

Polyolithium Compounds. 10. Preparation and Chemistry of Polyolithiated 2,4-Hexadiyne

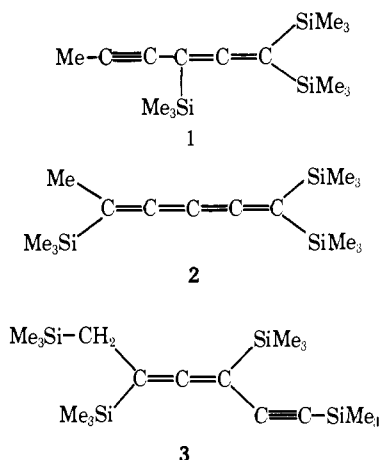
Witta Priester and Robert West*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received December 24, 1975

Abstract: 2,4-Hexadiyne can readily be metalated by *n*-butyllithium-TMEDA complex at room temperature to give the lithiated compound MeC_5Li_3 . Reaction of MeC_5Li_3 with organic and organometallic derivatizing agents yields a variety of isomeric products. Allenynes are the major products, although cumulenes and diacetylenes are also formed. Derivatization with trimethylchlorosilane yields small amounts of a hexasilylated product, hexakis(trimethylsilyl)-1,2,4,5-hexatetraene. Reasons for gem polymetalation are discussed.

Introduction

In 1973 Klein and Becker¹ reported on the polymetalation of diacetylenes. They found that 2,4-hexadiyne could be trilitiated at one of the methyl groups to give MeC_5Li_3 . Reaction of this trilitiated hydrocarbon with trimethylchlorosilane resulted in the isolation of two trisilylated products which they identified as **1** and **2**. They also found that by metalating in tetrahydrofuran (THF) rather than in hexane solution, a tetrasilylated product, compound **3**, could be formed. We have



repeated this reaction and found the structure assignment for **1** to be incorrect. We have also prepared numerous other derivatives of MeC_5Li_3 and have isolated a hexasilylated product from polyolithiated 2,4-hexadiyne.

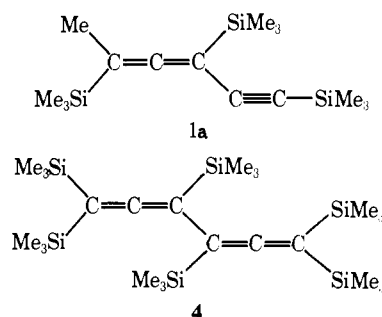
Results: Structure of Products

Polymetalation of 2,4-hexadiyne using *n*-butyllithium-tetramethylethylenediamine (TMEDA) complex at room temperature for 16 h resulted in a brown oil. Addition of tetrahydrofuran and trimethylchlorosilane at -78°C yielded a mixture of products from which two tris(trimethylsilyl) derivatives and a small amount of a hexasilylated derivative were isolated.

The tris derivatives were shown to be identical with Klein and Becker's¹ compounds by UV, IR, ^1H NMR, and mass spectral data. The tris(trimethylsilyl)hexatetraene **2** was 15% of the tris products in a typical run. The other tris derivative had infrared absorptions at 2135 and 1900 cm^{-1} , which can be assigned to acetylene and allene stretching modes, indicating that it is an allenyne. The original assignment of structure **1** for this compound followed from the 2:1 ratio for silylmethyl resonances in the proton NMR spectrum, determined in carbon tetrachloride. However, when the NMR spectrum is determined in benzene- d_6 the silylmethyl peaks separate into

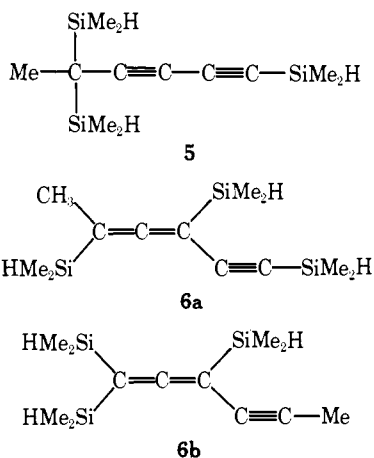
three resonances of equal intensity (Figure 1), showing that structure **1** cannot be correct. Moreover, the observed chemical shift for the methyl protons at δ 1.71 is inconsistent with a conjugated acetylenic methyl resonance, but consistent with an allenic methyl. We therefore assign structure **1a** for this compound.² Structure **1a** is similar to that of the tetrakis product **3**, which shows four distinct silylmethyl resonances in benzene- d_6 .

Identification of the hexasilylated product as the allene **4** was based on spectral and microanalytical evidence, as well as comparison with a known sample.³ Because compound **4**

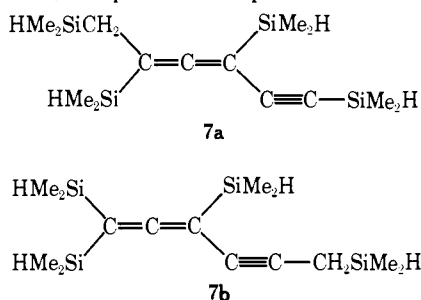


might have been derived from a small amount of the unknown lithiocarbon C_6Li_6 , various reaction conditions were tried in an attempt to increase its yield. However, metalation with large excess of *n*-butyllithium (25°C , 80°C) in the presence of hexamethylphosphoric triamide (0°C) or tetrahydrofuran (0°C) or TMEDA (25°C , 65°C) gave no improvement in yield.

Derivatization of MeC_5Li_3 with the less bulky silane, dimethylchlorosilane, resulted in formation of two trisubstituted products, **5** and **6**, and one tetrakis derivative, **7**. Compound **5** was readily identified as the substituted 1,3-hexadiyne by the chemical shift of the methyl singlet at δ 1.13 and by its UV spectrum (λ_{max} , 282, 266, 252, 240 nm). The infrared spectrum of compound **6** (2130 , 1915 cm^{-1}) identified the product as an allenyne (**6a** or **6b**). The chemical shift of the methyl singlet (CCl_4) at δ 1.70 indicated an allenic methyl group, but a 100-MHz ^1H NMR spectrum in deuteriobenzene showed only three doublets in the silylmethyl region, while the Si-H region showed a multiplet at δ 4.43 (2 H) and a septet at δ 4.18 (1 H). Compound **6a** has six diastereotopic methyl groups and therefore should give six doublets, while compound **6b** with only three diastereotopic methyl groups should give three doublets. Therefore a 270-MHz spectrum was determined (Figure 2), and at this higher field strength five doublets appear (the diastereotopic character of the methyl on the acetylenic silicon is not observed), proving the structure for allenyne **6** to be **6a**.

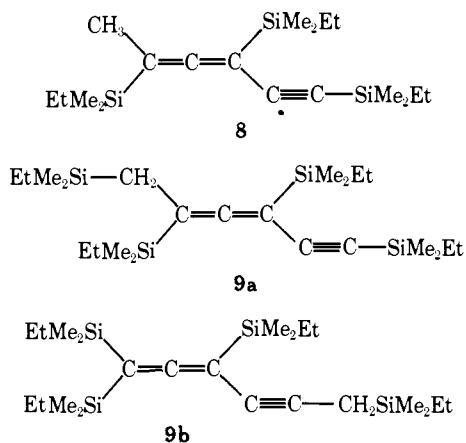


The tetrakis(dimethylsilyl) derivative was shown also to be an allenyne by its infrared spectrum. The 100-MHz ^1H NMR spectrum shows a multiplet in the silylmethyl region which is consistent with six overlapping doublets, two of relative intensity two. The silylmethyl region for the two possible allenyne, **7a** and **7b**, is expected to be quite different. Compound



7a could show up to eight diastereotopic methyl doublets, while compound **7b** could exhibit at most four methyl doublets. The structure is therefore assigned as **7a**. The Si-H region which shows two clearly defined septets and two overlapping septets is also as expected for this structure. Interestingly, the geminal nonequivalence of the diastereotopic methylene hydrogens is not observed in **7a**, although it is observed in the quite similar compound **3**.⁴

Derivatization of MeC_5Li_3 with ethyldimethylchlorosilane resulted in the formation of two products, a tris derivative **8** and a tetrakis derivative **9**, in yields of 39 and 10%, respectively.



