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


Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Received November 13, 1970

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(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).


[Reprinted from the Journal of the American Chemical Society, 94, 232 (1972).]
butyraldehyde 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. The rate constant for this latter reaction is almost certainly 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.  

Results and Discussion

Ether solutions of neophyl(tri-n-butylphosphine)copper(I) (3) were prepared by the reaction of 1 equiv of neopentyllithium with 1 equiv of tetrakisiodo(tri-n-butylphosphine)copper(I) at $-78^\circ$. For comparison of thermal decomposition products, neophyl(tri-n-butylphosphine)silver(I) (4) was prepared in a similar manner from tetrakisiodo(tri-n-butylphosphine)silver(I).

Treatment of solutions of these organometallic compounds with 1 equiv of dioxane/ethanol/acetic anhydride at $-78^\circ$ removed the lithium iodide formed in the preparations as an insoluble dioxanate. 

Both 3 and 4 are appreciably more stable than $n$-butyl(tri-n-butylphosphine)copper(I) or silver(I). Decomposition of ca. 0.1 N etheral solutions of 3 and 4 at temperatures above $30^\circ$ proceeded at convenient rates and in high yields to mixtures of hydrocarbon products containing both neophyl and benzylidemethylcarbinyl 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 diethynylmercury 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

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

<table>
<thead>
<tr>
<th>Product</th>
<th>$30^\circ$, 1800</th>
<th>$30^\circ$, 655, 155</th>
<th>$125^\circ$, $&lt;5^\circ$</th>
<th>$235^\circ$, $&lt;10^\circ$</th>
<th>$235^\circ$, $&gt;10^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C,H,CH(CH$_3$)$_3$ (5)</td>
<td>59.1</td>
<td>57.5</td>
<td>58.9</td>
<td>45.7</td>
<td>56</td>
</tr>
<tr>
<td>C,H,CH,CH,CH, (6)</td>
<td>6.6</td>
<td>6.1</td>
<td>7.0</td>
<td>17.9</td>
<td>17</td>
</tr>
<tr>
<td>C,H,CH,CH,CH, =CH, (7)</td>
<td>4.0</td>
<td>6.0</td>
<td>6.9</td>
<td>14.0</td>
<td>12</td>
</tr>
<tr>
<td>C,H,CH,CH, (8)</td>
<td>0.3</td>
<td>0.8</td>
<td>1.4</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>R =R* (9)</td>
<td>26.6</td>
<td>26.5</td>
<td>21.2</td>
<td>8.4</td>
<td>7.5</td>
</tr>
<tr>
<td>R =R* (10)</td>
<td>2.2</td>
<td>1.6</td>
<td>2.3</td>
<td>6.5</td>
<td>4.3</td>
</tr>
<tr>
<td>R =R* (11)</td>
<td>1.0</td>
<td>1.0</td>
<td>2.1</td>
<td>4.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Product balance</td>
<td>100</td>
<td>99</td>
<td>100</td>
<td>99</td>
<td>100</td>
</tr>
</tbody>
</table>

* 0.1 N in diethyl ether. * 0.05 N in n-heptane. * 0.05 N in p-dioxane. * Decomposition time (minutes): see text for explanation of this term. * R refers to neophyl; R' refers to benzylidemethylcarbinyl.
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 1 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 benzylidinemethylcarbinyl 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 benzylidinemethylcarbinyl radicals, and subsequent reaction of these radicals.

Exclusion of Benzylidinemethylcarbinylcopper(I) (12) as an Intermediate in the Formation of 10 and 11 during the Thermal Decomposition of 3. Although the data of Table 1 indicate that the benzylidinemethylcarbinyl 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 benzylidinemethylcarbinyl 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 benzylidinemethylcarbinylcopper(I) (12) by alkyl group displacement on 3, 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-butyl lithium is much more readily obtained than benzylidinemethylcarbinyl lithium. 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 benzylidinemethylcarbinyl moiety.

Table 1 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 reagents. 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. The absence of 15 of (16) An authentic sample of another possible mixed dimer from these reactions, 1-phenyl-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 gcpe analyses of these reaction mixtures.

