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METALATION AND SILYLATION OF ALLENE: A CONVENIENT SYNTHESIS OF TETRAKIS(TRIMETHYLSILYL)ALLENE

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SUMMARY

Allene is metalated by n-butyllithium at −50° in tetrahydrofuran/hexane (1/1) to produce allenyllithium. When allene was mixed with two or more equivalents of n-butyllithium and trimethylchlorosilane subsequently was added to the mixture, silylated derivatives (Id), (II), (III), (IV) and (V) were formed in varying amounts. A competitive reaction demonstrated that metalation of allene and the subsequent reaction sequence leading to (V) was competitive with the coupling of n-butyllithium with trimethylchlorosilane. Rapid formation of a dilithiated species in the metalation step appeared likely since metalation of allene with exactly two equivalents of n-butyllithium followed by addition of two equivalents of trimethylchlorosilane suppressed formation of (I) and produced a high yield (63%) of (II). By mixing one equivalent of allene with five equivalents of n-butyllithium followed by five equivalents of trimethylchlorosilane, a 70% isolated yield of (V) was obtained. A similar yield (63% isolated yield) was obtained by treating one equivalent of allene with two equivalents of n-butyllithium followed by two equivalents of trimethylchlorosilane and then adding, in succession, two equivalents more of each of the latter two reagents. A mechanism for formation of (V) was postulated involving (1) formation of lithioallene and 1,3-dilithiopropyne in the metalation step followed by (2) formation of (II) and stepwise sequential metalation and silylation to produce (III), (IV), and (V) in the silylation step.

RESULTS AND DISCUSSION

A number of unusual reactions describing the formation of tetrakis(trimethylsilyl)allene (V) have recently been reported[1-4]. This paper describes a rapid, convenient synthesis of (V) directly from allene by treating one equivalent of allene with 4–5 equivalents of n-butyllithium followed by addition of 4–5 equivalents of trimethylchlorosilane to the metalation mixture. The reaction proceeds via metalation of allene by n-butyllithium. Allenyllithium is also formed when allene is metalated in hexane at room temperature or in tetrahydrofuran/hexane (1/1) at −50° by one equivalent of n-butyllithium. The metalation of allene is not mentioned in recent

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reviews on the chemistry of allene[5-7].

The facile metalation of allene was demonstrated by allowing it to react with a molar equivalent of n-butyllithium in tetrahydrofuran/hexane (approx. 1/1) at −50° and subsequently adding, at the same temperature, a molar equivalent of benzophenone. Only 1,1-diphenyl-3-butyn-1-ol (70 area-%) and unreacted benzophenone (30 area-%) were detected by gas chromatographic analysis of the reaction mixture. Since the allenyl Grignard reagent behaves similarly upon treatment with benzophenone[8-10], the formation of allenyllithium was indicated. IR evidence for allenyllithium formation was obtained by evaporating most of the tetrahydrofuran/hexane solvent at 0° under vacuum and adding hexane. The resulting solution at room temperature was quickly analyzed by IR spectroscopy and indicated the presence of only allenyllithium by a strong absorption at 5.30 μ. No absorption in the acetylene region was observed. Metalation of allene by n-butyllithium in hexane at 25° gave a pale yellow solid showing strong absorption at 5.28 μ in the IR, thus providing further evidence for formation of allenyllithium.

Formation of the butynol probably proceeded by coordination of the allenyllithium with the carbonyl oxygen followed by reaction via a cyclic transition state, as has been suggested for the allenyl Grignard reagent[10]. Complex formation by organolithium reagents is well known, influencing both their state of aggregation[11,12] and reactivity[11,13-16].

The benzophenone recovered was either unconverted starting material or could have been derived from a ring metalated product from which benzophenone was regenerated on workup.

Allene behaves like fluorene (pK_a 23)* which is metalated by n-butyllithium at 25° in tetrahydrofuran/hexane, and is more reactive than ethylene (pK_a 36.5)* or benzene (pK_a 37)*. The latter, with sp^2 hybridized hydrogens, are not metalated by n-butyllithium in ether or hexane solvents[18-25]. Kinetic acidity in the metalation reactions of olefins and alkylaromatics has been shown to reflect both hybridization and charge stabilization (delocalization) effects[26,27]. Hybridization can be determined from ^{13}C–H coupling constants[28], which are 168.2, 250, 159, 157[28-32] and 130 Hz, respectively, for allene, propyne, benzene, ethylene, and fluorene (C_9–H). The almost linear increase in pK_a with increasing s-character of C–H bonds, when delocalization is not a factor, has been established*.