Both compounds were shown to have an allenyne structure by infrared spectroscopy. The chemical shift of the methyl singlet (CCl_4) at δ 1.68 for compound **8** indicated the product had an allenic methyl group, and the benzene- d_6 spectrum showed five peaks in the silylmethyl region, at δ 0.49 (3 H), 0.47 (3 H), 0.39 (6 H), 0.29 (3 H), and 0.28 (3 H), ruling out the isomeric allenyne. The tetrakis derivative was identified as **9a** by its proton NMR spectrum which showed six peaks in the silylmethyl

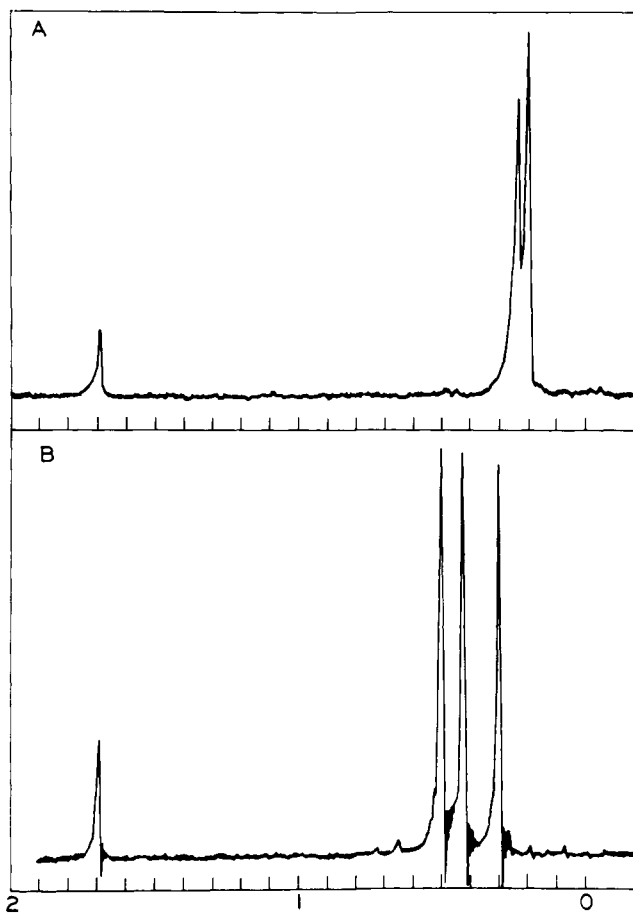
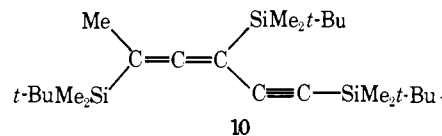


Figure 1. ^1H NMR spectrum of **1a** in (A) CCl_4 solution and (B) C_6D_6 solution.

region. The isomeric structure **9b** can be eliminated because it can have at most four singlets in this region.

Quenching MeC_5Li_3 with *tert*-butyldimethylchlorosilane resulted in the formation of only one trisubstituted product, again an allenyne, identified as **10** on the basis of its benzene- d_6



^1H NMR spectrum which showed five peaks in the silylmethyl region in a ratio of 1:1:1:2:1. The peaks with relative intensity 1 are assigned to the diastereotopic methyls on the allenic silicons and the peak of relative intensity 2 is assigned to the acetylenic silylmethyls. The *tert*-butyl region shows three singlets in a 3:3:3 ratio.

A lower boiling solid was also isolated from this reaction and identified as bis(*tert*-butyldimethylsilyl)acetylene (**11**).⁵ Formation of **11** indicates that decomposition of the C_6 -skeleton occurs either during lithiation or derivatization and accounts, in part, for the isolation of products in only fair to good yields.

Derivatization with bromotrimethylgermane yielded only one major trisubstituted product, the allenyne **12**. The ^1H NMR spectrum in CCl_4 showed a 2:1 ratio of trimethylgermyl groups, but the spectrum in benzene- d_6 clearly showed three equal intensity singlets at δ 0.43, 0.33, and 0.24, eliminating the isomeric allenyne structure.

Methylated and ethylated derivatives of MeC_5Li_3 were prepared by reaction with dimethyl sulfate and diethyl sulfate. Quenching with dimethyl sulfate resulted in the formation of

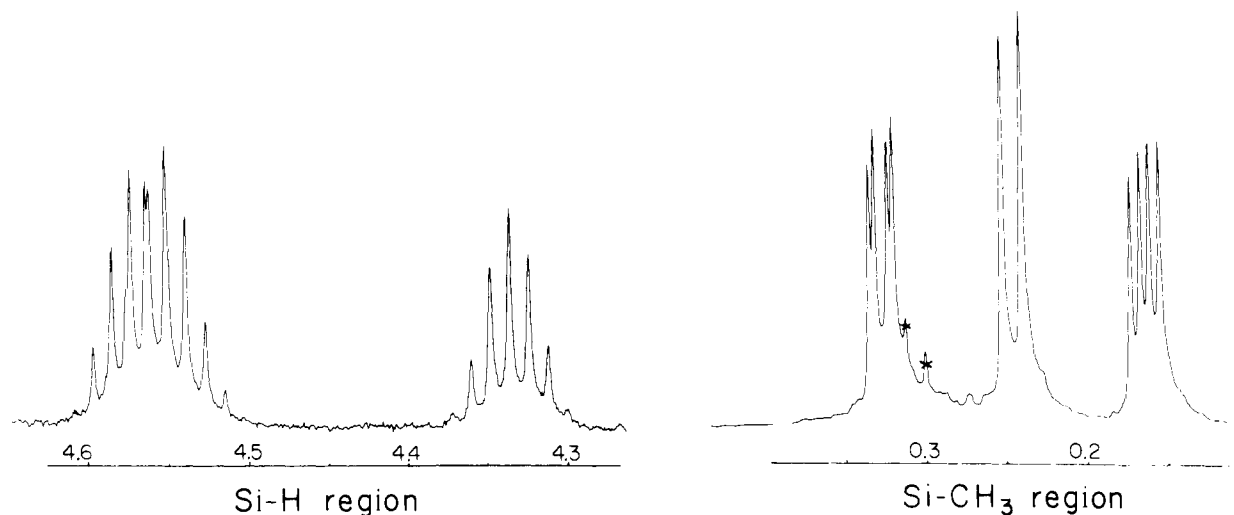
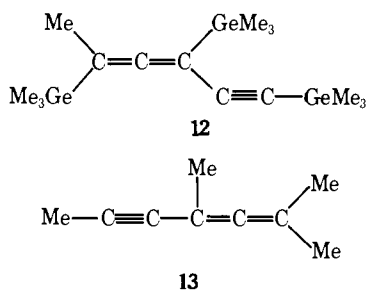


