Triphenylallenyllead: A Facile Preparation and Its Use as a Propargylating Reagent

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Summary: Triphenylallenyllead, which is easily prepared by reaction of the readily available $Ph_3PbMgBr$ (in situ, via 3 $PhMgBr$ + $PbCl_2$ in THF) with propargyl bromide, reacts with aldehydes in the presence of a Lewis acid ($BF_3{\cdot}OEt_2$ or $TiCl_4$) to give homopropargylic alcohols, $RCH(OH)CH_2C{\equiv}CH$, in good yield. Propargylation of ketones requires transmetalation of $Ph_3PbCH{=}C{=}CH_2$ with PhLi to $CH_2{=}C{=}CHLi$ and reaction of the latter with the ketone.

Introduction

There has been, and there continues to be, much interest in the propargylation of organic carbonyl compounds to give homopropargylic alcohols. Such syntheses have been effected using allenyl or propargyl derivatives of metals and metalloids, including Li, Mg, Zn, B, Al, Si, Sn, Sb, Ti, and Cr.[1-4] As pointed out by Brown et al.,[1] not all of these procedures are practical. Barbier-type procedures in which reactions were carried out between a propargyl halide, a carbonyl compound and a metal or a low valent metal compound also have been reported.[5,6]

By far the most work in this area has centered around group 14 allenyl derivatives. Danheiser and co-workers prepared allenylsilanes and reported their addition to aldehydes and ketones in the presence of $TiCl_4$ to yield the homopropargylic alcohols.[7] The first use of organotin compounds as propargyl anion equivalents was reported by Lequan and Cadiot in 1973.[8] They found that allenyltin compounds added to chloral to give predominantly homopropargylic alcohols in high yield. Tagliavini and coworkers investigated the addition of tri-*n*-butylallenyltin to aldehydes in the presence of di-*n*-butyltin dichloride and water.[9] The reactions proceeded smoothly, with the ratio of homopropargylic to homoallenic alcohol products dependent on the reaction conditions and on the aldehyde used. Marshall and Wang reported that chiral allenyltin compounds undergo stereospecific additions to aldehydes in the presence of Lewis acids to afford homopropargylic alcohols with good to excellent diastereoselectivity.[10] Japanese workers studied the propargylation of α,β-unsaturated carbonyl compounds with triphenylallenyltin compounds.[11] When $TiCl_4$ was the Lewis acid catalyst used, the reaction proceeded regioselectively, giving the 1,4 addition products in high yield. When ZnI_2 was used as catalyst, the 1,2 addition product was obtained. In either case, only propargylic products were formed.

Considering the wealth of information concerning silicon and tin propargyl anion equivalents, it is curious that no organolead propargyl group sources have been reported. A likely reagent for this purpose is triphenylallenyllead, and we report here its synthesis and use in the propargylation of several aldehydes and a ketone.

Results and Discussion

Synthesis of Triphenylallenyllead. Triphenylallenyllead is a known compound.[12] It was prepared in 70% yield by the reaction of propargylmagnesium bromide and triphenyllead chloride. The preparation of Ph_3PbCl by the reaction sequence shown in eqs 1 and 2[13] is tedious,

$$4PhMgX + 2PbCl_2 \rightarrow Ph_4Pb + Pb + 4MgX_2 \quad (1)$$

$$Ph_4Pb + HCl(g) \xrightarrow{CHCl_3} Ph_3PbCl + Ph_2PbCl_2 + Ph_4Pb \quad (2)$$

and a better route to triphenylallenyllead was desirable. In earlier work we prepared allylic lead compounds by the reaction of the triphenyllead Grignard reagent, $Ph_3PbMgBr$,[14] with allylic halides.[15] These syntheses were easily carried out and proceeded cleanly in high yield. We have found that the triphenyllead Grignard reagents reacts equally well with propargyl chloride or bromide in

