4 mm), n_D^{20} 1.5457). It had nmr δ 7.25 (m, 5, aromatic), 3.48 (s, 2, CH₂), and 1.47 (s, 6, CH₃), and ir (CS₂) 2970, 1380, 1370, 1290, 1245, 1225, 1035, 840, 760, 700, 560, and 550 cm⁻¹.

Dineophylmercury was prepared by an adaptation of a method used for the preparation of dicyclopropylmercury.²⁸ A 2 M solution of neophylmagnesium chloride was prepared from 68.0 g (0.40 mol) of neophyl chloride and 9.7 g (0.40 g-atom) of magnesium turnings in 200 ml of THF. Mercuric chloride (42.0 g, 0.16 mol; 0.8 equiv) dissolved in 75 ml of THF was added dropwise over a period of 45 min to the gently refluxing, stirred solution of the Grignard reagent. The reaction mixture was refluxed for an additional 10 hr, cooled to room temperature, and carefully hydrolyzed with 100 ml of water. The insoluble grey-white magnesium salts were separated from the THF and aqueous layers by suction filtration. The THF and aqueous layers were then separated and the aqueous layer was extracted with two volumes of ether. The combined ether and THF layers were washed twice with brine, dried (MgSO₄), and concentrated under aspirator vacuum. Any remaining volatile reaction components were removed by evacuating the residue to 0.1 mm at 50° for 48 hr. The crude dineophylmercury (56.3 g of a light yellow oil, 0.12 mol) was recrystallized three

(21) A large body of qualitative evidence from these laboratories indicates that alkylcopper(I) reagents are not sufficiently basic to abstract a proton from diethyl ether.

(22) Comparison of the product yields observed on thermal decomposition of dineophylmercury at a common temperature in solvents of differing hydrogen donor abilities dramatically illustrates this influence.

(23) 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).

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

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

(26) W. T. Smith, Jr., and J. T. Sellas, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 702.

(27) (a) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956); (b) J. D. Blackhurst, *J. Chem. Soc.*, 1958 (1960).

(28) G. F. Reynolds, R. E. Dessy, and H. H. Jaffe, *J. Org. Chem.*, **23**, 1217 (1958).

times from methanol-ether (2:1) at -78° ²⁹ to yield 41.8 g (0.09 mol, 56% based on HgCl_2) of white needles, mp $25-26^{\circ}$ (lit.²⁹ mp $26.0-26.5^{\circ}$), having ir (CCl_4 , CS_2) 2970, 1604, 1500, 1475, 1450, 1385, 1365, 1280, 1035, 905, 770, 700, 615, and 555 cm^{-1} , and nmr δ 7.19 (m, 5, aromatic), 1.30 (t, 2, CH_2 , $J(^{199}\text{HgCH}_2) = 92\text{ Hz}$), and 1.20 (t, 6, CH_3 , $J(^{199}\text{HgCH}_3) = 6.5\text{ Hz}$). The intensity of the ^{199}Hg satellites was approximately the expected 20% of the center bands.³⁰

Neophyllithium. A pentane solution containing 1.40 g (3.0 mmol) of dineophylmercury was added by funnel through the top arm of an 80-ml flame-dried Schlenk tube³¹ containing a magnetic stirring bar while flushing helium through the tube *via* the side arm. The top arm was then connected to a water aspirator isolated by a calcium sulfate drying tower and the pentane was removed under reduced pressure with the helium flow turned off. The tube was filled with He, the aspirator connection removed, and a pentane suspension of *ca.* 1.0 g (140 mg-atom) of freshly prepared lithium dispersion³² added by funnel through the top arm while flushing helium through the tube. As before, the top arm was connected to the aspirator and the pentane volume was reduced to *ca.* 8 ml. After cooling the tube and its contents to -78° under helium, the top arm and then the side arm were sealed while maintaining a helium atmosphere in the tube. At this point the contents of the tube were frozen with liquid nitrogen and a slight constriction was made in the side arm about 1 in. from the sealed end. After the tube warmed to room temperature, it was placed in a bath at $55-60^{\circ}$ and the contents were stirred magnetically. During the transmetalation reaction, white crystals of neophyllithium and black lithium amalgam were formed, and sank to the bottom of the tube. The reaction was complete within 2 hr (the excess lithium remained bright).³³

