

Butyllithium-induced dimerization of pent-3-en-1-yne and related additions

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Abstract

The enynes $\text{HC}\equiv\text{CCH}=\text{CHCH}_2\text{R}$ ($\text{R} = \text{H, Me, OMe, NMe}_2, \text{SMe}$), are converted into dimers by treatment with slightly more than two equivalents of butyllithium. The Z-configuration predominates in the dimers obtained after aqueous work-up. The lithiated enynes ($\text{R} = \text{H, Me, SMe}$) and acetylenic compounds $\text{LiC}\equiv\text{CCH}_2\text{R}$ ($\text{R} = \text{SMe, C}_6\text{H}_5$) add in an analogous way to the double bond of $\text{LiC}\equiv\text{CCH}=\text{CH}_2$.

Introduction

Since Ziegler showed that organolithium compounds add to olefins [1–3] this reaction has been extensively used for the initiation and propagation steps of the anionic polymerization of alkenes [4–8]. Additions to strained cyclic compounds [4,9–12] and intramolecular additions [4,12–16] are the most common and also the most useful applications in organic synthesis, whereas addition of lithium compounds to alkenes and to conjugated dienes and styrenes often cannot be disentangled from propagation, especially if the adducts are not stabilized by internal coordination or conjugation [4,17–28]. When pentadiene in tetrahydrofuran (THF) is metalated with butyllithium and subsequently treated with furan, (cyclic) dimers of pentadiene as well as higher oligomers are formed [17]. Miginiac, Mauzé and their co-workers [29–33] have extensively studied the addition of a number of organometallic compounds to conjugated enynes. In the case of enynes with a terminal triple bond, which were treated with an excess of BuLi or a number of allylic lithium compounds, they obtained the 4,3-adducts in yields of up to 50%. A few years ago we reported [34] the first results of the butyllithium-induced dimerization of pent-3-en-1-yne and some derivatives, a new type of regio- and stereospecific addition of dilithio-enynes to the double carbon-carbon bond of a lithiated con-

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jugated enyne system. This paper deals with detailed results of this study as well as with new examples and applications.

Results and discussion

a. Dimerization of $HC\equiv CCH=CHCH_2R$ ($R = H, Me, OMe, SMe, NMe_2$)

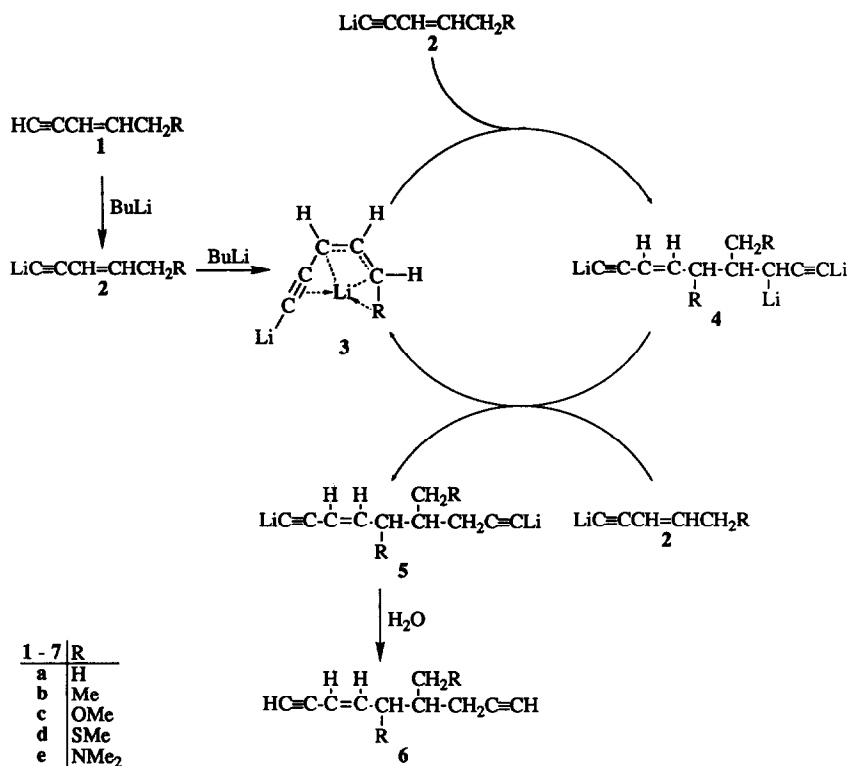
Treatment of pent-3-en-1-yne with two equivalents and a slight excess (5–10%) of BuLi at 0 °C in THF for 2 h afforded, after aqueous work-up, the dimer **6a** in ca. 70% yield [34]. These results and those obtained with hex-3-en-1-yne (**1b**) and the hetero-substituted derivatives **1c–e** are listed in Table 1. We assume that the dimerization reaction is initiated by the formation of small amounts of dilithiated enyne **3** (see Scheme 1). This species subsequently adds to the mono-lithiated enyne **2**, to give the tri-lithio adduct **4**, which in its turn undergoes a lithium/proton-exchange with **2**, giving **5** and **3**, respectively. The latter derivative prefers to add to **2**, which is less sterically hindered than the adduct **5**. This is consistent with the results of Miginiac et al. [33], who reported that the yield of the addition of butyllithium or allyllithium to branched enynes ($LiC\equiv CC(R^1)=C(R^2)(R^3)$) decreases with increasing steric hindrance.