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hexamethylenethane 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 benzylidimethylcarbonyl 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 benzylidimethylcarbonyl 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 be a copper hydride elimination-reduction process analogous to that established for \(n\)-butyl(tri-\(n\)-butylphosphine)copper(I), 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 deuterio(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 composition, structure, or extent of aggregation of the organometallic compounds in solution; 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). A mechanism involving tert-butyl free radicals as intermediates cannot be excluded at this time, although the low yield of hexamethylenethane observed as a product of reaction effectively precludes bimolecular disproportionation and combination between tert-butyl radicals as the source of the hydrocarbon products.

**Estimation of the Relative Importance of Radical and Nonradical Mechanisms in the Thermal Decomposition of 3 and 4.** Having established that neophyl and benzylidimethylcarbonyl 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 benzylidimethylcarbonyl radical. Ben-

### Table III. Relative Reactivities of Organocopper(I) Reagents [\(\text{RCu}(\text{Bu}_3\text{P})\)] toward Deuteriod(tri-\(n\)-butylphosphine)copper(I)

<table>
<thead>
<tr>
<th>(\text{RC} )</th>
<th>( \text{Rel Reactivity}^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3 )</td>
<td>1</td>
</tr>
<tr>
<td>( \text{CH}_3 \text{CH} = \text{CH} \text{CH}_3 )</td>
<td>3</td>
</tr>
<tr>
<td>( \text{C}_3 \text{H}_7 \text{C} = \text{CH} \text{CH}_3 )</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CH}_3 )</td>
<td>3</td>
</tr>
</tbody>
</table>

^a Relative reactivities between pairs of organocopper(I) reagents were determined in diethyl ether at \(-90^\circ\). Unless otherwise noted, the starting concentration of each organocopper(I) reagent was \(10^{-2}\) M, and that of DCuBu3P was 0.01 M. The deuterium label in the alkyl moiety was included to facilitate mass spectrometric analysis (see the Experimental Section). This datum was determined in ether-pentane (50:50, v/v).

(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 \(80^\circ\) 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 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.


zymidemethylenecarbonyl 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 hy-
drolysis. 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 con-
ducted probably reflects primarily a difference in the
activation energy for homolytic scission of carbon-
copper(l) and carbon–silver(l) 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 rear-
rangement observed in the products. However, as is
clear from earlier work, those factors which in-
fluence the lifetime of the radical intermediates at any
particular temperature also influence the distribution of
reaction products. Hence, the observation that simi-
lar product distributions are obtained from decomposi-
tion 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 differ-
ences in the activation energies for corresponding re-
actions 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 estab-
lishes that the thermal decomposition of 3, an aliphatic
copper(l) 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 pre-
vious demonstration that the thermal decomposition of
vinylidene (and presumably aromatic) copper(l) and
silver(l) reagents takes place by a nonradical mech-
anism.

Experimental Section

General Methods. All reactions involving organometallic com-
ponents were carried out under purified nitrogen or grade A
helium using the usual techniques for handling air-
and water-
sensitive compounds. Dioxane was purified by distillation under
nitrogen from a dark purple solution of sodium benzophenone di-
ion. Ether and tetrahydrofuran were distilled from lithium alu-
num 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 un-
corrected. Boiling points are uncorrected. Nmr spectra were run as
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
Model 177, 277B, or 325 spectrophotometers. All pmms were
determined on a Hitachi-Perkin-Elmer Model RMU-
6D mass spectrometer; spectra used for isotopic analysis
were obtained using low ionizing voltages. Microanalyses were
performed by Midwest Microlab, Inc., Indianapolis, Ind.

Analytical gpc analyses were performed on F and M Model 810
instruments equipped with flame ionization detectors using response
tables determined with authentic samples. All components derived
from 3 in a reaction mixture could be analyzed using a 6 ft × 1/8 in.
5% diethylene glycol succinate on 80-100 mesh Chromosorb W
column, temperature programmed from 60 to 210°. In addition,
an 8 ft × 1/8 in. 20°, UC-W98 on 80-100 mesh Chromosorb W
column could be used at 110° for analysis of the monomeric hydro-
carbon products more accurately than those obtained with the
diethylene glycol succinate column. Neophyl dimers were on oc-
casion analyzed separately using a 6 ft × 1/8 in. 13° SE-52 on 80-100
mesh Chromosorb W column. The yields of tert-butylbenzene for-
med in reactions of neoply lithium 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 neophyl-tert-butylphosphine copper(l) were
analyzed using an 8 ft × 1/8 in. 20°, UC-W98 on 80-100 mesh
Chromosorb W column.