To remove the contents from the tube the constriction on the side arm was scored with a glass scribe and the side arm was attached by a short length of Tygon tubing to one arm of a three-way stopcock, the opposite arm of which was sealed with a No-Air stopper. The remaining arm was connected to a vacuum-nitrogen manifold. After evacuating and filling the stopcock and connecting tubing with nitrogen a number of times, the side arm was broken at the constriction while under a nitrogen atmosphere. If a solvent other than pentane was to be used for the subsequent reactions of the lithium reagent, the pentane was removed by distillation at reduced pressure at this time. While protecting the solid residue from the distillation under a positive pressure of nitrogen, a stainless steel cannula was inserted through the rubber septum and the stopcock into the side arm of the Schlenk tube. The desired solvent (or more pentane) was added through the cannula by forced transfer under a positive pressure of nitrogen and, after the neophyllithium had dissolved, the solution was transferred from the tube to a suitable container through the cannula in the same manner. A saturated solution of neophyllithium in *n*-pentane or *n*-heptane at room temperature is *ca.* 0.1 *N*. Crystalline, ether-free neophyllithium can be obtained by cooling a pentane solution saturated at room temperature to -78° and removing the solvent, or by slowly distilling the pentane from a pentane solution under reduced pressure.

Proof of Identity of Neophyllithium. Hydrolysis of a sample of neophyllithium yields only *tert*-butylbenzene; no (<0.1%) *iso*-butylbenzene, neophyl alcohol, or neophyl dimers were detected in a hydrolyzed aliquot by glpc analysis. A solution of neophyllithium in ether at room temperature reacts with either ethylene dibromide or bromobenzene to yield neophyl bromide quantitatively. Hydrocarbon solutions of neophyllithium yield neophyl bromide quantitatively upon reaction with bromine at -78° .

2-Methyl-1-phenyl-2-propene (7). Enough of this material was obtained for determinations of glpc retention times and response factors by the following procedure. Dehydration of 2-methyl-1-phenylpropan-2-ol (22.5 g, 0.15 mol) was carried out at 110° using

2 drops of 20% aqueous sulfuric acid catalyst. The reaction products were distilled as they formed (bp $60-80^{\circ}$ (20 mm)), dried (MgSO_4), and redistilled. A sample of the desired material was collected from glpc of a fraction having bp $70-75^{\circ}$ (20 mm) (lit.³⁴ bp $69-70^{\circ}$ (20 mm)), and its identity was confirmed by comparison of its ir spectrum with that of an authentic sample in the Sadtler file (no. 2046).

2-Methyl-1-phenylpropan-1-ol. Approximately 160 ml of 1.6 *N* isopropyl Grignard reagent was added, with stirring and cooling, to 27.0 g (0.250 mol) of benzaldehyde dissolved in 150 ml of ether over a period of 1.5 hr at 15° . After stirring for an additional 30 min, the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride solution and worked up in the usual manner to yield 30.0 g (0.200 mol, 80%) of the desired alcohol, bp $101-104^{\circ}$ (8 mm), n_D^{20} 1.534 (lit.³⁵ bp $101-104^{\circ}$ (7 mm)).

2-Methyl-1-phenyl-1-propene (8). A solution of 12.9 g (86 mmol) of 2-methyl-1-phenylpropan-1-ol and 10.0 g (66 mmol) of phosphorus oxychloride in 75 ml of benzene was stirred at reflux for 20 min.³⁶ The ruby red mixture was cooled to 0° , the layers were separated, and the benzene layer was extracted with cold water until the water was neutral and then dried (MgSO_4). After removing benzene, 3.7 g (27 mmol, 31% yield) of the desired olefin (>95% pure by nmr) was obtained by fractional distillation, bp $92-95^{\circ}$ (22 mm) (lit.³⁴ bp $79-80^{\circ}$ (20 mm)). The identity of this material was confirmed by comparison of its ir spectrum with that in the Sadtler file (no. 2045).