Table 1

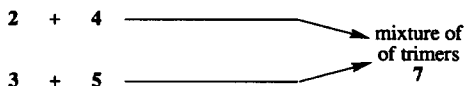
Dimerization of enynes **1a–e**

Enyne ^b	Reaction conditions ^a				Results (product ratio)				
	Equivalents of BuLi	Temp (°C)	Time (h)	Additive ^c	Yield (%)	Z/E ^d	Dimer 6	Trimer 7	Oligomers ^e
1a	1.00	0	1		0				
	1.03	0	1		10	90/10	95	5	
	1.09	0	1		86	95/5	86	14	
	2.00	0	1		86	80/20	72	14	14
	1.09	0	1.5	HMPT	87	85/15	82	18	
	1.09	0	1	HMPT	81	88/12	89	11	
	1.09	0	0.5	HMPT	83	89/11	91	9	
1b	1.09	0	2.25		15	92/8	47	3	50
	1.09	20	5.0	^t BuOK	18	90/10	75	25	
	1.09	0	2.0	TMEDA	0				
	1.09	0	3.5	HMPT	40	80/20	100		
	1.09+0.09 ^f	0	2.0+2.0 ^f	HMPT	80	83/17	99	1	
1c	1.09	0	0.75		70	95/5	30	25	45
	1.25	0	0.5		92	95/5	40	30	30
	1.25	0	0.25	HMPT	93	95/5	42	24	34
	1.25	0	1.0	HMPT	94	95/5	55	24	21
1d	1.25	0	4.5	HMPT	31	100/0	100		
1e	1.10	0	2.0		66	100/0	100		

^a Solvent hexane/THF (1/1 v/v). ^b Z/E ratios of starting enynes: **1a** and **1b** 40/60, **1c–e** 0/100. ^c If mentioned: 8 g of HMPT (hexamethylphosphoric triamide) per 0.05 mol of enyne **1a**, **b** or **d**, and 2 g HMPT per 0.05 mol of **1c** was added to the reaction mixture at –20 °C; 2 g ^tBuOK per 0.05 mol of enyne **1b** was added at –90 °C. ^d Z/E ratio of the dimer. ^e Remained as viscous residue after distillation. ^f After addition of 1.09 equiv. of BuLi and stirring for 2 h, 0.09 equiv. of BuLi was added and stirring was continued for an additional 2 h.



Side reactions:



Scheme 1

The rate of the dimerization decreases in the order $\text{R} = \text{OMe} \gg \text{H} > \text{NMe}_2 > \text{Me} > \text{SMe}$. In the cases of $\text{R} = \text{H}$ and OMe the dimerization reaction could not be disentangled from trimerization, and significant amounts (10–25%) of the trimers 7a and 7c, respectively, were formed. This is due to the relatively high reaction rates in these cases. In the cases of $\text{R} = \text{Me}$, OMe and SMe , the reaction times could be shortened if hexamethylphosphoric triamide (2–8 g per 0.05 mol of enyne) was added to the reaction mixture. The dimerizations were completely regiospecific with respect to the sites of attachment of the two enyne units. Dimers in which the allylic (or “skipped”) enyne was present could not be detected.

Starting with mixtures of *E*- and *Z*-isomers of 1 or even with pure *E*-1, the *Z*-configuration of the dimers 6 predominated in all cases. This stereospecificity may be explained by assuming that both *Z*- and *E*-1 are converted into 3 with the stereostructure depicted in Scheme 1, in which the represented internal coordination with R is only possible if it is a heterosubstituent. Starting from allylacetylene ($\text{HC}\equiv\text{CCH}_2\text{CH}=\text{CH}_2$), and following the procedure used for the dimerization of 1a, similar yields of 6a were obtained. This is the result of lithiation of

$\text{LiC}\equiv\text{CCH}_2\text{CH}=\text{CH}_2$ to give the dilithio derivative **3a** and a subsequent addition of **3a** to **2a**.