Concentrations of organolithium reagent solutions were deter-
mmed by the Gilman double titration method using 1,2-dibromo-
ethane. Solutions of methyl lithium (prepared from methyl
lithium in ether and n-butylthium in hexane were purchased from
Foote Mineral Co.; tert-butylthium in pentane was purchased from
Alpha Inorganics, Inc.

Neoply chloride, prepared by the alkylation of benzene with
3-chloro-2-methylpropene using sulfuric acid as a catalyst, had
bp 110-111° (13 mm); nD 1.2520.

Neophylmagnesium Chloride. A 2 M solution of neoply-
magnesium chloride was prepared by allowing 33.0 g (0.20 mol) of
neophyl chloride and 5.0 g (0.21 gatom) 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
either. 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 neophyl-
magnesium bromide with bromine in ether at 0°: 21 bp 85-86° (3 mm);
µ/ρ 1,5430 (lip, 25° bp 110°) (4.5 mm), µ/ρ 1,5331; lit.26 25° bp 93.1-
91.5° (4 mm), µb 1,5457. It had nmr δ 7.25 (m, 5, aromatic),
3.48 (s, 2, CH3), and 1.47 (s, 6, CH3), and ir(CCl4) 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 diphenylmercury.28 A 2 M solu-
tion of neophylmagnesium chloride was prepared from 68.0 g (0.40
moll of neophyl chloride and 9.7 g (0.40 gatom) 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 addi-
tional 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 fil-
tration. 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
(Me₂SO₄), and concentrated under aspirator vacuum. Any resid-
ual solvents or reagents were removed by evaporating the
residue to 0.1 ml at 50° for 48 hr. The crude dineophyl-
mercury (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(l) reagents are not sufficiently basic to
abstract a proton from diethyl ether.

(22) Comparison of product yields observed on thermal decom-
position 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).


(27) (a) H. H. Faiman and S. Weinstein, J. Amer. Chem. Soc., 78,

1217 (1958).
times from methanol ether (2:1) at -78 °C to yield 41.8 g (0.09 mol, 56.7% based on HeCl) of white needles, mp 25-26 °C (lit. 30 mp 26-28 °C, 5 mm Hg). The v(1, TCH) = 9.1 Hz, v(1, 3.CH, J(1H,CH) = 92 Hz), and J(1,2. CH, J(1H,CH) = 6.5 Hz). The intensity of the 1H NMR signals was approximately the expected 20% of the center bands.

Neophylithium. A pentane solution containing 1.40 g (3.0 mmol) of diphenylmercury was added by funnel through the top arm of an 80-ml flame-dried Schlenk tube, 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 dispersion was 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 °C 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 construction 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 °C where it was stirred magnetically. During the transmetallation reaction, white crystalline material of a sample of lithium amalgam was formed, and sank to the bottom of the tube. The reaction was complete within 2 hr (the excess lithium remained bright).

To remove the contents from the tube the construction on the side arm was scored with a glass scriber and the side arm was attached by a glass-to-glass stopcock and a rubber stopper. A sample of a three-way stopcock, the opposite arm of which was fitted with a No-Air stopcock. The 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 construction while under a nitrogen atmosphere. If a solvent other than pentane was to be used for the subsequent reactions of the lithium amalgam, pentane was removed at reduced pressure at this time. While protecting the solid residue from air, the reaction mixture was distilled 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 neophylithium 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 was ca. 0.1 M. Crystalline, ether-free neophylithium can be obtained by cooling a pentane solution saturated at room temperature to -78 °C 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-buty1benzene: no <0.01% 12-isobutylbenzene, neophyl alcohol, or neophyl dimers were detected in a hydrolyzed aliquot by gc 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 on standing with bromine.