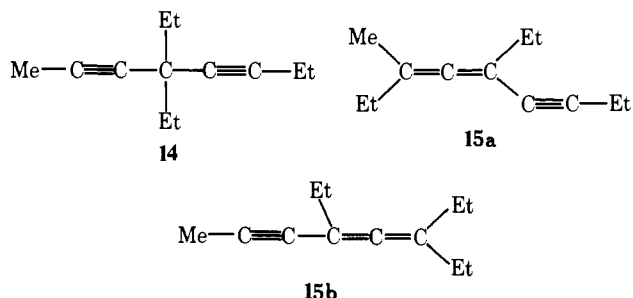
Figure 2. Expansion of silicon hydrogen and silicon methyl regions of 270-MHz ^1H NMR spectrum of **6a** in C_6D_6 .

many products; the major isomer formed corresponded to the allenyne **13**.⁶ This product was identified by its mass spectrum



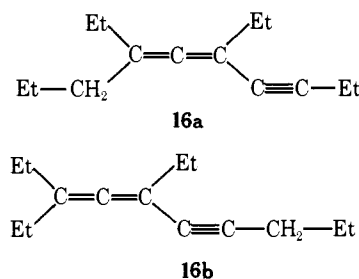
M^+ at m/e 120 (C_9H_{12}) and by its ^1H NMR spectrum which consisted of three singlets at δ 1.88 (acetylenic methyl), 1.70, and 1.66 in a ratio of 1:1:2.⁷ Surprisingly, no allene or acetylene absorption was present in the infrared spectrum. A Raman spectrum could not be obtained due to excessive fluorescence.

Derivatization of MeC_5Li_3 with diethyl sulfate resulted in the formation of two isomeric $\text{C}_{12}\text{H}_{18}$ products, **14** and **15**, in



approximately 30% yield (ratio 1:4). Compound **14** was readily identified by its ^1H NMR spectrum which showed four aliphatic methylene hydrogens at δ 1.54 and an acetylenic methyl resonance at δ 1.83. There is no acetylene absorption present in the IR, but the Raman spectrum shows an absorption at 2240 cm^{-1} . This identified compound **14** as the unconjugated acetylene, 4,4-diethyl-2,5-octadiyne. Compound **15** was identified as the allenyne on the basis of its UV spectrum which was almost identical with **14** [λ_{max} for **14** (cyclohexane) 218 nm (ϵ 5700), (214 sh (ϵ 5500)); λ_{max} for **15** (cyclohexane) 221 nm (ϵ 7400), 215 sh (ϵ 6700)].⁸ As with compound **14** no allene or acetylene absorption was present in the infrared spectrum, and a Raman spectrum could not be obtained. The chemical shift of the methyl singlet at δ 1.70 strongly indicates the product is **15a** rather than **15b**.

A tetrakis derivative was also isolated (17% yield). It was identified as an allenyne by its UV spectrum (λ_{max} 222 nm) and ^1H NMR spectrum (two acetylenic methylene hydrogens, six allenic methylene hydrogens). The structure should be similar to the other allenynes observed and thus is probably **16a** rather than **16b**.

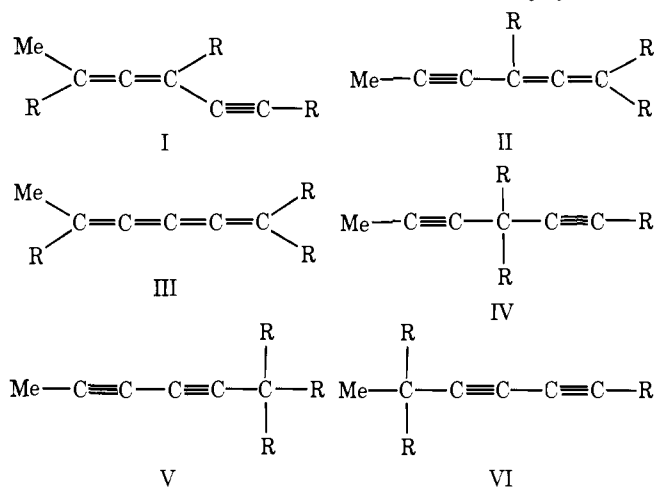


Discussion

Table I summarizes the tris derivatization results. Of the six possible isomeric products that can be obtained from MeC_5Li_3 , the allenyne I is the major product in all cases. This is not surprising since it is the only product which does not have more than one R group on any carbon atom and is therefore the product having the least steric interactions. When less bulky derivatizing agents are used, smaller amounts of isomers III, IV, and VI are formed. With diethyl sulfate, formation of the thermodynamically least favored diacetylene IV (the only one which lacks conjugation) is observed although V and VI should be more stable. The central carbon atom of a pentadienyl anion is the position of greatest reactivity and this, in addition to the relatively small size of the ethyl group, may account for formation of isomer IV with diethyl sulfate.⁹

Products having structure II are not observed. It seems likely that if they were to form they might readily trilithiate and derivatize under the reaction conditions since trimetalation of propargyl methyls is well known.¹⁰⁻¹² This may account for the formation of small amounts of the hexakis(trimethylsilyl) derivative **4** and our inability to increase its yield. Formation of the tetrakis derivatives probably also results from lithiation during derivatization. Vinylic methyl groups are readily monometalated by *n*-butyllithium-TMEDA complex,^{13,14} and products of structure I could be further lithiated and derivatized to give tetrakis products. However, attempts to lithiate the tris(trimethylsilyl) derivative **1a** led to products where *n*-butyllithium had added across the allenyne.

Cumulenes besides **2** may have been formed in some of these reactions; these compounds may be thermally and photo-

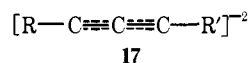
Table I. Ratio of Tris-Derivatized Products from MeC_3Li_3 

Derivatizing agent	R	I	II	III	IV	V	VI
Me_2SO_4	Me	I = II ^a	a				
Et_2SO_4	Et	80			20		
HSiMe_2Cl	HSiMe_2	60					40
SiMe_3Cl	SiMe_3	85		15			
GeMe_3Br	GeMe_3	100					
SiMe_2EtCl	SiMe_2Et	100					
$\text{SiMe}_2t\text{-BuCl}$	$\text{SiMe}_2t\text{-Bu}$	100					

^a Many products, allenyne (I = II) is major product.

chemically labile and could have polymerized during workup or distillation. However, none of the reactions produced large amounts of high boiling residues, indicating that cumulenes were never major products.

One of the most interesting questions raised by these results is why gem trilithiation is the course followed by 2,4-hexadiyne rather than metalation at both of the terminal methyl groups. Klein and Brenner¹⁵ have discussed the ease of formation of dicarbanions α to acetylenes in terms of the sesquiacetylene model which attributes the stability of these dianions to "the unusual occurrence of two identical four-electron three-center systems delocalized symmetrically", i.e., **17**. From this model



one might predict relatively easy formation of C_6Li_6 from 2,4-hexadiyne, which is not observed. Trilithiation appears to be rapid, but further lithiation is difficult. Let us examine the possible paths for polymetalation.