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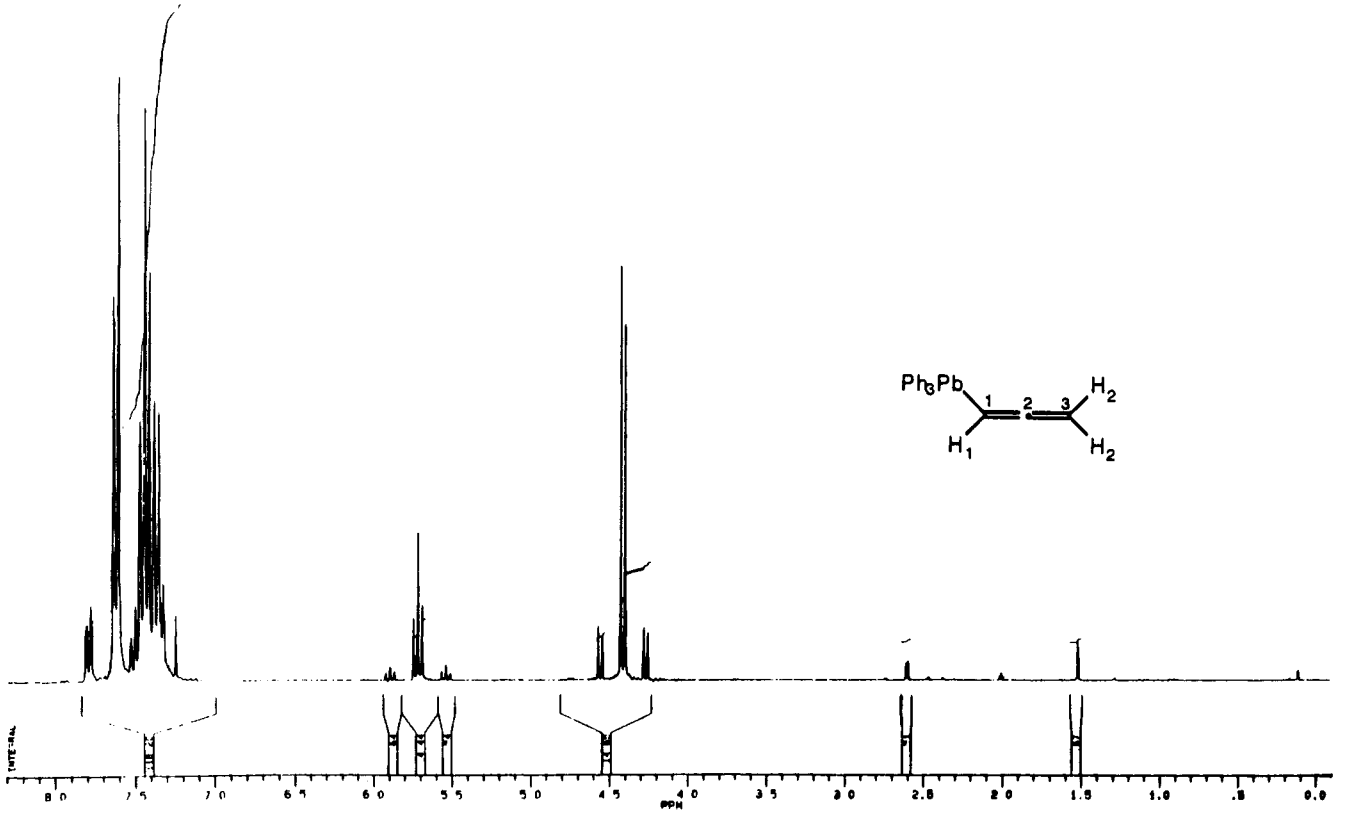

Figure 1. ^1H NMR spectrum of **1** (H_2O, δ 1.5).

tetrahydrofuran (THF) to give a white solid in 80% yield after aqueous workup. As determined by ^1H NMR spectroscopy, this product was not pure triphenylallenyllead; it contained 6% of the propargyl isomer (eq 3). This is close to the ratio (92/8) obtained in the reaction of propargylmagnesium bromide with Ph_3PbCl.[12]

$$3PhMgBr + PbCl_2 \longrightarrow Ph_3PbMgBr \xrightarrow{HC\equiv CCH_2Br} \underset{\textbf{1}\ (94\%)}{Ph_3Pb(H)C{=}C{=}C(H)H} + Ph_3PbCH_2C\equiv CH \quad (6\%) \qquad (3)$$