2-Methyl-1-phenylpropan-1-ol. Approximately 160 ml of 1.8 M isopropyl Grignard reagent was added, with stirring and cooling, to 27.0 g (0.25 mol) of benzaldehyde dissolved in 150 ml of ether over a period of 1.5 hr at 15 °C. 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 23.0 g (0.20 mol, 80%) of the desired alcohol, bp 101-104 °C (8 mm). J(3,3) = 1.534 (lit. 3. bp 104-105 °C (7 mm).

2-Methyl-1-phenyl-1-propane. (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. The ruby red mixture was cooled to 0 °C, the layers were separated, and the benzene layer was extracted with cold water until the water was neutral and then dried (MgSO4). After removing benzene, 3.7 g (27 mmol, 51%) of the desired olefin >95% pure by nmr) was obtained by fractional distillation, bp 92-95 °C (22 mm) (lit. J bp 79-80 °C (20 mm). The identity of this material was confirmed by comparison of its ir spectrum with that in the Safranl file (1995).

2-5-Dimethyl-2,5-diphenylhexane (9) was prepared in 16%, yield by the reaction of cumene with potassium 1,2-di-chloroethane in ether at 0 °C. It was isolated from the reaction mixture by fractional distillation, bp 142-145 °C (0.1 mm), and recrystallized from absolute ethanol at -20 °C, mp 60-61 °C (lit. J mp 60-61 °C, lit. 9 bp 158-154 °C (mp 60-61 °C). Its ir spectrum, ¢ 7.07 (m, 5 aromatic), 1.72 (s, 2 CH3), and 1.18 (s, 6, CH3) agrees with the reported values.


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 (0.45 g-atom) of magnesium, was cooled to 0 °C. A solution of 22.2 g (0.20 mol) of acetone (dried over Molecular Sieve 3A) in 50 ml of ether was added with stirring to the Grignard reagent over a period of 1.5 hr at a rate such that the reaction temperature never exceeded 5 °C. The mixture was stirred at 0 °C, 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, 53%) of the desired alcohol, bp 92-93 °C (0.8 mm), nD 1.5114 (lit. 5 bp 108.5-109 °C (4 mm), 1.5130), having nm h 7.52 (m, 5 aromatic), 1.93 (s, 2 CH3), 1.40 (s, 6 CH3), 0.92 (s, 6 CH3), and 1.25 (s, 10 OH).

2-Bromo-2,4-dimethyl-4-phenylpentan-2-ol. 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 H2SO4 over a period of 25 min. The reaction was stirred at 25 °C for an additional 1.5 hr, then poured into water. The organic layer was separated, washed with aqueous NaHCO3 solution, dried (MgSO4), and concentrated to yield 6.8 g of crude bromide as a yellow liquid. This material was decomposed on attempted purification, and was characterized only on the basis of its ir spectrum: 3 7.25 (m, 5 aromatic), 2.55 (s, 2 CH3) 1.36 (s, 6 CH3), and 1.25 (s, 6 CH3).

2,4-Diphenylpentan-4-1-phenylpentane (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 M) over 1.5 hr. The reaction mixture was stirred at reflux for an additional 3 hr, hydrolyzed (saturated aqueous NH4Cl), and worked up as usual. The hydrocarbon 10


(31) J. B. Conn and A. H. Blatt, ibid. 50, 551 (1928).


(33) This transmetallation reaction has proved to be very sensitive to impurities and to experimental technique. In particular the neophyllithium must be carefully purified for the transmetallation to take place.

(34) Even with scrupulous attention to detail, in our hands approximately one batch of neophyllithium out of four could not be reactivated to reduct with lithium.
formed, 1.9 g (7.1 mmol, 18%), based on tert-butyridine) was isolated by distillation, bp 104-105 100.4 mm. The distillate was crystallized from absolute ethanol at -20°C to yield white crystals, mp 32.5, showing mmr 7.71 (m, 5), aromatic, 7.05 (m, 5), aromatic, 2.65s (2, CH3), 1.80s (2, CH3), 1.35s (6, CH3), and 0.63s (9, CH3) for C₆H₃.