2,5-Dimethyl-2,5-diphenylhexane (9) was prepared in 16% yield by the reaction of cumyl potassium³⁷ with 1,2-dichloroethane in ether at 0° .³⁸ It was isolated from the reaction mixture by fractional distillation, bp $142-145^{\circ}$ (0.1 mm), and then recrystallized from absolute ethanol at -20° , mp $60-61^{\circ}$ (lit.³⁸ mp $60-61^{\circ}$; lit.³⁹ bp 158° (0.4 mm), mp 65°). Its nmr spectrum, δ 7.07 (m, 5, aromatic), 1.32 (s, 2, CH_2), and 1.18 (s, 6, CH_3), agrees with the reported³⁹ values.

Anal. Calcd for $\text{C}_{20}\text{H}_{26}$: C, 90.16; H, 9.84. Found: C, 90.14; H, 9.89.

2,4-Dimethyl-4-phenylpentan-2-ol. Approximately 50 ml of a 4 *N* ether solution of neophyl Grignard, prepared from 33.6 g (0.20 mol) of neophyl chloride and 5.0 g (0.20 g-atom) of magnesium, was cooled to 0° . A solution of 23.2 g (0.20 mol) of acetone (dried over Molecular Sieve 4A) in 30 ml of ether was added with stirring to the Grignard reagent solution over a period of 1.5 hr at a rate such that the reaction temperature never exceeded 5° . The mixture was stirred at 0° , hydrolyzed with saturated aqueous ammonium chloride solution, and worked up in the usual manner. Fractional distillation of the crude reaction mixture yielded 20.0 g (0.10 mol, 50%) of the desired alcohol, bp $92-93^{\circ}$ (0.8 mm), n_D^{20} 1.5114 (lit.⁴⁰ bp $108.5-109^{\circ}$ (4 mm), n_D^{20} 1.5130), having nmr δ 7.22 (m, 5, aromatic), 1.93 (s, 2, CH_2), 1.40 (s, 6, CH_3), 0.92 (s, 6, CH_3), and 1.25 (s, 1, OH).

2-Bromo-2,4-dimethyl-4-phenylpentane. 2,4-Dimethyl-4-phenylpentan-2-ol (5.76 g, 30 mmol) dissolved in 25 ml of pentane was added to a mixture of 6.9 ml of 48% aqueous HBr (60 mmol) and 1.9 ml of concentrated H_2SO_4 over a period of 25 min. The reaction was stirred at 25° for an additional 1.5 hr, then poured into water. The organic layer was separated, washed with aqueous NaHCO_3 solution, dried (MgSO_4), and concentrated to yield 6.8 g of crude bromide as a yellow liquid. This material decomposed on attempted purification, and was characterized only on the basis of its nmr spectrum: δ 7.25 (m, 5, aromatic), 2.53 (s, 2, CH_2) 1.30 (s, 6, CH_3), and 1.25 (s, 6, CH_3).

1,4-Diphenyl-2,2,4-trimethylpentane (10). 2-Bromo-2,4-dimethyl-4-phenylpentane (10.3 g, 40 mmol, *ca.* 90% pure) in 25 ml of ether was added to a stirred, refluxing solution of benzyl Grignard reagent (25 ml, *ca.* 1.6 *N*) over 1.5 hr. The reaction mixture was stirred at reflux for an additional 3 hr, hydrolyzed (saturated aqueous NH_4Cl), and worked up as usual. The hydrocarbon 10

(29) S. Winstein and T. G. Traylor, *J. Amer. Chem. Soc.*, **77**, 3747 (1955).

(30) The nmr spectrum of dineopentylmercury is very similar: $J(^{199}\text{HgCH}_2) = 94.0\text{ Hz}$; $J(^{199}\text{HgCH}_3) = 5.5\text{ Hz}$; *cf.* G. Singh, *J. Organometal. Chem.*, **5**, 577 (1966).