Triphenylallenyllead, **1**, was characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum (Figure 1) shows interesting splitting patterns. H(1) is coupled to the two H(2) protons in addition to the ^{207}Pb nucleus, resulting in a triplet of triplets centered at δ 5.7. The ^{207}Pb–H coupling constant is approximately 89 Hz. The two H(2) protons are coupled to H(1) and Pb through the π-system of the allenyl group, resulting in the observed triplet of doublets centered at δ 4.4. The ^{207}Pb–H coupling constant in this case is approximately 72 Hz. Small signals indicating the propargylic isomer also are present in the spectrum. The signals in the ^{13}C NMR spectrum of **1** were assigned on the basis of the assigned ^{13}C NMR spectra of similar allenyltin compounds.[16]

Propargylation Reactions of Triphenylallenyllead. As expected, it was found that triphenylallenyllead, **1**, is an effective propargyl anion equivalent. In the presence of a Lewis acid, it reacts cleanly with aldehydes to give the homopropargylic alcohols, **2**, in good yields (eq 4).

$$Ph_3PbCH{=}C{=}CH_2 + RCH{=}O \xrightarrow[CH_2Cl_2,\ -78\ ^\circ C]{\text{Lewis acid}} \xrightarrow{H_3O^+} \underset{\mathbf{2}}{R{-}CH(OH){-}CH_2C\equiv CH} \qquad (4)$$

R = Ph (**2a**), $C_6H_4CH_3$-*p* (**2b**), *n*-C_7H_{15} (**2c**), $PhCH_2CH_2$ (**2d**), $CH_2{=}CH$ (**2e**), C_2H_5 (**2f**), $(CH_3)_2CH$ (**2g**)

In a typical reaction, a CH_2Cl_2 solution of the aldehyde and the Lewis acid was cooled to −78 °C and, subsequently, a CH_2Cl_2 solution of **1** was added dropwise. After gradual warming to 0 °C over 2–2.5 h the alcohol **2** was isolated after aqueous workup. A variety of aldehydes was examined. The results are shown in Table 1.

In most cases, using $BF_3{\cdot}OEt_2$ as the Lewis acid resulted in acceptable yields of product. However, this catalyst was not suitable for such reactions of propionaldehyde and isobutyraldehyde. The use of $TiCl_4$ instead resulted in acceptable yields of product. Only in one instance (*n*-octylaldehyde) was any allenic isomer of the homopropargylic alcohol observed, despite the fact that the organolead reagent contained 6% of $Ph_3PbCH_2C\equiv CH$.

Propargylation of an α,β-unsaturated aldehyde can result in 1,2 addition or 1,4 addition. Reaction of **1** with acrolein gave only the 1,2 product, **2e**. No 1,4 product was observed.

This procedure proved to be ineffective for the propargylation of benzophenone. However, treatment of **1** with 1 molar equiv of phenyllithium in THF followed by

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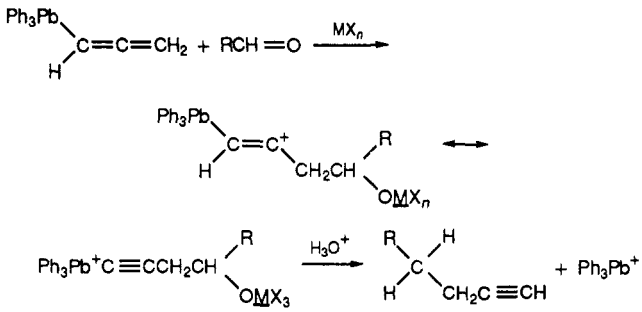
Table 1. Reactions of Triphenylallenyllead with Aldehydes in the Presence of a Lewis Acid

electrophile	Lewis acid	product	yield (%)[a]
benzaldehyde	none	**2a**	0
benzaldehyde	$MgBr_2$	**2a**	0
benzaldehyde	$BF_3{\cdot}OEt_2$	**2a**	80 (86)[b]
p-tolualdehyde	$BF_3{\cdot}OEt_2$	**2b**	77
octylaldehyde	$BF_3{\cdot}OEt_2$	**2c**	53[c]
hydrocinnamaldehyde	$BF_3{\cdot}OEt_2$	**2d**	65
acrolein	$BF_3{\cdot}OEt_2$	**2e**	55
propionaldehyde	$BF_3{\cdot}OEt_2$	**2f**	8
propionaldehyde	$TiCl_4$	**2f**	65
isobutyraldehyde	$BF_3{\cdot}OEt_2$	**2g**	10
isobutyraldehyde	$TiCl_4$	**2g**	66
benzophenone	$BF_3{\cdot}OEt_2$	**2h**	0

[a] Unless otherwise stated, yields determined using ^1H NMR spectroscopy with 1,1,2,2-tetrachloroethane as the internal standard (δ 5.96). [b] Yield determined by GLC analysis. [c] A mixture of allenic and propargylic isomers (allenic/propargylic = 1/5.2).