A parallel between kinetic and thermodynamic acidities is generally assumed[17,33], and is presumed to apply to the reactions under discussion. The higher kinetic acidity of allene may reflect a small s-character contribution, but a ^{13}C–H coupling constant closer to 250 Hz, corresponding to a pK_a of about 25, would be required if the increased acidity were due entirely to hybridization of the C–H bonds. As with fluorene, resonance stabilization of the carbanionoid allenyllithium can account for the increased acidity of allene. The electron pair in an allenyl carbanion is coplanar with the adjacent π-bond, thus permitting maximum overlap as a result of this favorable stereoelectronic arrangement. This view implies an appreciable degree of bond breaking in the transition state.

When allene was passed into a solution containing an equimolar amount of

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* See ref. 17. The correlation of kinetic and thermodynamic acidities is discussed in Chapter 1 of this reference.

n-butyllithium in hexane and tetrahydrofuran at −50°, a white solid formed. After 5 min at −50°, trimethylchlorosilane was slowly added. Gas chromatographic analysis* of the organic layer after hydrolysis gave only two peaks, retention time 1.38 min (Ia) and 1.50 min (Ib).

The same procedure was repeated using propyne in place of allene and only a single product, retention time 1.60 min (Ic), was detected. The latter was identified as 1-(trimethylsilyl)propyne by its IR[34] and proton NMR spectra.

Compounds (Ia) and (Ib) were separated by gas chromatography. The IR spectrum of the mixture had bands at 3.00 μ ($\equiv$C–H), 4.72 μ (C$\equiv$C stretch), 5.18 μ (C=C=C stretch), 8.00 μ ($-SiMe_3$) and no band at or near 9.73 μ ($\equiv$C–Me). Correlation of the IR allenic and acetylenic band intensities with the relative amounts of (Ia) and (Ib) in two different distillation cuts permitted assignment of structures. The 1.38 min peak was 3-(trimethylsilyl)propyne (Ia) and the 1.50 min peak was (trimethylsilyl)allene (Ib).

A series of reactions were run in which allene was treated with two or more equivalents of n-butyllithium followed by an equal amount of trimethylchlorosilane [eqn. (1)]. The reactions are summarized in Table 1. Also included in Table 1 (run 2) is a competitive reaction run as shown in eqn. (2) and a two-stage reaction (run 6).

$$CH_2{=}C{=}CH_2 + (1+x)\,\text{n-BuLi} \xrightarrow[-50^\circ]{THF/C_6H_{14}} \xrightarrow{(1+x)\,Me_3SiCl} (Id)+(II)+(III)+(IV)+(V)$$
$$(x=1,\ 3,\ \text{or}\ 4) \qquad (1)$$

TABLE 1

Run	Allene/BuLi/ Me$_3$SiCl	Me$_3$SiCl	Product composition (area-%)[a–c]				
			(Id)	(II)	(III)	(IV)	(V)
1	1/2/2	Neat	0	80.5	2.0	6.3	11.3
2	1/4/4[d]	Dilute	72	18 (63)	0.1 (0.4)	0.1 (0.4)	10 (36)
3	1/4/4	Diluted (1/1)[e]	23	27 (35)	< 0.05	<0.05	50 (65)[f]
4	1/4/4	Neat	19	26 (32)	0.8 (1.0)	0.6 (0.8)	54 (66)
5	1/5/5	Neat	18	9.9 (12)	< 0.05	< 0.05	72 (88)[g]
6	1/4/4[h]	Neat	12	5.5 (6)	0	0	83 (94)