(31) W. Schlenk and J. Holtz, *Chem. Ber.*, **50**, 262 (1917).

(32) P. D. Bartlett and E. B. Lefferts, *J. Amer. Chem. Soc.*, **77**, 2804 (1955).

(33) This transmetalation reaction has proved to be very sensitive to impurities and to experimental technique. In particular the dineophylmercury must be carefully purified for the transmetalation to take place. Even with scrupulous attention to detail, in our hands approximately one batch of dineophylmercury out of four could not be induced to react with lithium.

(34) F. G. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *J. Amer. Chem. Soc.*, **65**, 1469 (1943).

(35) J. B. Conant and A. H. Blatt, *ibid.*, **50**, 551 (1928).

(36) The method used was that of S. Lindenbaum, *Chem. Ber.*, **50**, 1270 (1917).

(37) K. Ziegler and H. Dislich, *ibid.*, **90**, 1107 (1957).

(38) H. Breederveld and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **76**, 297 (1957).

(39) C. Rüdhardt and H. Trautwein, *Chem. Ber.*, **95**, 1197 (1962).

(40) A. D. Petrov, G. I. Nikishkin, V. N. Gramenitskays, and V. D. Vorob'ev, *Zh. Obshch. Khim.*, **28**, 2315 (1958); *Chem. Abstr.*, **53**, 3145b (1959).

formed, 1.9 g (7.1 mmol, 18% based on tertiary bromide) was isolated by distillation, bp 104–105° (0.04 mm). The distillate was crystallized from absolute ethanol at –20° to yield white crystals, mp 32.0–32.5°, having nmr δ 7.15 (m, 5, aromatic), 7.05 (m, 5, aromatic), 2.30 (s, 2, CH₂), 1.80 (s, 2, CH₂), 1.35 (s, 6, CH₃), and 0.63 (s, 6, CH₃).

Anal. Calcd for C₂₀H₂₆: C, 90.16; H, 9.84. Found: C, 90.43; H, 9.66.

2-Bromo-2-methyl-1-phenylpropane, prepared in 80% yield by bubbling HBr through 2-methyl-1-phenylpropan-2-ol at room temperature, had: bp 63–65° (1 mm) (lit.⁴¹ bp 88–89° (5.3 mm)); ir (CCl₄) 3045, 2970, 2940, 1604, 1505, 1465, 1400, 1380, 1210, 1105, 700, 630, 610, 530 cm⁻¹; nmr δ 7.07 (s, 5, aromatic), 3.07 (s, 2, CH₂), 1.65 (s, 6, CH₃).

1,4-Diphenyl-2,2,3,3-tetramethylbutane (11). *Method A.* Ca. 40 ml of a 0.5 N ether solution of *n*-butylmagnesium bromide, prepared from 3.3 g (23 mmol) of *n*-butyl bromide and 0.8 g (33 mg-atom) of magnesium turnings, was stirred with 1.0 g (8 mmol) of anhydrous cobalt(II) chloride for 45 min at 0°. Then 3.3 g (15 mmol) of 2-bromo-2-methyl-1-phenylpropane, dissolved in 30 ml of ether, was added over a period of 1.5 hr. The reaction mixture was refluxed for 1 hr, cooled, and carefully hydrolyzed with 3% aqueous sulfuric acid. The reaction mixture was worked up in the usual manner to yield a yellow oil as the crude product. An nmr spectrum of this material indicated that isobutylbenzene and 2-methyl-1-phenyl-1-propene were the major products. By crystallization from ethanol, 142 mg (0.53 mmol, 7.1%) of hydrocarbon **11** was obtained as fine white needles, mp 131.5–132.5° (lit.³⁶ mp 131–132°), having nmr δ 7.00 (s, 5, aromatic), 2.57 (s, 2, CH₂), 0.78 (s, 6, CH₃), in reasonable agreement with that reported.³⁹

Method B. A solution of 3.5 g (26 mmol) of 2-methyl-1-phenyl-1-propene in 250 ml of ether was stirred for 147 hr at room temperature with 1.3 g of sodium-potassium alloy (prepared from 0.3 g of sodium and 1.0 g (26 mg-atom) of potassium) under a nitrogen atmosphere,³⁵ then hydrolyzed with wet ether. The crude product, a yellow oil, was purified as above to yield 0.80 g (3.0 mmol, 23%) of white needles, mp 131.5–132.5° (mmp with the sample prepared by method A, 131.5–132.5°).