Scheme 1



addition of benzophenone yielded the homopropargylic alcohol 1,1-diphenyl-3-butyn-1-ol, $Ph_2C(OH)CH_2C{\equiv}CH$, in 63% yield. This synthesis proceeds via allenyllithium, generated by transmetalation between 1 and PhLi (eqs 5 and 6). Reaction 5 finds precendent in the synthesis of

$$Ph_3PbCH{=}C{=}CH_2 + PhLi \rightarrow Ph_4Pb + CH_2{=}C{=}CHLi \quad (5)$$

$$CH_2{=}C{=}CHLi + Ph_2C{=}O \xrightarrow{H_3O^+} Ph_2C(OH)CH_2C{\equiv}CH \quad (6)$$

vinyllithium by the reaction of tetravinyllead with 4 molar equiv of PhLi[17] and in the generation of allenyllithium by reaction of methyllithium with allenyltin compounds.[18]

These propargylation reactions were carried out mostly on a small scale (~0.5 mmol). However, the reactions can be performed on a preparative scale. When 41 mmol of **1** was allowed to react with benzaldehyde in the presence of $BF_3{\cdot}OEt_2$, 4.0 g (67%) of alcohol **2a** was isolated by distillation, free of allenyl isomer, as indicated by its ^1H NMR spectrum.

The mechanism of the Lewis acid-catalyzed propargylation when $Ph_3PbCH{=}C{=}CH_2$ is the reagent used very likely is the same as that suggested by Danheiser et al. for the propargylation of aldehydes with allenylsilanes.[7b] The first step would involve addition of the electrophilic aldehyde–Lewis acid complex to C(3) of **1** to form a vinyl cation (Scheme 1). The latter can be stabilized via hyperconjugation through the Pb–C bond. Hydrolysis of the reaction mixture results in the loss of the Ph_3Pb group and formation of the homopropargylic alcohol.

This brief study has shown triphenylallenyllead to be a useful propargylation reagent. Its preparation is very simple and uses readily available starting materials. Aldehydes may be propargylated directly in the presence of a Lewis acid. In the case of ketones a simple, two-step, one-pot procedure, transmetalation of the allenyllead compound to allenyllithium and reaction of the latter with the ketone, is successful. The yields of these reactions have not been optimized and further attention to detail should give higher yields. This procedure may be recommended for small-to-medium scale preparations of homopropargylic alcohols.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise indicated. Solvents were dried by standard procedures. All reagents were of commercial origin. Gas chromatographic (GLC) analysis were performed on a Hewlett-Packard 5890A gas chromatograph equipped with a 6-ft. × 0.25-in. column packed with 10% SE-30 silicone rubber gum on Chromosorb P.

Preparation of $Ph_3PbMgBr$. A solution of PhMgBr (49 mL, 2.06 M) in THF was added to a 250-mL Schlenk flask equipped with a magnetic stir bar. Another 100 mL of THF was added, and the flask was placed in an ice bath. Lead dichloride (9.18 g, 0.033 mol) was added as a solid in one portion. The resulting mixture immediately turned yellow and then slowly orange. The ice bath was removed, and the reaction mixture was stirred overnight at room temperature under nitrogen to give a dark green mixture.