Feed Caled for C₆H₃: C, 90.16; H, 9.84. Found: C, 91.43; 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 11 mm (lit. bp 88-89 (5.3 mm)); r (r-CCl₃) 1435, 2970, 2940, 1604, 1505, 1485, 1408, 1380, 1210, 1105, 750, 600, 630, 580 (m, CH₃); mnr 7.07 (5, aromatic), 3.07 (2, CH₃), 1.65s (6, CH₃).

1,4-Diphenyl-2,2,3,3-tetramethylbutylamine (11). Method A. Ca. 40 ml of a 0.5 N ether solution of n-butyllithium bromide, prepared from 3.3 g (23 mmol) of n-butyll bromide and 0.8 g (6 mmol) of magnesium turnings, was stirred with 1.0 g (8 mmol) of anhydrous cobalt(II) chloride for 43 min at 0°C. Then 3.3 g (115 mmol) of 2,3-dimethyl-1-phenylpropylamine, 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 M 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 propane were the major products. By crystallization from benzene: yield 1.05g (60%); mnr 7.03 (5, aromatic), 5.25 (2, CH₃), 4.05 (4, CH₂), and 1.05s (9, CH₃) for C₆H₃.


2-Phenyl-1,2,4,6-tetramethylpenta-1 (15). tert-Butylthiophene (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°C, and the resulting solution was allowed to react with 50 ml of oxygen at -78°C. The reaction mixture was warmed to room temperature, hydrolyzed, dried (MgSO₄), and the product was isolated from the reaction mixture by glpc (9-10°C). DEGS on Chromosorb W at 80°C, and had ir (r-CCl₃) 3080, 3060, 3030, 3020, 2960, 2940, 2900, 1600, 1500, 1470, 1450, 1395, 1385, 1365, 1250, 1080, 800, and 700 cm⁻¹; mass spectrum (70 eV) 190 (111), M⁺ 120 (11), 119 (100), 91 (28). (r-CCl₃) 7.283 (S, aromatic), 1.73s (2, CH₃), 1.37t (6, CH₃), and 0.76s (9, CH₃).


Organocopper(1) and silver(1) Compounds. Neoplythyl(2-tert-butylphosphino)copper(I). [Tetakis(2-tert-butylphosphino)copper(I)] (199 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 (3.5 ml) was added, and the resulting solution was cooled to -78°C in a Dry ice-acetone bath. Neoplythyl(1.0 mmol, 0.01 mol of a 0.14 V ether solution), also cooled to -78°C, was added by cannula. The resulting bright yellow solution was shaken several times and returned to the -78°C bath. Dioxide (50 ml, 1.2 mmol was added, and the resulting white precipitate of lithium oxide dioxane 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(2-tert-butylphosphino)copper(I) were prepared by reaction at -78°C between tetakis(2-tert-butylphosphino)copper(I) and methyl lithium or tert-butylthiophene as described previously. Neoplythyl(2-tert-butylphosphinoyl)copper(I) was prepared by reaction of neoplythyl thiophene in ether at -78°C with tetakis(2-tert-butylphosphino)copper(I) and tert-butyl-
reaction flask was immersed in an ice bath and its internal temperature maintained at 50–60° by cautious addition of methyl trichloroacetate (176 g, 1.0 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$_1$ 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 (MgSO$_4$) and distilled through an 8-in. platinum spinning band column, yielding methyl acetate-2,2,2-d$_1$ (48.5 g, 0.63 mol, 63%$^\circ$), bp 56°.

Ethanol-2,2,2-d$_1$ was prepared from methyl acetate-2,2,2-d$_1$ (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 (MgSO$_4$) and distilled, yielding ethanol-2,2,2-d$_1$ (19.24 g, 0.39 mol, 62%), bp 76–80°.