Anal. Calcd for C₂₀H₂₆: C, 90.16; H, 9.84. Found: C, 89.87; H, 9.91.

2-Phenyl-2,4,4-trimethylpentane (15). *tert*-Butyllithium (1.30 ml of a 1.5 N solution in pentane, 1.95 mmol) was added to a solution of 1.93 mmol of **3** in a mixture of 22 ml of THF and 15 ml of ether at –78°, and the resulting solution was allowed to react with 50 ml of oxygen at –78°.⁴² The reaction mixture was allowed to warm to room temperature, hydrolyzed, dried (MgSO₄), and concentrated. Compound **15** was isolated from the reaction mixture by glpc (8-ft 20% DEGS on Chromosorb W at 80°), and had ir (CCl₄) 3080, 3060, 3030, 3020, 2960, 2900, 1604, 1500, 1470, 1450, 1395, 1385, 1365, 1250, 1030, 860, and 700 cm⁻¹; mass spectrum (70 eV) 190 (11) M⁺, 120 (11), 119 (100), 91 (28); nmr (CCl₄) 7.283 (5, m, aromatic), 1.73 (2, s), 1.37 (6, s), and 0.72 (9, s).

Anal. Calcd for C₁₄H₂₂: C, 88.25; H, 11.65. Found: C, 88.30; H, 11.58.

Organocopper(I) and -silver(I) Compounds. Neophyl(tri-*n*-butylphosphine)copper(I) was prepared as described previously for *n*-butyl(tri-*n*-butylphosphine)copper(I).³ Tetrakis[iodo(tri-*n*-butylphosphine)copper(I)]³ (393 mg, 0.25 mmol) was weighed into a flame-dried 40-ml centrifuge tube. The tube was capped with a No-Air stopper and flushed with nitrogen. Ether (3 ml) was added, and the resulting solution was cooled to –78° in a Dry Ice-acetone bath. Neophyllithium (1.0 mmol, 7.0 ml of a 0.14 N ether solution), also cooled to –78°, was added by cannula. The resulting bright yellow solution was shaken several times and returned to the –78° bath. Dioxane (100 μ l, 1.2 mmol) was added and the resulting white precipitate of lithium iodide dioxanate was packed on the bottom of the tube by centrifugation using a centrifuge bucket packed with Dry Ice. Ether solutions of methyl- or *tert*-butyl(tri-*n*-butylphosphine)copper(I) were prepared by reaction at –78° between tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] and methyl- or *tert*-butyllithium as described previously.³ Neophyl(tri-*n*-butylphosphine)silver(I) was prepared by reaction of neophyllithium in ether at –78° with tetrakis[iodo-*n*-butylphosphine]-silver(I).¹³ Neophyl(tri-*n*-butylphosphine)silver(I) and *tert*-butyl-

(tri-*n*-butylphosphine)copper(I) decompose rapidly if kept at temperatures greater than –78° for more than a few minutes; in consequence, the white precipitate of lithium iodide dioxanate which formed on addition of dioxane to solutions of these reagents was allowed to settle at –78° rather than being packed by centrifugation.