After initial monolithiation of one methyl group, there are two choices for the next site of metalation, gem dilithiation **18**, or lithiation at the other methyl group **19** (Figure 3). If lithiation at both methyl groups takes place, two different electronic arrangements leading to two different geometries are possible. A perpendicular geometry **19a** would result if the second hydrogen were removed such that the resulting p orbital is in a plane perpendicular to the first lithiation. The energy for this π arrangement can be approximated from Hückel molecular orbital calculations by the energy of two pentadienyl anions ($2 \times 5.46 \beta = 10.92 \beta$).¹⁶ The alternative planar geometry **19b** would result if the second hydrogen were removed such that the resulting p orbital is in the plane of the first lithiation. The π energy for this arrangement can be approximated by the energy of eight electrons in hexatriene and four electrons in butadiene ($6.10 \beta + 4.42 \beta = 10.52 \beta$). The energy difference of 0.4β between **19a** and **19b** should greatly favor the perpendicular geometry. This energy difference results from filling an antibonding molecular orbital in **19b**, while in

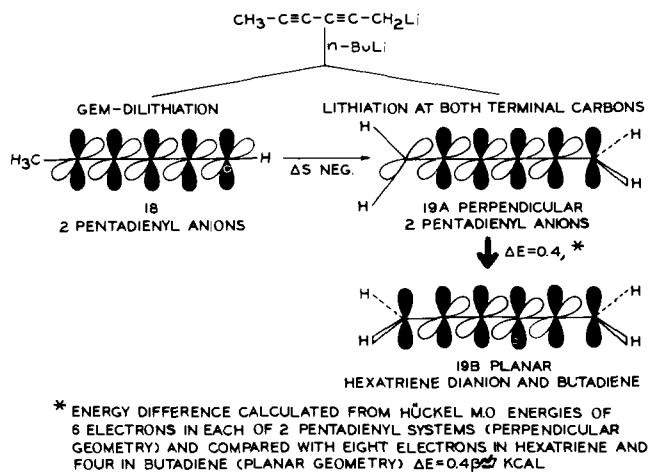


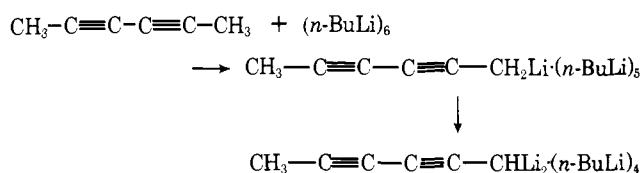
Figure 3. Dilithiation of 2,4-hexadiyne.

19a nonbonding molecular orbitals are filled. Gem dilithiation also results in two pentadienyl anions with filled nonbonding molecular orbitals.

Unfortunately it is not possible to calculate the energy difference between **18** and **19a**. Electron repulsions should favor **19a** where the negative charges are spread over six carbons rather than **18** where the charges are spread over five carbons. The entropy term should favor **18** since this structure would allow free rotation at the methyl group, whereas in **19a** all the atoms are in fixed geometries. Heats of formation for lithiated hydrocarbons are not known at the present time, so enthalpy terms cannot be determined.

Another factor that surely plays an important role in determining the course of polyolithiation is aggregate structure. It is well known that monolithiated hydrocarbons form tetramers or hexamers in solution, and it is likely that polyolithiated hydrocarbons have similar structures. The observed preference for gem dilithiation may result from the proximity of *n*-butyllithium to the monolithiated hexadiyne in the aggregate complex (see Scheme I). The geminal hydrogens are ideally

Scheme I



located to undergo metalation. Whatever the determining factors are, it is clear from the products observed that gem dilithiation is preferred.

After gem dilithiation, the third hydrogen of the methyl group is now acidic, being in an orbital of high s character, and is rapidly metalated to give MeC_3Li_3 . Further lithiation is then much more difficult since it requires formation of hexatriene dianions with filled antibonding molecular orbitals. Gem trilithiation may also be favored because the resulting trianion can associate with another trianion to give a simple aggregate having an octahedral array of lithium atoms (Figure 4).^{17,18}

From the foregoing discussion, it can now be understood why propyne can be perolithiated.¹⁰ After lithiation of the acetylenic hydrogen, two nonbonding propargyl molecular orbitals are filled when the second and third hydrogens are replaced by lithium. The remaining hydrogen is in an orbital of high s character and is readily metalated. Analogously 2-butyne is gem trilithiated;¹⁹ the explanation is similar to that used for 2,4-hexadiyne. After monometalation, 2-butyne can either gem dilithiate or lithiate at the other methyl group to give either a

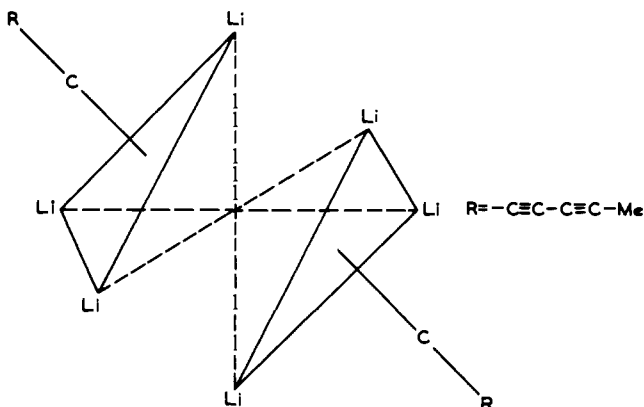


Figure 4.

planar or perpendicular dianion. The energy of two allyl anions (2.818 β , perpendicular geometry) is lower than the energy of ethylene and a butadienyl dianion (2.6 β , planar geometry). This 0.2 β energy difference results in the planar dianion being disfavored. The product is therefore determined by the relative thermodynamic stabilities of the perpendicular dianion and the gem-dilithiated dianion. Again, thermodynamic considerations and aggregate structure must favor gem polymetalation.

Experimental Section

General Procedures. All reactions involving organolithium compounds were carried out in an atmosphere of dry nitrogen. Hydrocarbon and ether solvents were freshly distilled from Na:K alloy before use. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Gas chromatographic analyses and separations were made on a Varian Aerograph Model A-700 chromatograph with thermal conductivity detectors, or on a Barber-Colman Model 5430 thermal conductivity gas chromatograph. The following columns were used: (A) 15 ft \times 1/4 in. 20% SE 30 on Chromosorb W; (B) 15 ft \times 1/4 in. 20% QF-1 on Chromosorb W.

n-Butyllithium in hexane was obtained from Foote Mineral Co. Trimethylchlorosilane, Dow Corning Corp., was distilled before use. *tert*-Butyldimethylchlorosilane was purchased from Willow Brook Labs, Inc. Diethyl sulfate, Aldrich Gold Label, and dimethyl sulfate were stirred over anhydrous sodium carbonate until neutral to Congo red paper and then distilled. Trimethylbromogermane was prepared by reaction of tetramethylgermane with bromine in 1-bromopropane.²⁰ Ethyldimethylchlorosilane was prepared using a modification of the procedure of Lewis,²¹ utilizing EtMgCl rather than EtMgBr to prevent formation of undesired bromochlorodimethylsilane.

Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 457, Beckman ir 33; ¹H NMR, Varian A-60A, HA-100, JEOL MH-100, and Bruker WH-270; mass spectra, AEI-MS 902 at 70 eV; ultraviolet-visible, Cary 14 or 15.

General Procedure for Polyolithiation of 2,4-Hexadiyne. *n*-Butyllithium in hexane was placed in a reaction vessel fitted with a mechanical stirrer, a pressure-equalizing dropping funnel and a condenser. To the stirred solution, 0.25 molar equiv of tetramethylethylenediamine (TMEDA) was added dropwise. The mixture was allowed to stir for 30 min, resulting in the formation of *n*-butyllithium-TMEDA complex as a white suspension. With stirring 0.33 molar equiv of 2,4-hexadiyne in hexane was then added dropwise over a period of 2 h and stirred at room temperature for an additional 16–24 h. At this time a dark brown oil was present with infrared absorption at 1825, 1740, and 1650 cm^{-1} .