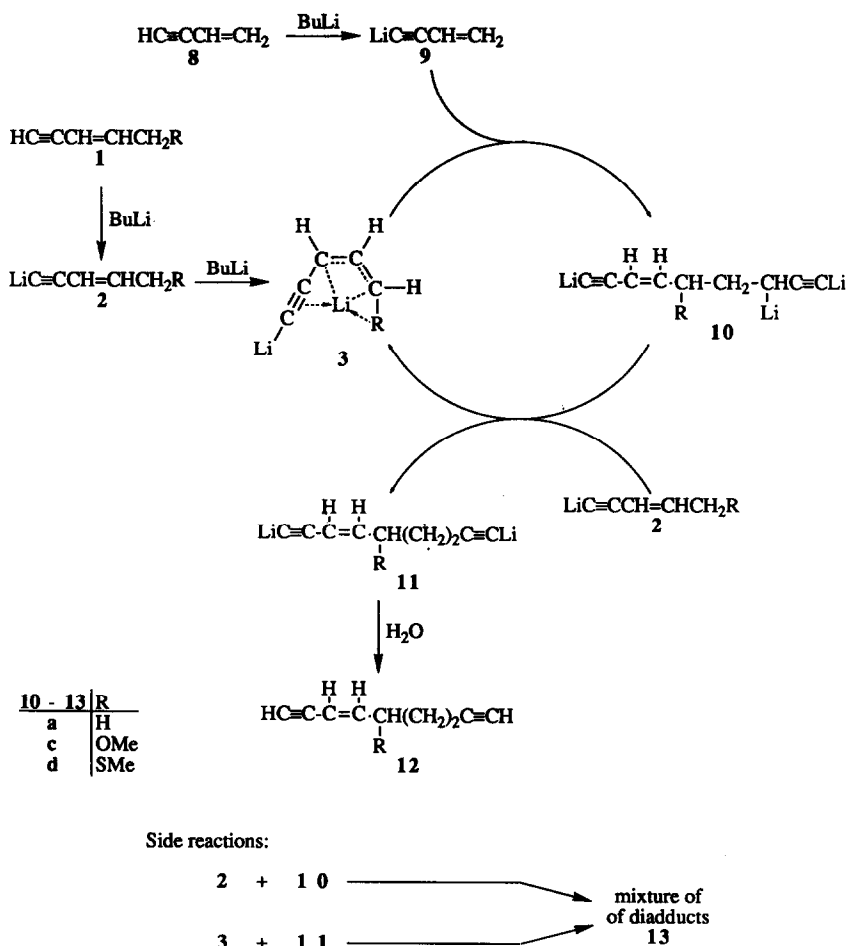
The preference for the *Z*-configuration in the intermediate **3a** was shown by treatment of allylacetylene with two equivalents of BuLi and subsequent protonation. The relatively high kinetic acidity of the "skipped" CH_2 group of allylacetylene allows rapid and complete formation of **3a**, which prevents further dimerization. The intermediate **3a** was trapped by quenching with water. In the ^1H NMR spectrum of the organic layer (the volatility of the products did not allow their separation from the solvents) the signals belonging to *Z*- $\text{HC}\equiv\text{CCH}=\text{CHCH}_3$, $\text{HC}\equiv\text{CCH}_2\text{CH}=\text{CH}_2$, and *E*- $\text{HC}\equiv\text{CCH}=\text{CHCH}_3$ could be observed at 3.10, 2.85–3.00, and 2.70 ppm, respectively, with an integral ratio of 50/42/8. Thus, the *Z/E* ratio of the quench product was 86/14, which is comparable with the *Z/E* ratio of the dimers **6a**. The stereochemical course of the dimetalation of the enynes **1** resembles that of the metalation of (heterosubstituted) allyl or 1-alkenyl compounds leading to the thermodynamically more stable *Z*-allylic anion [35–41], the $\text{LiC}\equiv\text{C}$ moiety being comparable with a coordinating heterosubstituent. The dimetalation of **1a** was achieved by using the basic mixture BuLi · $^t\text{BuOK}$ in THF at -70°C . Reaction with one equivalent of oxirane afforded a mixture *Z*-, *E*- $\text{HC}\equiv\text{CCH}=\text{CH}(\text{CH}_2)_3\text{OH}$, *Z*-, and *E*- $\text{HC}\equiv\text{CC}(\text{CH}_2\text{CH}_2\text{OH})=\text{CHCH}_3$ with a ratio of ca. 5/1/1/1, indicating that *Z*- $\text{KC}\equiv\text{CCH}=\text{CHCH}_2\text{K}$ predominated in the reaction mixture. The latter two products are the result of functionalization at the allylic position, and subsequent base-catalyzed isomerization to the thermodynamically more stable conjugated isomers. However, care should be taken in drawing conclusions from these dimetalation–functionalization experiments. Dilithiation of allylacetylene with BuLi in THF and subsequent silylation with trimethylchlorosilane afforded $\text{Me}_3\text{SiC}\equiv\text{CCH}=\text{CHCH}_2\text{SiMe}_3$ in 60% yield with a *Z/E* ratio of 54/46. Dimetalations of the enynes **1b–e** with BuLi/ $^t\text{BuOK}$ in THF at -70°C gave after aqueous work-up mixtures of a number of isomers, among which *Z*-, *E*-**1b–e** in about equimolar ratios (see Experimental section). These results are not in keeping with the regio- and stereospecific dimerizations of these enynes. This stereospecificity can be explained by assuming that in the addition-reaction the *Z*-isomer reacts faster than the *E*-isomer (compare [38]).