Thermal decomposition reactions were run in sealed 8-mm Pyrex tubes whose walls had been neutralized with 5% aqueous ammonium hydroxide solution and dried in a vacuum oven at 120° prior to use. These tubes were filled with organometallic solutions using the following procedure. A tube was attached to one arm of a three-way stopcock using Tygon tubing, and the opposite arm was sealed with a No-Air stopper; the remaining arm of the stopcock was attached to the vacuum-nitrogen manifold. The tube was flame-dried under vacuum, filled with nitrogen, and reevacuated a number of times, and then immersed in a Dry Ice-acetone bath. The tube was connected to the storage vessel containing the organometallic solution by a stainless steel cannula inserted through the stopcock and the No-Air stopper, charged with ca. 2 ml of the organometallic solution (or with accurately measured quantities of solutions of known concentrations for decompositions of mixtures of organometallic compounds, degassed by several freeze-thaw cycles (liquid nitrogen), and sealed. The filled tube was finally immersed in a bath at the temperature desired for the thermal decomposition. During the decompositions the initially clear solutions became dark and turgid as metallic copper or silver formed. At the end of the decompositions, when metal formation had stopped, the solutions became colorless and transparent. The time required to react to this stage is the number reported as the "decomposition time" in Table I, and is probably ca. 10–15 half-lives for the decomposition. Decompositions reported in Table I were carried out for several hours longer than the "decomposition time," in order to ensure complete decomposition. Mixtures of **3** and *tert*-butyl(tri-*n*-butylphosphine)copper(I) (Table II) were allowed to decompose for 18 hr at 30°, then heated to 60° for 4 hr. Absolute yields of products were determined by glpc analysis using appropriate internal standards. The product identities were confirmed by comparison of the infrared spectra of samples collected by glpc with those of authentic samples.

Thermal Decomposition of Dineophylmercury. Degassed *n*-heptane and *p*-dioxane solutions of dineophylmercury (0.05 N), containing *n*-pentadecane as an internal standard, were decomposed thermally at 230–240° for 1 week in neutral-walled 8-mm Pyrex tubes.

Methyl Trichloroacetate. Trichloroacetonitrile (216 g, 1.5 mol) was added to a stirred solution of sodium (1.6 g, 0.075 mol) in methanol (145 g, 4.5 mol) maintained in an ice bath over a 30-min period.⁴³ After an additional 30 min of stirring, the mixture was poured with vigorous stirring onto a slurry of 200 ml of concentrated hydrochloric acid and 200 ml of crushed ice. The organic layer was separated, the aqueous layer was extracted with methylene chloride, and the combined organic layers were washed with aqueous sodium carbonate and dried (MgSO₄). Methyl trichloroacetate (178 g, 1.01 mol, 68% yield), isolated by distillation through a 120-cm Nester-Faust Teflon spinning band column, had bp 143–145° (760 mm) (lit.⁴⁴ bp 152° (748 mm)).

Methyl Acetate-2,2,2-d₃. Reagent zinc dust (300 g, 4.7 g-atom), hexamethylphosphoramide (150 ml), benzene (150 ml), and diglyme (150 ml) were placed in a 1-l. three-necked, round-bottomed flask fitted with a Dean-Stark trap, a mechanical stirrer, and a thermometer extending down into the slurry; one arm of the flask was closed with a serum stopper. Azeotropic distillation was used to dry the apparatus and reaction mixture. Three 3-ml portions of deuterium oxide were added and removed by azeotropic distillation in order to exchange possible sources of protons. The Dean-Stark trap was replaced by a distillation head and most of the benzene was separated from the reaction mixture. The distillation head was replaced by a reflux condenser, and 10 ml of deuterium oxide was added to the reaction mixture. The mixture was heated to 80°, and methyl trichloroacetate (2 ml) was added. An immediate 5–10° temperature rise indicated initiation of the reaction.⁴⁵ The

(43) For a description of the conversion of nitriles to methyl imidates see: F. C. Schaeffer and G. A. Peters, *J. Org. Chem.*, **26**, 412 (1961); R. Rogers and D. G. Nelson, *Chem. Rev.*, **61**, 179 (1961); T. C. Plecheter, S. Koehler, and E. H. Cardes, *J. Amer. Chem. Soc.*, **90**, 7072 (1968).

(44) A. I. Vogel, *J. Chem. Soc.*, 1849 (1948).

(45) If the reduction did not initiate at 80°, the reaction temperature was increased to 90 or 100°. If more than 0.1–0.2 mol of ester was added before the reduction had begun, the exotherm resulting on initiation was uncontrollable.