Derivatization with Trimethylchlorosilane. Using the general procedure for polyolithiation of 2,4-hexadiyne, 1.17 g (15 mmol) of 2,4-hexadiyne in 50 ml of hexane was allowed to react with 112 ml of 1.6 M *n*-butyllithium (180 mmol) complexed with 5.2 g (45 mmol) of TMEDA. The reaction mixture was quenched at -78°C with 26 g (220 mmol) of Me_3SiCl in 100 ml of THF. The reaction mixture was stirred at room temperature for 16 h, washed with dilute hydrochloric acid, dried (MgSO_4), and rotary evaporated. The crude product (11.4 g) was chromatographed on 300 g of neutral alumina with hexane as eluent. The first six 150-ml fractions contained the products, silylated

Table II. Lithiation of 2,4-Hexadiyne and Derivatization with Trimethylchlorosilane

Run no.	Lithiation conditions	Presence of 4 ^a	Comments
1	8 equiv <i>n</i> -BuLi/3 equiv TMEDA/25 $^\circ\text{C}$ /16 h	Tr	Ratio 1a:2, 85:15
2	12 equiv <i>n</i> -BuLi/3 equiv TMEDA/65 $^\circ\text{C}$ /16 h	None	Mixture of many products
3	32 equiv <i>n</i> -BuLi/7.5 equiv TMEDA/25 $^\circ\text{C}$ /16 h	Tr	Ratio 1a:2, 72:28
4	12 equiv <i>n</i> -BuLi/3 equiv TMEDA/0 $^\circ\text{C}$ /26 h	Tr	Best conditions for formation of 1a (75% yield)
5	8 equiv <i>n</i> -BuLi/no TMEDA/65 $^\circ\text{C}$ /16 h	Tr	Many other products besides 1a, 2, 3 and 4
6	12 equiv <i>n</i> -BuLi/3 equiv TMEDA/HMPA/0 $^\circ\text{C}$ /16 h	Tr	Low yield of products
7	12 equiv <i>n</i> -BuLi/3 equiv TMEDA/0 $^\circ\text{C}$ /10 h, the THF/ -30°C /1 h	Tr	
8	36 equiv <i>n</i> -BuLi/no TMEDA/solvent removed, 70 $^\circ\text{C}$ /16 h, then 80 $^\circ\text{C}$ /5 h	Tr	Low yield of products
9	8 equiv <i>tert</i> -BuLi/8 equiv TMEDA/25 $^\circ\text{C}$ /16 h	None	Ratio 1a:3, 57:43

^a Determined by GLC on column B (240 $^\circ\text{C}$).

alkynes and allenes. These were further separated into two fractions, 3.2 g bp 60–70 $^\circ\text{C}$ (150 μm) and 0.2 g bp 80–130 $^\circ\text{C}$ (150 μm), by Kugelrohr distillation. The lower boiling fraction was separated into two components by GLC (column A, 240 $^\circ\text{C}$). These were identified as 1a (85% of area, retention time 3.9 min) and 2¹ (15% of area, retention time 4.6 min) (75% total yield). Ethanol was added to the higher boiling fraction and white crystals separated. Recrystallization from ethanol yielded pure 4, mp 112–113 $^\circ\text{C}$ (lit.³ mp 111–112 $^\circ\text{C}$). The following spectral and microanalytical data were obtained.

2,4,6-Tris(trimethylsilyl)-2,3-hexadien-5-yne (1a). ¹H NMR (C_6D_6) δ 1.53 (s, 3 H), 0.23 (s, 9 H), 0.16 (s, 9 H), 0.03 (s, 9 H); (CCl_4) 1.68 (s, 3 H), 0.12 (s, 9 H), 0.08 (s, 18 H); IR (CCl_4) 2960, 2920, 2900, 2860, 2135, 1900, 1255, 855 cm^{-1} ; UV (EtOH) λ_{max} 252 nm (ϵ 12 700), 241 (12 100), 235 sh (10 900); mass spectrum *m/e* (rel intensity) 296 (6), 295 (10), 294 (33, M⁺), 279 (6), 208 (10), 207 (23), 206 (100), 191 (13), 97 (15), 73 (95). Anal. Calcd for $\text{C}_{15}\text{H}_{30}\text{Si}$: C, 61.19; H, 10.28; Si, 28.53. Found: C, 61.01; H, 10.32; Si, 28.43.

1,2,4,6-Tetrakis(trimethylsilyl)-2,3-hexadien-5-yne (3). ¹H NMR (C_6D_6) δ 1.42 (d, $J = 14$ Hz, 1 H), 1.13 (d, $J = 14$ Hz, 1 H), 0.36 (s, 9 H), 0.28 (s, 9 H), 0.24 (s, 9 H), 0.20 (s, 9 H); other spectral data reported in ref 1.

1,1,3,4,6-Hexakis(trimethylsilyl)-1,2,4,5-hexatetraene (4). ³ Anal. Calcd for $\text{C}_{24}\text{H}_{54}\text{Si}_6$: C, 56.46; H, 10.59; Si, 32.94. Found: C, 56.64; H, 10.66; Si, 33.27. Other conditions for lithiation of 2,4-hexadiyne are summarized in Table II. No significant increase in yield of 4 was observed.

MeC_5Li_3 and Dimethylchlorosilane. Using the general procedure outlined above, 3.9 g (50 mmol) of 2,4-hexadiyne was reacted with 110 ml of 1.5 M *n*-butyllithium (160 mmol) and 7.8 ml (55 mmol) of TMEDA. After 16 h of stirring at room temperature, 50 ml of THF was added at 0 $^\circ\text{C}$. This solution was added dropwise to 15.0 g (160 mmol) of dimethylchlorosilane in 50 ml of THF at 0 $^\circ\text{C}$. After stirring at room temperature for 16 h, the mixture was refluxed for 2 h. Saturated NH_4Cl (100 ml) was added and the layers were separated and washed. Rotary evaporation and distillation [25–90 $^\circ\text{C}$ (100 μm)] yielded 11.8 g of product. Separation into three components was accomplished by GLC (column A, 180 $^\circ\text{C}$): 5 (26% of total area, 24% yield), 6a (40% area, 37% yield) and 7a (22% area, 16% yield) with retention times of 16.2, 9.0, and 18.3 min, respectively.

1,5,5-Tris(dimethylsilyl)-1,3-hexadiyne (5). ¹H NMR (C_6D_6) δ 4.40 (m, $J = 3.5$ Hz, 2 H), 4.31 (m, $J = 4$ Hz, 1 H), 1.13 (s, 3 H), 0.19–0.00 (five peaks, 18 H); IR (CCl_4) 2960, 2910, 2870, 2200, 2140, 1260, 1225, 955, 945, 850 cm^{-1} ; UV λ_{max} (cyclohexane) 282 nm (ϵ 1350), 266 (4650), 252 (5080), 240 (5020); mass spectrum *m/e* (rel intensity) 252 (12), 238 (29), 237 (100), 193 (18), 179 (33), 178 (20), 177 (22), 153 (21), 139 (21), 97 (22), 83 (21), 73 (76), 59 (45); exact mass 252.1180 (calcd for $\text{C}_{12}\text{H}_{24}\text{Si}_3$: 252.1188).