Table 2

Additions of enynes to vinylacetylene

Enyne	Equivalents ^a of BuLi	Time ^a (h)	<i>Z/E</i> ^b	Yield (%)			
				adduct 12	diadducts 13	dimer 6	oligomers ^c
Allylacetylene	2.4	1.5	82/18	43	13	17	27
1c	2.4	0.75	95/5	10	25	25	40
1d	2.4	2.0	100/0	63 ^d	14	10	13
1d	2.2	4.0	100/0	25	11	8	10
1e	2.4	4.0				60	40

^a Reaction conditions were: 0.05 molar scale; after BuLi was added at -100°C stirring at 0°C ; hexane/THF (1/1 v/v) as solvent, and HMPT (10 g per 0.05 mol of enyne) as co-solvent (except in the case of **1e**). ^b *Z/E* ratio of the adduct. ^c Remained as viscous residue after distillation. ^d The isomer $\text{H}_2\text{C}=\text{C}=\text{CHCH}=\text{C}(\text{SMe})\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ was for 6% present in the product.



Scheme 2

b. Additions of enynes to vinylacetylene

In Table 2 are listed the results of the experiments in which 1:1 mixtures of allylacetylene or 1c-e and vinylacetylene were treated with a slight excess of butyllithium in the presence of a small amount of HMPT. In the case of allylacetylene or 1d moderate yields of the desired adduct (12a, d, respectively) were obtained after aqueous work-up. Dimers (6a, d) and diadducts (13a, d, see Scheme 2) were formed in low yields in these cases. Reaction without HMPT or in the presence of TMEDA led in the case of the thioether to much lower yields (10–20%) and to the formation of larger amounts of oligomeric material. In the case of 1-methoxy-2-penten-4-yne (1c) and vinylacetylene dimerization, oligomerization, and formation of the diadduct were the main processes. In the case of *N,N*-dimethyl-2-penten-4-yne (1e) no addition to vinylacetylene was observed, and the dimer 6e was obtained in 60% yield.

c. Addition of propargylic compounds to vinylacetylene and 3-hexen-1-yne

Table 3

Addition of propargylic compounds to vinylacetylene (**8**) and 3-hexen-1-yne (**1b**)

Propargylic compound	Enyne	Ratio 14 /enyne	Equivalents ^a of BuLi	Time ^a (h)	Yield (%)		
					adduct 19	diadduct 21 ^b	oligomer ^c
14a	8	1/1	2.2	4.0	58 ^d	17	25
14a	8	1/1.6	3.0	4.0	37	20	40
14b	8	1/1	2.4	4.0			34
14b	8	1/1	2.9 ^e	5.0	6	4 ^f	40
14c	8	1/1	2.2	1.0			44
14d	8	1/1	2.2	2.75	23	23	15
14d	8	2/1	3.3	1.5	32	27	10
14d	8	1/2	3.3	3.0	13	52	21
14e	8	1/1	2.2	1.5	10		50
14a	1b	1/1	2.4	4.0	55 ^d (19f)		

^a Reaction conditions were: 1 equiv. = 0.05 mol; after BuLi was added at -100°C stirring at 0°C ; hexane/THF (1/1 v/v) as solvent, and HMPT (10 g per 0.05 mol of enyne) as co-solvent (except in the case of **14e**). ^b Yield based on **14a**–**e**, this yield is twice as high as when compared to vinylacetylene. ^c Yield based on amount of adduct which theoretically could be formed. Thus the yields compared to vinylacetylene were much higher. Remained as viscous residue after distillation. ^d The product was contaminated for 5% with the isomer $\text{H}_2\text{C}=\text{C}(\text{Ph})\text{CH}(\text{R}'')\text{CH}_2\text{C}\equiv\text{CH}$. ^e In this case hexyne was dilithiated (with BuLi·TMEDA in hexane and reflux for 2 h) prior to the reaction in THF with lithiated vinylacetylene (with 0.9 equivalent of BuLi). ^f Two isomers; in this case also **17b** has added to **9**.

reaction of 1-hexyne with vinylacetylene (**8**) the oligomerization of **8** was the predominating process, probably due to the relatively slow propargylic lithiation of **15b**, which gave rise to addition of the excess of BuLi to **8**, followed by oligomerization. This explanation seems reasonable, since benzylacetylene can be readily dilithiated with BuLi in ether at -50°C [42] whereas the dilithiation of hexyne in the same solvent requires heating under reflux for 2 h [49]. In keeping with this assumption, the smooth dilithiation of methyl propargyl thioether (**14b**) [51] in the presence of lithiated vinylacetylene gave reasonable yields of the adduct (**19c**). Large amounts of the diadduct **21c** were also obtained, due to abstraction of the propargylic proton of the adduct **18c** and subsequent addition to **9**.

Attempts to prepare adducts from methyl propargyl ether ($\text{HC}\equiv\text{CCH}_2\text{OMe}$), the propargylic amine $\text{HC}\equiv\text{CCH}_2\text{NMe}_2$, and vinylacetylene by a similar procedure gave low yields or failed completely, the main or exclusive products being oligomers of vinylacetylene. These results are similar to that obtained for the reaction of 1-hexyne with vinylacetylene mentioned above, and also in these cases the abstraction by butyllithium of a propargylic proton of the lithiated acetylenic compounds **15c** and **15e** is too slow [53].