[a] Based on GLC analysis of total reaction mixtures and presented as uncorrected area-%. The mixtures were analyzed on 6′ × 1/8″ 10% SE-30 on 80–100 Diatoport-S columns at a 50 ml/min He flow rate and a temperature held at 50° 8 min and then programmed at 10°/min to 225°. [b] Figures in parentheses are normalized values permitting comparison of the relative distribution of (II)–(V) in these runs. [c] Minor amounts of (trimethylsilyl)allene and 3-(trimethylsilyl)propyne may have been present also, but were masked by the large solvent peaks. [d] This was a competitive reaction [see eqn. (2) and text]. In all others the allene and butyllithium were mixed at −50° and then trimethylchlorosilane was added. [e] The trimethylchlorosilane was diluted with a equal volume of THF to assess the importance of local concentration of the chlorosilane on product distribution. [f] A 42% isolated yield of (V) was obtained from this mixture. [g] A 70% isolated yield of (V) was obtained from this mixture. [h] This was a two stage run in which two equivalents of n-butyllithium followed by two equivalents of trimethylchlorosilane were added and then the sequential addition of two additional equivalents of each of the latter two reagents was repeated. A 62% isolated yield of (V) was obtained by distillation.

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* A 6 ft by $\frac{1}{8}$ in 10% SE-30 on 80–100 Diatoport-S column at a temp. of 40° and helium flow of 50 ml/min in an F&M Scientific Model 700 thermal conductivity instrument was used.

$$CH_2{=}C{=}CH_2 + 4\ Me_3SiCl \xrightarrow[-50^\circ]{THF} \xrightarrow[-50^\circ]{4\ n\text{-}BuLi} (Id) + (II) + (III) + (IV) + (V) \qquad (2)$$

[(Id) = $Me_3SiCH_2CH_2CH_2CH_3$, (II) = $Me_3SiCH_2C{\equiv}CSiMe_3$,
(III) = $(Me_3Si)_2CHC{\equiv}CSiMe_3$, (IV) = $(Me_3Si)_2C{=}C{=}CHSiMe_3$,
(V) = $(Me_3Si)_2C{=}C{=}C(SiMe_3)_2$]

Formation of appreciable amounts of (II) and (V) (Table 1, run 2) in the competitive reaction [eqn. (2)] indicated that the rate of metalation of allene and of subsequent metalation and silylation steps leading to (V) were of the same order of magnitude as the coupling reaction of n-butyllithium with trimethylchlorosilane. Thus one mole of allene could compete with four moles of trimethylchlorosilane for four moles of n-butyllithium. Similar effective competition for n-butyllithium with trimethylchlorosilane by fluorene[35], bromobenzene[35], and styrene[36] has been reported by Bey and Weyenberg. Allene behaves similarly to fluorene, but the reaction sequence is much more complex because the allenyl-3-propynyl rearrangement and the presence of four rather than two replaceable hydrogen atoms increase the number of possible trimethylsilyl substituted intermediates from two to twelve*. Both compounds undergo polysilylation. This can be attributed to the ability of the first trimethylsilyl substituent to enhance α-proton acidity (or γ-proton acidity in α,β-unsaturated systems) and consequently to enhance the metalation rate by stabilizing carbanions via d_π–p_π interaction[35,37,38].

Structure determination of (II), (III), (IV), and (V) was based on IR, proton NMR, mass spectrometry, and gas chromatography data. Authentic (III) and (V) were prepared by the method of West *et al.* for comparison. By passing samples directly from the gas chromatograph exit port into a mass spectrometer, the peaks corresponding to (Id), (II), (III), (IV), and (V) were shown to have molecular weights, respectively, of 130, 184, 256, 256, and 328. IR analysis indicated that (II) and (III) were nonterminal acetylenes (4.7 μ absorption for C≡C, no absorption at 3.0 for ≡CH) and that (IV) and (V) were allenic (strong absorption at 5.3 μ). Furthermore, in the product from a run to which D_2O was added to the final mixture after trimethylchlorosilane had been added (see Experimental), combined gas chromatography and mass spectrometry showed 73% of the (II) formed was monodeuterated (mol.wt. 185) and the remainder was dideuterated (mol.wt. 186), indicating the presence of two acidic hydrogen atoms. The mass spectra of (III) and (IV) were essentially identical, and both were present only as monodeuterated products (mol.wt. 257). The deuterated species are taken as evidence for the presence of acidic protons that are exchangeable in the presence of organolithium reagents, but no conclusion is drawn concerning the composition of the mixture quenched since transmetalation could have been occurring during the quenching step**.