Preparation of Triphenylallenyllead. A solution of $Ph_3PbMgBr$ (0.03 mol in THF) was cooled in an ice bath. Propargyl bromide (5.2 g of 80% wt/wt in toluene, 0.035 mol) was added to the solution while the reaction temperature was maintained below 15 °C. Upon completion of the addition a gray suspension was present. The reaction mixture was stirred at room temperature overnight. Subsequently, the suspension was poured into saturated aqueous ammonium chloride and the resulting mixture was poured through a pad of Celite. The separated aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with saturated aqueous NaCl and dried over anhydrous $MgSO_4$. Low boiling components were removed using a rotary evaporator, leaving a yellow-orange oil. The latter was chromatographed on silica gel using hexane as eluent to yield $Ph_3PbCH{=}C{=}CH_2$, **1**, as a white solid after the solvent had been evaporated at a reduced pressure. Yields typically were 75–80%. The crude oil also can be recrystallized from hexane to yield pure **1**. Compound **1** was obtained as a 94/6 mixture of allenic and propargylic isomers, mp 62–63 °C (lit.[12] mp 64 °C). IR (cm^{-1}, $CDCl_3$): 3061 (m), 1923 (s), 1572 (m), 1476 (m), 1430 (s), 1063 (m), 1017 (m), 996 (m). ^1H NMR (250 MHz, $CDCl_3$): δ 4.25–4.56 (td, 2 H, $^4J_{H-H}$ = 6.8 Hz, J_{Pb-H} = 72 Hz), 5.50–5.92 (tt, 1 H, $^4J_{H-H}$ = 6.8 Hz, J_{Pb-H} = 89 Hz), 7.28–7.81 (m, 15 H, Ph). The propargyl isomer shows resonances centered at 2.0 and 2.6 ppm. Comparison of the integrated intensities of these signals with those of the allenyl isomers established the 94/6 allenyl/propargyl isomer ratio. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 66.8, 83.8, 128.9, 129.0, 129.6, 136.8, 137.4, 150.3, 209.6. Anal. Calcd for $C_{21}H_{18}Pb$: C, 52.82; H, 3.80. Found: C, 52.88; H, 3.88.

Standard Procedure for the Propargylation of Aldehydes by 1 with $BF_3{\cdot}OEt_2$ Catalyst. A small vial was equipped with a stir bar and an argon inlet needle. The appropriate aldehyde (0.42 mmol) and 1 mL of CH_2Cl_2 were added, and the vial was cooled in a −78 °C bath. The catalyst, $BF_3{\cdot}OEt_2$, 0.63 mmol, was injected into the reaction mixture by syringe. After this mixture had been stirred for 10 min, a solution of 0.42 mmol of **1** in 1 mL of CH_2Cl_2 was added dropwise by syringe. After completion of

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the addition the reaction mixture was warmed slowly to 0 °C over 2.5 h. At this point the reaction mixture generally was orange in color. The reaction was quenched by addition of saturated aqueous NH_4Cl. The resulting mixture was filtered, and the layers were separated. Hexane was added to the organic phase to precipitate solid byproducts, and the resulting suspension was filtered. The aqueous layer was extracted twice with hexane and the combined organic layers were dried over anhydrous $MgSO_4$. Low-boiling volatiles were evaporated by heating, and the residual oil was mixed with $Cl_2CHCHCl_2$ for ^1H NMR analysis. Product yields and isomer ratios were determined by comparing integrals of propargylic and allenic protons. In the reaction of **1** with PhCHO the product yields also was determined by GLC analysis. The identity of the products in all cases was confirmed by comparison of spectral data with those reported in the literature: **2a**,[19] **2b**,[20] **2c**,[21] **2d**,[7b] and **2e**.[22]

1-Phenyl-3-butyn-1-ol, **2a**, colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ 2.06 (t, 1 H, J = 2.8 Hz), 2.41 (s, 1 H), 2.63 (dd, 2 H, J_1 = 2.6 Hz, J_2 = 6.2 Hz), 4.86 (t, 1 H, J = 6.3 Hz), 7.2–7.4 (m, 5H).

1-*p*-Tolyl-3-butyn-1-ol, **2b**, colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ 2.05 (t, 1 H, J = 2.7 Hz), 2.34 (s, 3 H), 2.62 (dd, 2 H, J_1 = 2.7 Hz, J_2 = 6.3 Hz), 4.83 (m, 1 H), 7.0–7.8 (m, 4H).

1-Undecyn-4-ol, **2c**, colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ 0.89 (t, 3 H, J = 6.0 Hz), 1.15–1.69 (m, 12 H), 1.87 (d, 1 H, J = 5.13 Hz), 2.04 (t, 1 H, J = 2.5 Hz), 2.30–2.40 (m, 2 H), 3.73 (m, 1 H); (allenic isomer) δ 4.13–4.17 (m), 4.79–4.85 (m), 5.25 (m).