The combination of the sluggish dimerization of 3-hexen-1-yne (**1b**) and the smooth dilithiation of benzylacetylene (**14a**) permitted successful addition of **14a** to **1b**. The adduct **19f** was isolated in 55% yield.

Experimental section

a. General remarks

^1H NMR (90 MHz) spectra were recorded on a Varian EM390 apparatus, with CCl_4 as solvent and tetramethylsilane (δ 0.00 ppm) as internal standard, and ^{13}C

NMR (20 MHz) spectra on a Varian CFT20 apparatus with CDCl_3 as solvent and internal standard (δ 77.0 ppm), unless indicated otherwise. Mass spectra were obtained with a linked Kratos MS80 GLC-MS system. THF was distilled from LiAlH_4 and stored over sodium-lead alloy under nitrogen. Butyllithium (ca. 1.6 M hexane solution; the determination of the concentration is described below) and potassium tert-butoxide were purchased and used as supplied. The starting compounds (enynes and propargylic compounds) were prepared as described previously [54]. All reactions were carried under nitrogen in a 500 mL three-necked, round-bottomed flask equipped with a mechanical stirrer, gas inlet, outlet, and thermometer.

b. Dimerizations of 1a-e (typical procedure, see also Table 1)

A mixture of 0.050 mol of enyne **1a-b** and 60 mL of THF was cooled to -70°C and a solution of BuLi in hexane (ca. 1.6 M, amounts are listed in Table 1) was added dropwise during ca. 2 min. During the addition the mixture was efficiently stirred and the temperature kept between -70 and -50°C ; the temperature was subsequently raised during 5 min to 0°C . When HMPT was used as co-solvent (see Table 1) the mixture was subsequently cooled to -40°C , after which 2 or 8 g of HMPT were added. After this addition the flask was immersed in an ice-bath for the period given in Table 1, then the reaction mixture was poured into a precooled (0°C) saturated aqueous solution of ammonium chloride or in the case of **6e** into a potassium carbonate solution with efficient swirling. The aqueous layer was extracted with ether. When HMPT had been used, the combined organic solutions were washed with dilute aqueous hydrochloric acid (pH 1). After drying over magnesium sulfate, or in the case of **6e** over potassium carbonate, the solvents were removed *in vacuo*. The residue was subjected to GLC followed by fractional distillation.

6a ($\text{R} = \text{H}$), b.p. $60-64^\circ\text{C}$ (12 mmHg), n_{D}^{20} 1.4765 ($Z/E = 90/10$). **7a**, b.p. $80-90^\circ\text{C}$ (0.15 mmHg), n_{D}^{20} 1.4882 ($Z/E = 88/12$), mixture of trimers; mass spectrum m/e (% of base peak) (main isomer) no M^+ , 197 ($M^+ - \text{H} \cdot$, 0.2), 183 (1), 168 (4), 155 (20), 141 (32), 129 (41), 117 (97), 105 (32), 91 (100), 77 (57), 65 (48), 53 (15), 39 (27).

6b ($\text{R} = \text{Me}$), b.p. $83-84^\circ\text{C}$ (12 mmHg), n_{D}^{20} 1.4802 ($Z/E = 83/17$). **7b**, mixture of trimers; mass spectrum m/e (% of base peak) (main isomer) no M^+ , 239 ($M^+ - \text{H} \cdot$, 0.6), 225 (3), 211 (27), 183 (22), 169 (65), 155 (90), 141 (100), 129 (80), 115 (58), 105 (42), 91 (70), 77 (72), 65 (22), 55 (50), 41 (40).

6c ($\text{R} = \text{OMe}$), b.p. 85°C (0.15 mmHg), n_{D}^{20} 1.4787 ($Z/E = 95/5$). **7c**, b.p. $110-130^\circ\text{C}$ (0.15 mmHg), n_{D}^{20} 1.4950 ($Z/E = 100/0$), mixture of trimers; mass spectrum m/e (% of base peak) (main isomer) no M^+ , 229 ($M^+ - [\text{H} \cdot + \text{MeOCH}_2\text{CH} \cdot]$, 6), 217 (10), 191 (6), 178 (9), 165 (12), 153 (10), 141 (10), 129 (12), 115 (15), 95 (100), 77 (8), 65 (8), 45 (23).

6d ($\text{R} = \text{SMe}$), b.p. 120°C (0.1 mmHg), n_{D}^{20} 1.5561 ($Z/E = 100/0$), 31% yield. **1d** was recovered in 45% yield, n_{D}^{20} 1.5310 ($Z/E = 55/45$).