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[*] Three mono-, four di-, three tri-, and two tetrasilyl derivatives are possible when substition products of both allene and propyne are considered. Several pairs have a common carbanionic precursor or give a common carbanionic species, if the lithiated species are considered to be ionic. With fluorene only a monosilyl and a disilyl derivative are possible.

[**] Ref. 17, pp. 44–45 and 76–77 discusses the problems in correlating deuterium quenching data with composition of the mixture quenched.

The reaction system is quite complex and a complete study to provide data necessary to describe a detailed mechanism for the formation of (V) has not been undertaken. Nevertheless, a plausible hypothetical path can be deduced from the data available. Thus, metalation of allene by butyllithium yields lithioallene as the initial species. Further rapid metalation to produce a dilithiated species is indicated

$$\mathrm{CH_2{=}C{=}CH_2 + RLi \rightarrow CH_2{=}C{=}CHLi + RH} \tag{3}$$

by the results of run 1, Table 1, in which no (Id) was formed. At a 1/2 ratio of allene to butyllithium the dilithiated species formed rapidly and essentially no unreacted butyllithium remained to form (I) when trimethylchlorosilane was added. The ditlithiated species is formulated as 1,3-dilithiopropyne. Rapid formation of homologous 1,3-dilithioalkynes when higher terminal acetylenes were metalated by two or more equiva-

$$\mathrm{CH_2{=}C{=}CHLi + RLi \rightarrow LiCH_2C{\equiv}CLi + RH} \tag{4}$$

lents of n-butyllithium has been described by others[1,39]. Furthermore, the analogous di-Grignard reagent is formed quantitatively when the allenyl Grignard reagent is metalated with one equivalent of the ethyl Grignard reagent[9]. It is also formed by disproportionation of the allenyl Grignard on heating[8-10].

Reaction of 1,3-dilithiopropyne with trimethylchlorosilane produces (II). Formation of (III), (IV) and (V) can then proceed by stepwise metalation and silylation of (II).

$$\mathrm{(II) + RLi \rightarrow \underset{(IIa)}{[Me_3SiCH{=}C{\equiv}CSiMe_3]^-Li^+} + RH} \tag{5}$$

$$\mathrm{(IIa) + Me_3SiCl \rightarrow (III) + (IV) + LiCl} \tag{6}$$

$$\mathrm{(III)\ or\ (IV) + RLi \rightarrow \underset{(IIIa)}{[(Me_3Si)_2C{=}C{\equiv}CSiMe_3]^-\,Li^+} + RH} \tag{7}$$

$$\mathrm{(IIIa) + Me_3SiCl \rightarrow (V) + LiCl} \tag{8}$$

The species (IIa) and (IIIa) possibly are ionic since the carbanions would be stabilized by d_π–p_π resonance with the silicon substituents[36,38]. This factor also explains the increased reactivity of (II), (III), and (IV) toward metalation, as required for rapid formation of (V). An enhanced reactivity of (IIa) and (IIIa) (compared to n-butyllithium) toward trimethylchlorosilane is also required for rapid formation of (V). This is in accord with the proposed mechanism since, for benzylic species, it has been shown that resonance stabilized ionic organolithium reagents are more nucleophilic than alkyllithium reagents[36]. Intermediate (IIIa) should form faster and be more nucleophilic than (IIa) since it has an additional silicon substituent. The distributions of (II), (III), (IV), and (V) observed in the various reaction mixtures is also explained since metalation of (II) would be the slow step and (III) and (IV) would not accumulate in the mixture. Metalation of (III) by n-butyllithium and conversion of (IIIa) to (V) by reaction with trimethylchlorosilane has been described[2]. Conversion of (IIIa) to (V) is probably sterically controlled, as suggested by West *et al.*[2], to give the less strained allenic isomer.

Formation of tri- or tetralithiated species in the metalation reaction is considered unlikely in view of the low temperatures and short reaction time. The successive metalation steps leading to tri or tetralithiated species would be expected to occur progressively more slowly, as the increasing accumulation of negative charge should decrease acidity and slow the metalation rate. Furthermore, stepwise silylation of a tri- or tetralithiated species would not be expected to give high yields of (II) and (V) and almost negligible yields of (III) or (IV) (*cf.* ref. 2).