(41) H. C. Duffin, E. D. Hughes, and C. Ingold, *J. Chem. Soc.*, 2734 (1959).

(42) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).

reaction flask was immersed in an ice bath and its internal temperature maintained at 50–60° by cautious addition of methyl trichloroacetate (176 g, 1 mol) and deuterium oxide (88 g, 4.4 mol), adding 0.44 mol of deuterium oxide in one portion after each 0.1-mol portion of ester. The reaction temperature was maintained at 50–60° for 2 hr after addition was completed. The reflux condenser was replaced by a connection to a high capacity liquid nitrogen-cooled trap, the pot was warmed to 70°, and methyl acetate-2,2,2-*d*₃ was swept into the trap by a stream of nitrogen directed through a needle projecting below the surface of the stirred slurry. The organic layer obtained from the thawed condensate in the trap was dried (MgSO₄), and distilled through an 8-in. platinum spinning band column, yielding methyl acetate-2,2,2-*d*₃ (48.5 g, 0.63 mol, 63%), bp 56°.

Ethanol-2,2,2-*d*₃ was prepared from methyl acetate-2,2,2-*d*₃ (48.5 g, 0.63 mol) dissolved in 50 ml of ether by reduction with lithium aluminum hydride (25 g, 0.67 mol) in 300 ml of ether at ~0°. The mixture was refluxed for 30 min, and quenched with water (25 ml), 15% aqueous NaOH (25 ml), and additional water (75 ml). The ether was decanted and the residual aluminum salts were refluxed with two 100-ml portions of ether. The product was isolated by a careful, preliminary spinning band distillation; the material boiling between 36 and 90° was dried (MgSO₄) and redistilled, yielding ethanol-2,2,2-*d*₃ (19.24 g, 0.39 mol, 62%), bp 76–80°.

1-Bromoethane-2,2,2-*d*₃ was prepared from ethanol-2,2,2-*d*₃ in 91% yield by a procedure analogous to that of Kamm and Marval.⁴⁶

1-Butanol-4,4,4-*d*₃ was prepared in 52% yield by the reaction of ethyl-2,2,2-*d*₃ magnesium bromide with ethylene oxide, using a procedure analogous to that of Huston and Langham.⁴⁷

1-Bromobutane-4,4,4-*d*₃ was prepared in 71% yield by a procedure analogous to that of Kamm and Marval.⁴⁸ The mass spectrum of this material (8 eV) indicated an isotopic composition of 92.0% *d*₃, 6.5% *d*₂, and 1.5% *d*₁ material, corresponding to a minimum of 97.5 atom % deuterium incorporation per carbon-chlorine bond reduced in the preparation of methyl acetate-2,2,2-*d*₃.

n-Butyl-4,4,4-*d*₃-lithium. 1-Bromobutane-4,4,4-*d*₃ (9.6 g, 65 mmol) diluted to a total volume of 15 ml with pentane was added using a constant rate syringe drive over the course of 2 hr to 2 g of lithium dispersion (Foote Mineral Co.) in 40 ml of refluxing pentane. The solution was centrifuged and then filtered through a plug of glass wool to yield 50 ml of 0.88 *N* *n*-butyl-4,4,4-*d*₃-lithium (44 mmol, 69%). *s*-Butyllithium was prepared from 2-chlorobutane by an analogous procedure. *tert*-Butyllithium was purchased from Foote Mineral Co. Deuterido(tri-*n*-butylphosphine)copper(I) was prepared from copper(I) bromide and diisobutylaluminum deuteride using procedures already described.⁴⁸

Competition between *s*-Butyl- and *n*-Butyl-4,4,4-*d*₃(tri-*n*-butylphosphine)copper(I) for Deuterido(tri-*n*-butylphosphine)copper(I).

(46) C. S. Marval and O. Kamm, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 25.

(47) R. C. Huston and C. C. Langham, *J. Org. Chem.*, **12**, 90 (1947).