2,4,6-Tris(dimethylsilyl)-2,3-hexadien-5-yne (6a). 270 MHz ^1H NMR (C_6D_6) δ 4.62–4.53 (m, 2 H), 4.33 (septet, $J = 3.68$ Hz, 1 H), 1.61 (s, 3 H), 0.35 (d, $J = 3.67$ Hz, 3 H), 0.34 (d, $J = 3.49$, 3 H), 0.25 (d, $J = 3.68$, 6 H), 0.16 (d, $J = 3.68$, 3 H), 0.16 (d, $J = 3.68$ Hz, 3 H); ^1H NMR (CCl_4) δ 1.70 (s, allenic methyl); IR (CCl_4) 2970, 2130, 1915, 1250, 890, 875, 865, 837, cm^{-1} ; UV λ_{max} (cyclohexane) 255 nm (ϵ 12 300), 241 (11 900), 235 sh (11 300); mass spectrum m/e (rel intensity) 253 (4), 252 (11), 238 (26), 237 (100), 179 (30), 178 (19), 177 (22), 168 (10), 165 (9), 163 (16), 153 (20), 101 (10), 99 (20), 97 (28), 83 (25), 73 (75), 60 (40); exact mass, 252.1185 (calcd for $\text{C}_{12}\text{H}_{24}\text{Si}_3$; 252.1188).

1,2,4,6-Tetrakis(dimethylsilyl)-2,3-hexadien-5-yne (7a). 100 MHz ^1H NMR (C_6D_6) δ 4.57 (m, 2 H), 4.40 (septet, $J = 3.6$ Hz, 1 H), 4.25 (septet, $J = 3.5$ Hz, 1 H), 1.38 (d, $J = 3.4$ Hz, 2 H), 0.37 (d, $J = 3.5$ Hz, 3 H), 0.36 (d, $J = 3.5$ Hz, 3 H), lines at 0.26, 0.232, 0.222, 0.212, 0.196, 0.187, 0.175, interpreted as 0.241 (d, $J = 3.7$ Hz, 6 H), 0.214 (d, $J = 3.6$ Hz, 3 H), 0.205 (d, $J = 3.5$ Hz, 6 H), 0.194 (d, $J = 3.7$ Hz, 3 H); IR (CCl_4) 2962, 2130, 1905, 1250, 895, 877, 838 cm^{-1} ; IR (CCl_4) 2962, 2130, 1905, 1250, 895, 877, 838 cm^{-1} ; UV λ_{max} (cyclohexane) 253 nm (sh) (ϵ 15 400), 243 (16 500), 235 sh (14 900), 213 (21 800); mass spectrum m/e (rel intensity) 310 (3), 296 (10), 295 (31), 252 (18), 251 (49), 250 (38), 239 (12), 238 (27), 237 (95), 236 (49), 235 (60), 223 (22), 222 (32), 221 (100), 212 (11), 211 (11), 209 (12), 208 (10), 207 (32), 197 (44), 179 (30), 178 (28), 177 (70), 167 (32), 166 (10), 165 (40), 164 (11), 163 (43), 154 (45), 141 (48), 97 (39), 85 (71), 83 (70); exact mass, 310.1429 (calcd for $\text{C}_{14}\text{H}_{30}\text{Si}_4$; 310.1425).

Derivatization with Ethyldimethylchlorosilane. MeC_5Li_3 , prepared from 50 mmol of 2,4-hexadiyne as described above, was cooled to -78 $^\circ\text{C}$, and 50 ml of THF was added. To this solution was added 19.5 g (160 mmol) of ethyldimethylchlorosilane dropwise. The mixture was allowed to warm to room temperature and then refluxed for 2 h. After workup 19.5 g of crude products were obtained. Kugelrohr distillation yielded a fraction [9.0 g, bp 30–110 $^\circ\text{C}$ (100 μm)] which was separated by GLC (column B, 190 $^\circ\text{C}$) into two components, compounds **8** (39% yield) and **9a** (10% yield). The following spectral characteristics were observed.

2,4,6-Tris(ethyldimethylsilyl)-2,3-hexadien-5-yne (8). ^1H NMR (CCl_4) δ 1.68 (s, 3 H), 1.11–0.83 (m, 9 H), 0.74–0.44 (m, 6 H), 0.12 and 0.11 (18 H); HA-100 NMR (C_6D_6) δ 1.76 (s, 3 H), 1.42–0.58 (m, 15 H), 0.49 (3 H), 0.47 (3 H), 0.39 (6 H), 0.29 (3 H), 0.28 (3 H); IR (neat) 2960, 2920, 2880, 2140, 1895, 1250, 1040, 965, 845, 825, 790, 705 cm^{-1} ; UV λ_{max} (cyclohexane) 255 nm (ϵ 16 000), 241 (15 000), 233 sh (13 900); mass spectrum m/e (rel intensity) 337 (16), 336 (M^+ , 45), 235 (11), 234 (42), 221 (16), 206 (27), 97 (13), 87 (49), 83 (11), 73 (24), 59 (100); exact mass, 336.2124 (calcd for $\text{C}_{18}\text{H}_{36}\text{Si}_3$; 336.2125).

1,2,4,6-Tetrakis(ethyldimethylsilyl)-2,3-hexadien-5-yne (9a). ^1H NMR (C_6D_6) δ 1.47–0.23 (m, 22 H), 0.22 (s, 3 H), 0.15 (s, 9 H), 0.13 (s, 3 H), 0.12 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H); IR (neat) 2960, 2910, 2880, 2140, 1885, 1255, 1020, 970, 845, 825, 790, 710 cm^{-1} ; UV λ_{max} (cyclohexane) 255 nm (ϵ 12 200), 243 (12 900), 235 sh (11 400); mass spectrum m/e (rel intensity) 422 (100), 393 (3), 354 (5), 335 (4), 293 (5), 292 (16), 265 (3), 264 (9), 263 (6), 235 (4), 234 (4), 233 (3), 199 (9), 195 (3), 155 (3), 141 (5), 127 (3), 97 (3), 88 (4), 87 (40), 73 (20), 61 (3), 60 (7), 59 (90); exact mass 422.2670 (calcd for $\text{C}_{22}\text{H}_{46}\text{Si}_4$; 422.2677).

Derivatization with *tert*-Butyldimethylchlorosilane. Using the experimental procedure described above 3.9 g (50 mmol) of 2,4-hexadiyne was added to 112 ml of 1.6 M *n*-butyllithium (160 mmol) previously mixed with 5.2 g (45 mmol) of TMEDA. After stirring for 16 h the mixture was cooled to 0 $^\circ\text{C}$, and 50 ml of THF was added. *tert*-Butyldimethylchlorosilane (31.5 g, 210 mmol) in 100 ml of THF was then added. After 40 h of reflux a Gilman color test 1^{22} was still positive. The solution was stirred at room temperature for an additional 48 h after which the color test was negative. Saturated ammonium chloride (100 ml) was added, and the organic phase was washed with dilute hydrochloric acid to remove excess amine. After drying with MgSO_4 and evaporation of solvents, 26 g of a dark viscous oil remained. A portion of the crude product (5.7 g) was chromatographed on 200 g of neutral alumina eluting with hexane. The product mixture (2.9 g) was collected in the first five 100-ml fractions. Kugelrohr distillation yielded two fractions and 0.9 g of residue. The first fraction contained 0.25 g of bis(*tert*-butyldimethylsilyl)acetylene⁵ (**11**), bp 25–60 $^\circ\text{C}$ (100 μm), and the higher boiling fraction, bp 80 $^\circ\text{C}$ (60 μm), was almost pure **10** (1.1 g, 25% yield), which was further

purified for analytical purposes by preparative GLC on column B (230 $^\circ\text{C}$, retention time 6.75 min).