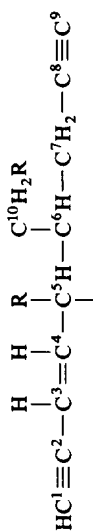
6e ($\text{R} = \text{NMe}_2$), b.p. 97°C (0.15 mmHg), n_{D}^{20} 1.4944 ($Z/E = 100/0$), 66% yield. Spectroscopic data of the dimers **6a-e** are listed in Table 4.

c. Additions of enynes to vinylacetylene (typical procedure, see also table 2)

A mixture of 0.050 mol of allylacetylene (or **1c-e**), 0.050 mol of vinylacetylene, and 60 mL of THF was cooled to -70°C , after which a solution of 0.120 mol of

Table 4

Spectroscopic data for the dimers 6a-e:



Dimer (R)	¹ H NMR δ (ppm)	¹³ C NMR (Z-isomer) δ (ppm)	Mass spectrum (Z-isomer) m/e (% of base peak)
1a (H)	5.80-6.10 (H ⁴ , m), 5.35-5.55 (H ³ , m), 2.97 (Z-H ¹ , d, 2.3 Hz), 2.67 (E-H ¹ , d, 2.3 Hz), 2.20-2.45 (2H ⁵ , m), 2.00-2.18 (2H ⁷ , m), 1.84 (H ⁹ , t, 3 Hz), 1.65-1.90 (H ⁶ , m), 0.99 (3H ¹⁰ , d, 6.5 Hz)	143.0 (C ⁴), 109.5 (C ³), 82.5 (C ⁸), 81.6 (C ¹), 80.0 (C ²), 69.4 (C ⁹), 36.1 (C ⁵), 32.4 (C ⁶), 25.1 (C ⁷), 18.8 (C ¹⁰)	132 (M ⁺ , 3), 131 (20), 117 (100), 103 (14), 91 (96), 77 (46), 65 (40), 51 (10), 41 (21), 39 (26)
1b (Me)	5.70-5.94 (H ⁴ , m), 5.30-5.46 (H ³ , m), 2.95 (Z-H ¹ , d, 3 Hz), 2.77-3.13 (H ⁵ , m), 2.66 (E-H ¹ , d, 3 Hz), 2.18 (2H ⁷ , m), 1.80 (H ⁹ , t, 2.5 Hz), 1.22-1.60 (2H ¹⁰ , H ⁶ , m), 0.98 (Me ⁵ , d, 7 Hz), 0.90 (Me ¹⁰ , t, 6 Hz)	149.6 (C ⁴), 107.6 (C ³), 82.7 (C ⁸), 81.2 (C ¹), 80.2 (C ²), 69.1 (C ⁹), 43.8 (C ⁶), 36.9 (C ⁵), 23.3 (C ¹⁰), 19.4 (C ⁷), 17.0 (Me ⁵), 11.3 (Me ¹⁰)	160 (M ⁺ , 0.5), 159 (3), 145 (20), 131 (85), 117 (47), 105 (33), 91 (57), 79 (95), 77 (100), 65 (20), 53 (26), 41 (15), 39 (17)
1c (OMe)	5.30-6.00 (2H ^{3,4} , m), 4.10-4.35 (H ⁵ , m), 3.30-3.50 (H ¹⁰ , 2d, 5.3 Hz), 3.28 (OMe ⁵ , s), 3.24 (OMe ¹⁰ , s), 3.03 (Z-H ¹ , d, 1.5 Hz), 2.14-2.40 (H ⁷ , m), 1.85-2.05 (H ⁶ , m), 1.77 (H ⁹ , t, 2.5 Hz)	143.0/143.2 (C ⁴), 112.2/112.0 (C ³), 83.0/82.8 (C ¹), 82.3/82.2 (C ⁸), 79.0 (C ²), 77.7/77.4 (C ⁹), 69.2/69.1 (C ⁵), 58.3 (OMe ⁵), 56.4 (OMe ¹⁰), 42.7/42.4 (C ⁶), 16.7/16.3 (C ⁷), ratio diastereomers 60/40	192 (M ⁺ , 0.5), 191 (3), 177 (10), 161 (16), 159 (21), 147 (14), 121 (15), 95 (100), 77 (5), 65 (6), 45 (19), 41 (9), 39 (7)
1d SMe	5.73-5.96 (H ⁴ , m), 5.50-5.63 (H ³ , m), 3.92-4.12 (H ⁵ , m), 3.05 (Z-H ¹ , d, 3 Hz), 2.35-2.80 (4H ^{7,10} , m), 2.07 (SMe ⁵ , s), 2.04 (SMe ¹⁰ , s), 1.90 (H ⁹ , t, 1.5 Hz), 1.65-2.20 (H ⁶ , m)	141.9 (C ⁴), 108.9 (C ³), 82.4 (C ¹), 80.9 (C ²), 79.2 (C ⁸), 70.1 (C ⁹), 47.9 (C ⁶), 40.4 (C ⁵), 35.1 (C ¹⁰), 19.4 (C ⁷), 15.5 (SMe ⁵), 13.7 (SMe ¹⁰)	no 224 (M ⁺), 209 (M ⁺ - Me ⁵ , 25), 185 (8), 177 (10), 161 (13), 137 (12), 128 (40), 123 (21), 115 (30), 111 (22), 91 (23), 77 (20), 65 (34), 61 (100), 45 (10), 39 (10), 32 (10)
1e (NMe ₂)	5.62-6.00 (2H ^{3,4} , m), 3.40-3.60 (H ⁵ , m), 3.02 (Z-H ¹ , d, 1.5 Hz), 2.30-2.65 (4H ^{7,10} , m), 2.21 (4Me ^{5,10} , s), 1.90-2.15 (H ⁶ , m), 1.86 (H ⁹ , t, 2.5 Hz)	141 (C ⁴), 112.1 (C ³), 82.5 (C ⁸), 79.9 (C ²), 77.1 (C ¹), 69.3 (C ⁹), 64.3 (C ⁵), 59.4 (C ¹⁰), 45.7 (2NMe ⁵), 41.2 (2NMe ¹⁰), 37.0 (C ⁶), 17.6 (C ⁷)	220 ([M + 2H] ⁺ , 0.5) 219 (M ⁺ + H ⁺ , 0.5) 218 (M ⁺ , 0.2), 174 (40), 160 (20), 134 (30), 108 (40), 94 (12), 58 (100)