Propyne, for which tri- and tetralithiated species have been reported[2] when the metalation is run in refluxing hexane for several hours, has been used in place of allene. The product composition was qualitatively similar to that obtained with allene, but the yield of (II)–(V) was decreased. This could be attributed to slower metalation of 1-lithiopropyne to give 1,3-dilithiopropyne or to a slower metalation of 1-(trimethylsilyl)propyne which might also be the precursor to (II). The reaction sequence for conversion of (II) to (III), (IV), and (V) is probably identical for allene and propyne.

The synthetic utility of these reactions is apparent from the fact that distillation of the reaction mixture from run 5, Table 1 provided (V) in 70% isolated yield. A 43% yield of (V) was realized from the mixture from run 3. Furthermore, run 1 provides a useful preparation of (II) (63% isolated yield).

Finally, these reactions provide another example where trimethylchlorosilane derivatization cannot be used as a diagnostic tool for characterizing organolithium intermediates present in reaction mixtures. This will be the case in those instances where rapid transmetalations can occur during the course of the derivatization reaction[16,39,40], as appears to be the case in the reaction mixtures leading to formation of (V).

EXPERIMENTAL

All reactions involving organolithium compounds were run under an atmosphere of oxygen-free argon. Gaseous allene and propyne were metered by means of a precalibrated flowmeter. A cold finger cooled with Dry Ice/acetone was used to assure that no allene or propyne escaped from the reaction mixtures.

Allene was 97% minimum purity purchased from the Matheson Company. The n-butyllithium solution, approximately 1.6 *N* in hexane, was obtained from Foote Mineral Company and was titrated shortly before use by the Gilman–Cartledge double titration method using 1,2-dibromoethane[42].

Mass spectral data was obtained with an Atlas CH-4 spectrometer. Proton NMR spectra were run on a Varian HA-100 spectrometer. Gas chromatography data was obtained with an F&M 700 chromatograph equipped with thermal conductivity detectors using 6′×1/8″ 10% SE-30 on 80–100 Diatoport-S columns, a helium flow rate of 50 ml/min, and an isotherm of 90° for 8.0 min followed by a temperature increase at 10°/min to 250°, unless otherwise indicated. IR spectra were recorded on a Perkin–Elmer Infracord.

Metalation and silylation of allene

To a solution prepared by mixing 62.5 ml of freshly distilled tetrahydrofuran at −50° with 59.3 ml of a 1.69 *N* hexane solution of n-butyllithium (0.10 mole) was added 1.00 g (0.025 mole) of gaseous allene over a period of 9.6 min. The mixture was stirred 5 min longer at −50°. Then 10.9 g (0.10 mole) of trimethylchlorosilane was added while maintaining the temperature at −50°. The mixture was stirred for an additional 25 min after the addition was complete and then excess 10% aqueous ammonium chloride solution was added to quench the reaction. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. A small portion of the solution was analyzed by gas chromatography and the remainder was distilled to give 5.78 g (70%) of (V), b.p. 83–84° (0.5 mm), mol.wt. 328 (mass spectrosc.). The product was shown to be identical with material prepared by the method of West *et al.*[2] by comparison of IR (5.3 μ, C=C=C; 8.0 μ, $SiMe_3$) and NMR (9.88, singlet) spectra and gas chromatographic retention times (16.9 min).

The reaction was repeated except that trimethylchlorosilane was diluted with 10 ml of tetrahydrofuran prior to addition. Distillation yielded 3.48 g of (V) (42%).

Competitive reaction of n-butyllithium with allene and trimethylchlorosilane

A solution of 8.7 g of trimethylchlorosilane in 50 ml of dry tetrahydrofuran was cooled to −50° and 0.8 g (0.02 mole) of allene was added. Then 47.5 ml of a 1.68 *N* hexane solution of n-butyllithium (0.08 mole) was added slowly while maintaining the temperature at −50°. The mixture was stirred at the same temperature for 30 min after addition was complete and then excess 10% aqueous ammonium chloride was added. The organic layer was separated, washed with water, dried over magnesium sulfate, and then analyzed by gas chromatography using a temperature program of 35° for 8 min, then 10° per min to 250°. The results of the analysis are given in Table 1, run 2. Retention times for (Id), (II), (III), (IV), and (V) were, respectively, 7.5 min, 17.75 min, 22.0 min, 22.4 min, and 26.0 min.