2,4,6-Tris(*tert*-butyldimethylsilyl)-2,3-hexadien-5-yne (10). MP 38–40 $^\circ\text{C}$; ^1H NMR (C_6D_6) δ 1.58 (s, 3 H), 1.13 (s, 9 H), 1.05 (s, 9 H), 1.01 (s, 9 H), 0.27 (s, 3 H), 0.19 (s, 3 H), 0.17 (s, 6 H), 0.09 (s, 3 H), 0.05 (s, 3 H); IR (neat) 2120, 1900, 1250 cm^{-1} ; UV λ_{max} (MeOH) 256 nm (ϵ 13 000), 240 (13 000), 232 sh (11 300); mass spectrum m/e (rel intensity) 422 (14), 421 (30), 420 (72), 363 (30), 290 (14), 275 (16), 251 (34), 235 (27), 234 (86), 233 (100), 219 (26), 209 (80), 179 (36), 155 (94), 151 (70), 115 (32), 99 (33), 97 (95); exact mass, 420.3068 (calcd for $\text{C}_{24}\text{H}_{48}\text{Si}_3$; 420.3063).

MeC_5Li_3 and Bromotrimethylgermane. Following the general procedure previously described, 65 ml of 1.4 M *n*-butyllithium (90 mmol), 4.4 ml (27 mmol) TMEDA, and 1.56 g (20 mmol) of 2,4-hexadiyne were reacted. After 16 h at room temperature, the mixture was cooled to 0 $^\circ\text{C}$, 50 ml of THF was added, and the resultant solution of organolithiums was added dropwise to 19.7 g (100 mmol) of bromotrimethylgermane in 50 ml of THF at 0 $^\circ\text{C}$. This mixture was refluxed for 3 h, and then 50 ml water was added. After washing the organic layer with dilute HCl and drying over MgSO_4 , the solvents were removed to yield 9.2 g of crude products. Kugelrohr distillation resulted in 5.7 g of material, bp 25–120 $^\circ\text{C}$ (200 μm). GC analysis (Column A, 210 $^\circ\text{C}$) indicated that 80% of this material was product **12**, (52% yield).

2,4,6-Tris(trimethylgermyl)-2,3-hexadien-5-yne (12). ^1H NMR (CCl_4) δ 1.73 (s, 3 H), 0.33 (s, 9 H), 0.26 (s, 18 H); ^1H NMR (C_6D_6) δ 1.66 (s, 3 H), 0.43 (s, 9 H), 0.33 (s, 9 H), 0.24 (s, 9 H); IR (CCl_4) 2975, 2910, 2142, 1900, 1415, 1240 cm^{-1} ; UV λ_{max} (cyclohexane) 255 nm (ϵ 14 300), 245 (14 500); mass spectrum m/e (rel intensity) 434 (4), 433 (4), 432 (11); 431 (7), 430 (20), 429 (9.5), 428 (22), 427 (9), 426 (18), 425 (4), 424 (10), 422 (3.5), 300 (14.5), 299 (9), 298 (46), 297 (23), 296 (60), 295 (20), 294 (58), 293 (14.5), 292 (27), 290 (11), 282 (4), 280 (8), 279 (8.5), 180 (7), 179 (6), 178 (6), 143 (5), 141 (4.5), 139 (6), 137 (5), 123 (6), 121 (28), 119 (100), 118 (25), 117 (75), 115 (55), 105 (7), 104 (6.5); exact mass, 432.0009 (calcd for $\text{C}_{15}\text{H}_{30}\text{Ge}_3$; 432.0005).

Derivatization with Dimethyl Sulfate. Using the general procedure described above, 17.8 ml (120 mmol) of TMEDA was added to 225 ml of 1.6 M *n*-butyllithium (360 mmol) and stirred for 30 min. 2,4-Hexadiyne (7.8 g, 100 mmol) in 100 ml of hexane was added dropwise. After the mixture was stirred for 24 h and cooled to 0 $^\circ\text{C}$, 50 ml of THF followed by 45 g (360 mmol) of dimethyl sulfate was added. The reaction mixture was stirred at room temperature overnight and then refluxed for 2 h. Water was added. The organic layer was washed with dilute hydrochloric acid to remove excess amines and then washed with water and dried (MgSO_4). Kugelrohr distillation yielded 1.7 g of product, bp 50–100 $^\circ\text{C}$ (70 μm) and 4.4 g of high boiling residue which was discarded. GLC analysis on column B at 100 $^\circ\text{C}$ showed many peaks. The major peak, retention time 4.75 min, was collected and identified as 2,4-dimethyl-2,3-heptadien-5-yne (**13**).⁶

Derivatization with Diethyl Sulfate. Fifty mmol of MeC_5Li_3 , prepared by addition of 50 mmol of 2,4-hexadiyne to 180 mmol of *n*-BuLi and 170 mmol of TMEDA as described above, was cooled to -78 $^\circ\text{C}$. THF (50 ml) and then diethyl sulfate (25 ml, 190 mmol) in 50 ml of THF was added. The mixture was warmed to room temperature and refluxed overnight. Two hundred ml of 20% KOH in EtOH water (1:1) was added to hydrolyze excess diethyl sulfate, and the mixture was refluxed for 3 h. After washing with water and dilute HCl, drying (MgSO_4), and Kugelrohr distillation, 5.5 g of product, bp 20–120 $^\circ\text{C}$ (0.5 Torr), was isolated. GLC analysis (column B at 130 $^\circ\text{C}$) showed two major tris products, **14** and **15a** (ratio 1:4; 45% total area) and three tetrakis products (55% total area), the major isomer (54%) of which was identified as **16a**. The following retention times and yields were observed: **14**, 2.2 min (6%); **15a**, 2.8 min (24%); **16a**, 4.8 min (17%).

4,4-Diethyl-2,5-octadiyne (14). ^1H NMR (CCl_4) δ 2.20 (q, $J = 8$ Hz, 2 H), 1.83 (s, 3 H), 1.54 (q, $J = 6.5$ Hz, 4 H), 1.15 (t, $J = 8$ Hz, 3 H), 1.05 (t, $J = 6.5$ Hz, 6 H); IR (CCl_4) 2970, 2930, 2880, 2860, 1460, 1380, 1355, 1323; Raman (neat) 2240 cm^{-1} ; UV λ_{max} (cyclohexane) 221 nm (ϵ 7400), 215 sh (6700); mass spectrum m/e (rel intensity) 162 (2), 147 (12), 134 (12), 133 (100), 105 (20), 91 (23), 77 (17), 41 (16); exact mass, 162.1407 (calcd for $\text{C}_{12}\text{H}_{18}$; 162.1408).

2,4-Diethyl-2,3-octadien-5-yne (15a). ^1H NMR (CCl_4) δ 2.30 (q, $J = 7$ Hz, 2 H), 2.04 (m, 4 H), 1.70 (s, 3 H), 1.16 (t, $J = 7$ Hz, 3 H), 1.03 (t, $J = 8$ Hz, 6 H); IR (film) 2970, 2940, 1455, 1379, 1322 cm^{-1} ; UV λ_{max} (cyclohexane) 221 nm (ϵ 7400), 215 sh (6700); mass spec-

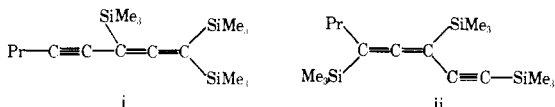
trum m/e (rel intensity) 163 (6), 162 (37), 147 (32), 133 (68), 119 (52), 117 (28), 115 (28), 105 (86), 95 (21), 93 (23), 91 (86), 81 (20), 79 (37), 77 (55), 69 (30), 67 (25), 65 (30), 63 (21), 55 (56), 53 (34), 51 (31), 41 (100), 39 (50); exact mass, 162.1408 (calcd for $C_{12}H_{18}$: 162.1408).