BuLi in 75 mL of hexane (or 0.110 mol in 69 mL) was added during 2 min. During the addition the mixture was efficiently stirred and the temperature kept between -70 and -50°C . After the addition the temperature was allowed to rise to 0°C , 10 g of HMPT was added at -60°C (except in the attempt to add **1e** to vinylacetylene, in which case stirring at 0°C was performed after the addition of BuLi). The flask was immersed in an ice-bath for the period given in Table 2. Work-up was carried out as described in section b. The crude product was subjected to GLC, and subsequently distilled (for the yields see Table 2).

12a ($\text{R} = \text{H}$), b.p. $60\text{--}70^{\circ}\text{C}$ (12 mmHg), n_{D}^{20} 1.4661 ($Z/E = 82/18$); mass spectrum m/e (% of base peak) (Z -isomer) 118 (M^{+} , 10), 117 (100), 115 (40), 103 (20), 91 (35), 78 (66), 65 (20), 51 (16), 39 (20); ^1H NMR (60 MHz) δ 5.20–6.30 (2H, $\text{CH}=\text{CH}$, m), 2.90 ($Z\text{-HC}\equiv\text{CC=}$, d, 1.2 Hz), 2.65 ($E\text{-HC}\equiv\text{CC=}$, d, 1.2 Hz), 1.4–2.5 (7H, $\text{HC}\equiv\text{C}(\text{CH}_2)_3$, m); the distilled product contained 24% of dimer **6a**, and 15% of diadducts **13a**, mass spectrum m/e (% of base peak) (main isomer) 170 (M^{+} , 1), 169 (2), 167 (2), 154 (18), 141 (30), 131 (52), 115 (60), 103 (22), 91 (100), 77 (64), 65 (41), 53 (25), 51 (25), 39 (38).

12c ($\text{R} = \text{OMe}$), b.p. $40\text{--}50^{\circ}\text{C}$ (0.1 mmHg), mass spectrum m/e (% of base peak) (Z -isomer) 148 (M^{+} , 2), 147 (7), 133 (6), 115 (23), 95 (100), 77 (7), 65 (12), 51 (7), 41 (11), 39 (11); the distilled product was contaminated with 40% of dimer **6c** and 40% of diadducts **13c**, mass spectrum m/e (% of base peak) (main isomer) no M^{+} , 199 ($[\text{M} - \text{H}]^{+}$, 4), 185 (6), 161 (6), 153 (5), 141 (15), 129 (13), 115 (10), 95 (100), 77 (8), 65 (12), 51 (5), 41 (8), 39 (7).

12d ($\text{R} = \text{SMe}$), b.p. $45\text{--}47^{\circ}\text{C}$ (0.1 mmHg), n_{D}^{20} 1.5287, mass spectrum m/e (% of base peak) (Z -isomer) 164 (M^{+} , 5), 149 (15), 134 (5), 125 (8), 115 (100), 91 (25), 77 (10), 65 (22), 51 (7), 39 (11), 32 (3), 28 (8); ^1H NMR (200 MHz, CDCl_3 as solvent and internal standard δ 7.26 ppm) δ 5.72 ($\text{C}=\text{CHC}\equiv\text{C}$, ddd, 2×10.6 Hz, 0.8 Hz), 5.54 ($\text{CH}=\text{CC}\equiv\text{C}$, dd, 10.6 Hz, 2.3 Hz), 3.82–3.95 (CHS , m), 3.07 ($\text{HC}\equiv\text{CC}=\text{C}$, dd, 2.3 Hz, 0.8 Hz), 2.17–2.32 ($\text{CH}_2\text{C}\equiv\text{C}$, m), 2.02 (SMe , s), 1.94 ($\text{HC}\equiv\text{CCCH}_2$, 2.6 Hz), 1.61–1.92 (CH_2CH , m); ^{13}C NMR (50 MHz) δ 144.1 ($\text{C}=\text{CC}\equiv\text{C}$), 109.0 ($\text{C}=\text{CC}\equiv\text{C}$), 83.2 ($\text{CH}_2\text{C}\equiv\text{CH}$), 82.3 ($\text{HC}\equiv\text{CC}=\text{C}$), 79.6 ($\text{HC}\equiv\text{CC}=\text{C}$), 68.9 ($\text{HC}\equiv\text{CCCH}_2$), 44.7 (CHS), 32.7 ($\text{CH}_2\text{C}\equiv\text{CH}$), 16.4 (CH_2CH), 13.9 (SCH_3). The product contained 6% of the isomer $\text{H}_2\text{C}=\text{C}=\text{CHCH}=\text{C}(\text{SMe})\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$: ^1NMR δ (characteristic signals) 5.40–5.50 ($\text{CH}=\text{CS}$, m), 5.12 ($\text{C}=\text{C}=\text{CH}$, dd, 2×7 Hz), 4.88–4.93 ($\text{H}_2\text{C}=\text{C}=\text{C}$, m). **13d**, b.p. $70\text{--}90^{\circ}\text{C}$ (0.1 mmHg), n_{D}^{20} 1.5410, mass spectrum m/e (% of base peak) (main isomer) no M^{+} , 201 ($M^{+} - \text{Me}^{\cdot}$, 2), 173 (3), 167 (7), 165 (7), 152 (15), 141 (28), 128 (40), 123 (100), 115 (45), 91 (55), 77 (30), 65 (50), 51 (13), 45 (12), 39 (24), 32 (12), 28 (27); contained ca. 50% dimer **6d**.