D_2O quenched metalation and silylation of allene

A mixture of 25 ml of dry tetrahydrofuran and 22 ml of a 1.9 *N* hexane solution of n-butyllithium (0.042 mole) were cooled to −50° and 0.4 g (0.01 mole) of allene was added over a period of 5 min. The mixture was stirred an additional 5 min, 4.55 g (0.042 mole) of trimethylchlorosilane was added over a 10 min period, and the stirred mixture was maintained at −50° for an additional 45 min. A solution of 1.7 g (0.082 mole) of D_2O in 2 ml of tetrahydrofuran was cooled to −30° and added. The mixture was allowed to warm to room temperature and filtered. Hexane (50 ml) was added to the filtrate, which was then washed with water, dried over magnesium sulfate, and evaporated on a rotary film evaporator to give 2.0 g of residual yellow oil. Gas chromatographic analysis indicated the presence of (Id)–(V) with the following retention times and relative area-%: (Id), 0.8 min, 4.0; (II), 3.55 min, 4.0; (III), 12.2 min, 1.2; (IV), 12.8 min, 1.8; (V), 16.95 min, 84.8. In addition a new product with retention time of 3.85 min (4.2 rel. area-%), tentatively identified as a bis(trimethylsilyl)allene on the basis of its retention time and mass spectrum, was detected. The allene structure was verified by an IR absorption at 5.25 μ.

Mass spectra, obtained by passing the sample into a mass spectrometer as it was eluted from the exit port of the gas chromatograph, indicated the following molecular weights from the products: (II), 185 (73%) and 186 (27%); 3.85 min product, 185 (36%) and 186 (64%); (III), 257; (IV), 257; (V), 328.

Preparation of 1,3-*bis(trimethylsilyl)propyne*

A solution of 30 ml of freshly distilled tetrahydrofuran and 29.7 ml of 1.68 *N* n-butyllithium (in hexane) was cooled to −50° and 1.00 g (0.025 mole) of allene was added over a 9 min period. The reaction mixture was stirred an additional 5 min, then 5.43 (0.05 mole) of trimethylchlorosilane was added dropwise over a 10–12 min period while maintaining the temperature at −50°. The mixture was stirred an additional 30 min at −50° and then poured into 100 ml of 10% ammonium chloride solution. The organic layer was washed, dried, and analyzed by gas chromatography. The analysis (Table 1, run 1) showed that no n-butyltrimethylsilane had been formed and about 80 area-% of the product was (II). Distillation of the mixture provided 2.9 g (63%) of (II), b.p. 35° (2.5 mm), shown to be essentially pure by gas chromatography (retention time 3.55 min).

The proton NMR of (II) (~50% solution $CDCl_3$) showed a singlet at τ 8.58 (2 protons) and two overlapping absorptions at τ 9.88 and 9.94 (18 protons). IR absorptions were present at 4.6 μ (C≡C), 8.00 μ ($SiMe_3$), and 11.85 μ (SiMe), with no absorption at or near 3.0 μ (≡C–H). (Found: C, 58.67; H, 11.03; Si, 30.39; mol.wt. mass spectrosc., 184. $C_9H_{20}Si_2$ calcd.: C, 58.62; H, 10.93; Si, 30.46%.)

Metalation and silylation of propyne

To 53 ml of a 1.5 *N* hexane solution of n-butyllithium (0.08 mole) at −50° was added 0.8 g (0.02 mole) of propyne. The mixture was stirred for 5 min and then cooled to −70°. Then 8.7 g (0.08 mole) of trimethylchlorosilane was added dropwise and the temperature rose to −45°. The mixture was stirred for 30 min at −50°, allowed to warm to −35° and quenched with 10% aqueous ammonium chloride. The organic layer was separated, washed with water, dried, and evaporated on a rotary film evaporator to give 1.8 g of residual yellow oil. Gas chromatographic and mass spectral analysis indicated the presence of the following with the retention times and relative area-% shown: (Id), 1.1 min, 2.0; (II), 3.7 min, 15.9; $(Me_3Si)_2C_3H_2$, 4.1 min, 20.2; (III), 12.2 min, 1.8; (IV), 12.8 min, 5.2; unknown, 14.4 min, 2.0; (V), 16.9 min, 52.8. IR analysis of a mixture of (II) and its isomer indicated the isomer was allenic by the presence of a peak at 5.25 μ (C=C=C) in addition to a 4.6 μ (C≡C) absorption.