4,6-Diethyl-4,5-hexadien-7-yne (16a). 1H NMR (CCl_4) δ 2.24 (m, 2 H), 1.92 (m, 6 H), 1.36 (m, 2 H), 1.20–0.72 (m, 12 H); IR (neat) 2950, 2920, 2860, 1455, 1445, 1370, 1315, 1060, 900 cm^{-1} ; UV λ_{max} (cyclohexane) 222 nm (ϵ 6000); mass spectrum m/e (rel intensity) 190 (26), 175 (13), 162 (22), 161 (100), 147 (28), 133 (10), 131 (18), 119 (68), 117 (22), 115 (15), 107 (15), 105 (81), 93 (23), 91 (60), 79 (24), 77 (32); exact mass 190.1728 (calcd for $C_{14}H_{22}$: 190.1722).

Acknowledgment. This work was supported by the U.S. Air Force Office of Scientific Research (NC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR 74-2644.

References and Notes

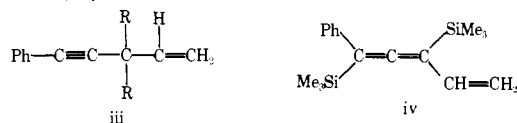
- (1) J. Klein and J. Y. Becker, *J. Chem. Soc., Perkin 2*, 599 (1973).
- (2) Klein and Becker also examined the products from metalation followed by derivatization with trimethylchlorosilane of 2,4-octadiene. The structure assigned to the major product was the allenyne i. The similarity of these



reactions to those of 2,4-hexadiyne prompts us to suggest that this assignment is also in error. The chemical shift of the methylene protons at δ 1.93 indicate they are attached to an allenic carbon atom and not an acetylenic one. We propose that further investigation will show the correct structural assignment to be ii.

- (3) D. H. Ballard, T. Brennan, and H. Gilman, *J. Organomet. Chem.*, **22**, 583 (1970).

- (4) For a review on NMR chemical shift nonequivalence in prochiral groups, see W. B. Jennings, *Chem. Rev.*, **75**, 307 (1975).
- (5) R. West and L. Quass, *J. Organomet. Chem.*, **18**, 55 (1969).
- (6) This compound has been prepared by derivatization of C_5Li_4 with dimethyl sulfate: T. L. Chwang and R. West, *J. Am. Chem. Soc.*, **95**, 3324 (1973).
- (7) The reported chemical shifts for compound **13** are all downfield by 0.35 ppm. This discrepancy can perhaps be explained by external Me_4Si being used in ref 6.
- (8) This is similar to the UV spectrum of 2-methyl-2,3-heptadien-5-yne (λ_{max} 220 nm in hexane); L. Skattebøl, *Tetrahedron Lett.*, 2175 (1965).
- (9) Similarly, J. Klein, S. Brenner, and A. Medlik, *Isr. J. Chem.*, **9**, 177 (1971), have shown that the dilithiated derivative of 5-phenyl-1-penten-4-yne reacts with alkyl halides to give exclusive formation of the unconjugated anyne iii while reaction with trimethylchlorosilane resulted in conjugated allenes as the major products, i.e., iv:



- (10) R. West and P. C. Jones, *J. Am. Chem. Soc.*, **87**, 3788 (1965).
- (11) T. L. Chwang and R. West, *J. Am. Chem. Soc.*, **95**, 3224 (1973).
- (12) J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, **32**, 1674 (1967).
- (13) J. Klein and A. Medlik, *J. Chem. Soc., Chem. Commun.*, 275 (1973).
- (14) R. B. Bates, W. A. Beavers, M. G. Green, and J. H. Klein, *J. Am. Chem. Soc.*, **96**, 5640 (1974).
- (15) J. Klein and S. Brenner, *J. Am. Chem. Soc.*, **91**, 3094 (1969).
- (16) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π Electron Calculations", W. H. Freeman, San Francisco, Calif., 1965.
- (17) R. Zerger, W. Rhine, and G. Stucky, *J. Am. Chem. Soc.*, **96**, 6048 (1974).
- (18) T. F. Schaaf, W. Butler, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, **96**, 7593 (1974).
- (19) T. L. Chwang, Ph.D. Thesis, University of Wisconsin, 1971.
- (20) W. Priester and R. West, *Inorg. Synth.*, in press.
- (21) R. N. Lewis, *J. Am. Chem. Soc.*, **69**, 717 (1947).
- (22) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. 1, 3d ed, Methuen, London, 1967, p. 31.

Photochemistry of Organochalcogen Compounds. 3. Photochemistry of Bis(benzoylmethyl)tellurium Dichloride

D. G. Marsh,* J. Y. C. Chu, J. W. Lewicki, and J. L. Weaver

Contribution from the Xerox Corporation, Webster Research Center,
Webster, New York 14580. Received May 31, 1975

Abstract: The photochemical β -cleavage and Norrish type II reactions for bis(benzoylmethyl)tellurium dichloride (**1**) have been investigated. No room temperature emission is observed for **1**, but at 77 K in methyltetrahydrofuran glass, phosphorescence is detected with quantum yield $\phi_p = 0.18$ and lifetime $\tau_p = 24$ ms. The spectroscopic triplet state is assigned as originating principally from a $^3\pi, \pi^*$ state with appreciable $^3n, \pi^*$ character. Photolyses of **1** with 313 nm light in degassed fluid solutions at 298 K result in the formation of acetophenone, chloroacetophenone, and tellurium metal as the principal photoproducts. In H atom donating solvents, the quantum yield of acetophenone produced may exceed 2, while chloroacetophenone is formed only in trace amounts. In inert solvents, chloroacetophenone and tellurium are formed in major amounts with lesser amounts of acetophenone and trace amounts of dibenzoylthane also produced. The formation of acetophenone and chloroacetophenone *cannot* be quenched with normal triplet quenchers but the triplet state of **1** can be sensitized with xanthene-9-one. These results suggest that β -cleavage and Norrish type II processes may occur from a very short-lived $^3\pi, \pi^*$ state probably identical with the spectroscopically observed triplet state.

Introduction

The photodecomposition of organic selenium and tellurium compounds has been known for over a century,^{1,2} and quite often these photoreactions are accompanied by formation of elemental selenium and tellurium. Not all organochalcogen compounds are unstable, for example, the carbon-tellurium bond in diaryl tellurium dihalides is generally quite stable.³ In spite of the interesting differences in photochemical behavior of organochalcogen compounds, the literature contains scant

molecular structure-property relationships, and no detailed photochemical studies have been reported until quite recently. Chu, Marsh, and Günther⁴ have reported details of the photochemistry of benzyl diselenide in which photolytic C-Se bond scissions and subsequent free-radical processes are responsible for the formation of elemental selenium and other observed photoproducts.

A recent patent⁵ has disclosed the photo- and thermal decomposition of bis(benzoylmethyl)tellurium dichloride (**1**), and some preliminary results of the photochemistry have been