(48) G. M. Whitesides and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 6611 (1970).

Tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] (0.4177 g, 0.267 mmol) in ether (10.0 ml) was treated at –78° with *s*-butyllithium (0.534 mmol, 0.606 ml, 0.880 *N*) and *n*-butyl-4,4,4-*d*₃-lithium (0.534 mmol, 0.450 ml, 1.180 *N*) in a 12-ml centrifuge tube sealed with a rubber septum. Lithium iodide was precipitated as its insoluble dioxanate with 1.2 equiv of dioxane. After centrifugation at –78°, the supernatant solution, 9.0 ml out of a total volume of 9.9 ml, containing 0.93 mmol of alkylcopper(I) reagents, was transferred by cannula to a 12-ml centrifuge tube. A solution of deuterido-(tri-*n*-butylphosphine)copper(I) (0.10 mmol, 1.0 ml, 1.0 *N*) in ether was added to this tube at –78° as rapidly as possible by syringe. Residual alkylcopper(I) reagents were decomposed thermally by allowing the contents of the tube to stand at room temperature for 1 hr. Yields of *n*-butane (56%), 1-butene (36%), and *cis*- and *trans*-2-butene (12%) were determined quantitatively using a 6-ft, 0.125-in. 80–100 mesh Durapak⁴⁹ column at room temperature. Samples of *n*-butane and 1-butene were collected for mass spectral analysis using a 4-ft 3% Apiezon N on alumina column at 70°. Mass spectral analysis, after correction for the *d*₂ and *d*₁ species present in the *n*-butylcopper(I), indicated the presence of *n*-butane-*d*₄ (9.0%), -*d*₃ (31.3%), -*d*₁ (11.4%), and -*d*₀ (18.3%), and 1-butene-*d*₃ (60.9%) and -*d*₀ (39.1%).

Competition between *tert*-Butyl- and *n*-Butyl(tri-*n*-butylphosphine)-copper(I) for Deuterido(tri-*n*-butylphosphine)copper(I). Tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] (0.4082 g, 1.041 mmol) in ether (10.0 ml) was treated with *n*-butyllithium (0.52 mmol, 0.35 ml, 1.49 *N*) and *tert*-butyllithium (0.52 mmol, 0.42 ml, 1.24 *N*). After removal of lithium iodide by precipitation with dioxane and transfer of the supernatant solution of alkylcopper(I) reagents (0.94 mmol total, 9.1 ml) to a second 12-ml centrifuge tube, deuterido(tri-*n*-butylphosphine)copper(I) (0.10 mmol, 1.0 ml, 1.0 *N*) was added as rapidly as possible by syringe. After thermal decomposition of the sample, glpc analysis (Durapak column) indicated the presence of isobutane (31.6%), *n*-butane (25.8%), 1-butene (25.8%), and isobutylene (16.7%). Mass spectral isotopic analysis of samples of isobutane and *n*-butane (10 eV) indicated the presence of isobutane-*d*₁ (52%) and -*d*₀ (48%), and *n*-butane-*d*₁ (20.5%) and -*d*₀ (79.5%).

Competition between *tert*-Butyl- and Neophyl(tri-*n*-butyl)copper(I) for Deuterido(tri-*n*-butylphosphine)copper(I). Tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] (0.4078 g, 1.04 mmol) in ether (5.0 ml) was treated with neophyllithium (0.52 mmol, 6.58 ml, 0.079 *N*) in pentane and *tert*-butyllithium (0.52 mmol, 0.425 ml, 1.24 *N*) in pentane. Addition of DCu(PBu₃) (10.10 mmol), decomposition, and analysis were carried out as described previously, indicating the presence of isobutane-*d*₁ (0.55 mmol) and *tert*-butylbenzene-*d*₁ (0.049 mmol) among the products.

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(49) Durapak (type *n*-octane/Poracil C) available from Waters Associates, Framingham, Mass., makes possible a base-line separation between *cis*- and *trans*-2-butene in 8 min. It is the most efficient column for separating C₁ to C₆ hydrocarbons we have used.