1,1-Diphenyl-3-butyn-1-ol

A solution of 1.28 g (0.02 mole) of n-butyllithium was prepared by adding 8.6 ml of 2.33 *N* n-butyllithium in hexane to 25 ml of tetrahydrofuran at −50°. Then 0.8 g (0.02 mole) of allene was passed into the solution. After 5 min at −50°, 3.44 g (0.02 mole) of benzophenone was added and the mixture was maintained at −50° an additional hour. Aqueous 10% ammonium chloride (100 ml) was added and the mixture was extracted with hexane. The hexane solution was dried and concentrated to give 3.0 g of residual yellow oil. Gas chromatographic analysis showed 69 area-% of a single product and 31 area-% of unreacted benzophenone.

Proton NMR analysis (CCl_4) indicated that the material was 1,1-diphenyl-3-butyn-1-ol by the following data: τ 2.68 (aromatic multiplet, 10 protons), τ 6.94 (≡C–CH_2–, doublet, $J_{1,4}$ 2.6 Hz, 2 protons) and τ 8.07 (H–C≡, triplet, $J_{1,4}$ 2.6 Hz, 1 proton).

The IR spectrum was in accord with the structure showing the acetylenic C–H at 3.00 μ and a weak, sharp band at 4.71 μ for C≡C stretch.

Allene metalation in hexane

Into a 100 ml flask equipped with a gas inlet and Dry Ice cold finger was placed 31.3 ml (0.05 mole) of a 1.6 *N* n-butyllithium solution in hexane. Then 2.0 g (0.05 mole) of allene was introduced, while cooling the flask to maintain the temperature at 25°. Some refluxing of allene occurred after addition was completed (~ 10 min) but before all the allene was consumed. After 15 min the straw-yellow solution originally obtained became opaque and was transformed to a slurry as a finely divided yellow solid formed. Vacuum was applied to remove any unreacted allene and about 15 ml of hexane. An IR analysis of a mineral oil mull of the yellow solid was obtained. In addition to a strong absorption at 5.28 μ ($>C{=}C{=}C{<}_{\mathrm{Li}}$; *vs.* 5.32 μ for the allenyl Grignard[8,10]) weak absorptions at 4.50 μ, 4.28 μ, and 5.57 μ were present in the 4–6 μ range.

Monometalation and monosilylation of allene

Allene (4.80 g, 0.12 mole) was passed into a solution prepared by adding 51.5 ml of 2.33 *N* n-butyllithium (0.12 mole) in hexane to 50 ml of tetrahydrofuran at −50°. A white solid formed after about 2/3 of the allene had been added. After 5 min at −50°, 13.0 g (0.12 mole) of trimethylchlorosilane was slowly added while maintaining the temperature at −50° to −40°. The mixture was stirred for 1 h at −50° and then 100 ml of 10% aqueous ammonium chloride was added. The organic layer was separated, washed with water, dried, and distilled. Solvents were distilled and then several distillation cuts boiling over the range of 82–92° were collected. Gas chromatographic analysis (isothermal at 40°) revealed only two peaks, retention time 1.38 min and 1.50 min, in the different cuts. IR analysis of the mixture gave absorptions at 3.00 μ (C−H), 4.72 μ (C≡C stretch), 5.18 μ (C=C=C stretch), 8.00 μ ($-SiMe_3$), and no band at or near 9.73 μ (≡C−Me). Correlation of the acetylenic and allenic absorption intensities with the relative amounts of the two species permitted identification of the 1.38 min species as 3-(trimethylsilyl)propyne and the 1.50 min species as (trimethylsilyl)allene.

Monometalation and monosilylation of propyne

The procedure above was repeated using propyne in place of allene. Only a single product, GLC retention time (isothermal, 40°) 1.60 min, was obtained. It was identified as 1-(trimethylsilyl)propyne by its proton NMR spectrum and by its IR which was essentially identical to the published spectrum[34].

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