1-Phenyl-5-hexyn-3-ol, **2d**, colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ 1.78–2.00 (m, 2 H), 2.05 (t, 1 H, J = 2.7 Hz), 2.20 (s, 1 H), 2.35–2.42 (m, 2 H), 2.62–2.95 (m, 2 H), 3.77 (broad s, 1 H), 7.10–7.40 (m, 5 H).

1-Hexen-5-yn-3-ol, **2e**, colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 2.05 (t, 2 H, J = 2.3 Hz), 2.45 (td, 2 H, J_1 = 2.7 Hz, J_2 = 6.2 Hz), 4.27 (q, 1 H, J = 5.3 Hz), 5.16–5.34 (m, 2 H), 5.86–5.97 (m, 1 H).

Synthesis of 2a: Preparative-Scale Reaction. A 500-mL round-bottomed flask was charged with PhCHO (4.2 mL, 41 mmol) and 100 mL of CH_2Cl_2. The flask was placed in a dry ice–acetone cold bath, and 7.6 mL (62 mmol) of $BF_3{\cdot}OEt_2$ was added by syringe. A solution of 19.68 g (41 mmol) of **1** in 100 mL of CH_2Cl_2 was cannulated into the flask, and the reaction mixture was allowed to warm slowly to 0 °C under an atmosphere of nitrogen. Addition of saturated aqueous NH_4Cl solution followed. The resulting mixture was filtered through a pad of Celite, and the layers were separated. Hexane was added to the organic layer to precipitate solid byproducts, and the suspension was filtered. The aqueous layer was extracted twice with hexane. The combined organic layers were washed with distilled water and saturated aqueous NaCl solution. Most of the low-boiling components were removed using a rotary evaporator, and the residue was taken up in hexane and filtered. Evaporation of low-boiling components was followed by reduced pressure distillation of the residual liquid. 1-Phenyl-3-butyn-1-ol, **2a**, bp 55–60 °C/0.1 Torr, was obtained in 67% yield as a clear, colorless liquid. Its ^1H NMR spectrum was identical to that given above.

Standard Procedure for the Propargylation of Aldehydes by 1 with $TiCl_4$ Catalyst. The procedure was identical to the $BF_3{\cdot}OEt_2$ procedure (above) except that $TiCl_4$ (0.63 mmol) was the Lewis acid used. After the reaction mixture had been stirred for 2.5 h, it was tan in color. The identity of the products was confirmed by comparison of their ^1H NMR spectra with those reported in the literature: **2f**[23] and **2g**.[24]

5-Hexyn-3-ol, **2f**, colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, 3 H, J = 6.3 Hz), 1.53 (m, 2 H), 2.00 (t, 1 H, J = 2.8 Hz), 2.30–2.39 (m, 3 H), 3.64 (broad, 1 H).

5-Methyl-1-hexyn-4-ol, **2g**, colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (d, 2 H, J = 6.8 Hz), 0.92 (d, 2 H, J = 6.8 Hz), 1.7–1.8 (m, 1 H), 2.01 (t, 2 H, J = 2.7 Hz), 2.30–2.40 (m, 2 H), 3.50 (broad, 1 H).

Generation of Allenyllithium and Its Reaction with Benzophenone. A 25-mL, round-bottomed flask was charged with 0.5 g (1.0 mmol) of **1** and 6 mL of THF. The flask was placed in a $CHCl_3$–dry ice bath (−60 °C), and 0.47 mL of a 2.23 M solution of PhLi in Et_2O was added by syringe. A white precipitate (Ph_4Pb, by mixture mp) formed almost immediately. The reaction mixture was stirred at −60 °C for 30 min, and then a solution of 0.18 g (1.0 mmol) of Ph_2CO in 4 mL of THF was added. After the resulting mixture had been stirred for 1 h in the cold bath, it was quenched with saturated aqueous NH_4Cl solution. The mixture was filtered, and the aqueous layer was extracted with ethyl acetate. The combined organic phases were dried over anhydrous $MgSO_4$ and low-boiling materials were removed under reduced pressure. The residue, a clear oil, was essentially pure 1,1-diphenyl-3-butyn-1-ol, by NMR. The yield was 0.14 g (63%). Its ^1H NMR spectrum matched that reported in the literature.[19]

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