1-Bromoethane-2,2,2-d$_1$ was prepared from ethanol-2,2,2-d$_1$ in 91%$^\circ$, yield by a procedure analogous to that of Kamm and Marval.14

1-Butanol-2,2,2-d$_1$ was prepared in 52%$^\circ$, yield by the reaction of ethyl-2,2,2-d$_1$ magnesium bromide with ethylene oxide, using a procedure analogous to that of Huston and Langham.47

1-Bromobutane-2,2,2-d$_1$ was prepared in 71%$^\circ$, yield by a procedure analogous to that of Kamm and Marval.14 The mass spectrum of this material (8 eV) indicated an isotopic composition of 92.0%$^\circ$, 6.5%$^\circ$, and 1.5%$^\circ$ 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$_1$.

n-Butyl-1,4,4,4-d$_4$-lithium. 1-Bromobutane-2,2,2-d$_1$ (9.6 g, 65 mmol) was 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 (Foose 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-1,4,4,4-d$_4$-lithium (44 mmol, 69%$^\circ$). n-Butyl-lithium was prepared from 2-chlorobutane by an analogous procedure. tert-Butyl-lithium was purchased from Foose Mineral Co. Deuteridotri-n-butylphosphine-copper(I) was prepared from copper(I) bromide and disobutylicuminum deuteride using procedures already described.48

Competition between 1-Bu$^-$- and 1-Bu$^-$trit-butylphosphine-copper(I) for Deuteridotri-n-butylphosphine-copper(I). Tetrakis[iodotri-n-butylphosphine-copper(I)] (0.4177 g, 0.26 mmol) in ether (10.0 ml) was treated at −78° with n-butyl-lithium (0.534 mmol, 0.606 ml, 0.880 N) and n-butyl-1,4,4,4-d$_4$-lithium (0.534 mmol, 0.450 ml, 1.180 V) 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 deuteridotri-n-butylphosphine-copper(I) (0.10 mol, 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%$^\circ$), 1-butene (36%$^\circ$), and cis- and trans-2-butene (12%$^\circ$) were determined quantitatively using a 6-ft, 0.125-in. 80–100 mesh Durapak column at room temperature. Samples of n-butane and 1-butene were collected for mass spectral analysis using a 4-ft 3%$^\circ$ Apiezon N on alumina column at 70°. Mass spectral analysis, after correction for the n$_1$ and d$_1$ species present in the n-butylcopper(I), indicated the presence of n-butane-d$_1$ (9.0%$^\circ$), d$_1$-n-butane (11.4%$^\circ$), and d$_1$-1-butene (18.3%$^\circ$), and 1-butene-d$_1$ (60.9%$^\circ$) and d$_1$-1-butene (39.1%$^\circ$).

Competition between tert-Butyl- and n-Butyl(tri-n-butylphosphine)-copper(I) for Deuteridotri-n-butylphosphine-copper(I). Tetrakis[iodotri-n-butylphosphine-copper(I)] (0.4082 g, 1.041 mmol) in ether (10.0 ml) was treated with n-butyl-lithium (0.52 mmol, 0.25 ml, 1.49 V) and tert-butyl-lithium (0.52 mmol, 0.42 ml, 1.24 V). 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, deuteridotri-n-butylphosphine-copper(I) (0.10 mol, 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%$^\circ$), n-butane (25.8%$^\circ$), 1-butene (25.8%$^\circ$), and isobutylene (16.7%$^\circ$). Mass spectral isolation analysis of samples of isobutane and n-butane (10 eV) indicated the presence of isobutane-d$_1$ (52%$^\circ$) and d$_1$-n-butane (48%$^\circ$), and n-butane-d$_1$ (20.5%$^\circ$) and d$_1$-n-butane (79.5%$^\circ$).

Competition between tert-Butyl- and Neopentyl(tri-n-butylphosphine)-copper(I) for Deuteridotri-n-butylphosphine-copper(I). Tetrakis[iodotri-n-butylphosphine-copper(I)] (0.4078 g, 1.04 mmol) in ether (5.0 ml) was treated with neopentyl-lithium (0.52 mmol, 6.58 ml, 0.079 N) in pentane and tert-butyl-lithium (0.52 mmol, 0.425 ml, 1.24 V) in pentane. Addition of DCUPH$_2$I (10.10 mmol, decomposition and analysis were carried out as described previously, indicating the presence of isobutane-d$_1$ (0.55 mmol) and tert-butylisobutene-d$_1$ (0.049 mmol) among the products.

Acknowledgment. We are indebted to Mr. Philip Kendall for assistance in obtaining the data in Table III.