d. Addition of propargylic compounds (14a–e) to vinylacetylene (8) and 3-hexen-1-yne (1b) (see also table 3)

The procedure described in section c was followed; the amounts of reagents (1 equivalent = 0.050 mol) and reaction times are listed in Table 3.

In the case of the reaction of **8** with 1-hexyne (**14b**) after treatment with 2.9 equiv. of BuLi, **14b** was dilithiated by heating under reflux a mixture of 0.050 mol of **14b**, 25 g of TMEDA, and 0.150 mol of BuLi in 130 mL of hexane for 2 h. THF (30 mL) was then added through the condenser and stirring was continued for an additional 15 min at 30°C ; under these conditions the excess of BuLi reacts with THF to give ethene and $\text{LiOCH}=\text{CH}_2$. In another flask a solution of 0.050 mol of

vinylacetylene in 50 mL of THF was cooled to -80°C , after which a solution of 0.045 mol of BuLi in 30 mL of hexane was added during 2 min, with the temperature kept below -70°C . The mixture was cautiously poured into the mixture containing **16b** at -80°C , after which 10 g of HMPT was added. The flask was immersed in an ice-bath. The subsequent procedure was as described in section c.

19a ($\text{R}' = \text{Ph}$, $\text{R}'' = \text{H}$), b.p. 80°C (0.15 mmHg), n_{D}^{20} 1.5322; mass spectrum m/e (% of base peak) 168 (M^{+} , 10), 167 (68), 141 (4), 153 (28), 128 (76), 115 (100), 102 (3), 89 (10), 77 (3), 63 (7), 51 (5), 39 (3); ^1H NMR δ 7.35–7.10 (5H, Ph, m), 3.74 ($\text{CHC}\equiv\text{C}$, td, 7.2 Hz, 2.6 Hz), 2.18–2.34 ($\text{CH}_2\text{C}\equiv\text{C}$, m), 2.16 ($\text{HC}\equiv\text{CCH}$, d, 2.6 Hz), 1.87–2.05 (CH_2CH , m), 1.85 ($\text{HC}\equiv\text{CCH}_2$, t, 2.0 Hz); ^{13}C NMR δ 140.2 (C1, Ph), 128.3 (2C, *m*-Ph), 127.1 (2C, *o*-Ph), 126.7 (*p*-Ph), 84.7 ($\text{HC}\equiv\text{CCH}$), 83.1 ($\text{HC}\equiv\text{CCH}_2$), 71.4 ($\text{HC}\equiv\text{CCH}$), 69.1 ($\text{HC}\equiv\text{CCH}_2$), 36.5 (CH_2CH), 36.0 ($\text{CHC}\equiv\text{CH}$), 16.1 ($\text{CH}_2\text{C}\equiv\text{CH}$). The product was contaminated to the extent of 5% with the isomeric allenyne $\text{H}_2\text{C}=\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$, characteristic signal: ^1H NMR δ 5.07 ($\text{H}_2\text{C}=\text{C}=\text{C}$, t, 3 Hz). **21a**, b.p. $100\text{--}120^{\circ}\text{C}$ (0.15 mmHg), n_{D}^{20} 1.5395; mass spectrum m/e (% of base peak) 220 (M^{+} , 4), 219 (5), 205 (12), 181 (13), 167 (70), 165 (100), 152 (80), 128 (31), 115 (33); ^1H NMR δ 7.14–7.52 (5H, Ph, m), 2.43 ($\text{HC}\equiv\text{CCPh}$, s), 2.00–2.20 (8H, CH_2CH_2 , m), 1.73 (2H, $\text{HC}\equiv\text{CCH}_2$, t, 1.5 Hz); ^{13}C NMR δ 140.1 (C1, Ph), 128.3 (2C, *m*-Ph), 126.9 (*p*-Ph), 126.1 (2C, *o*-Ph), 85.1 ($\text{HC}\equiv\text{CCPh}$), 83.7 (2C, $\text{HC}\equiv\text{CCH}_2$), 74.7 ($\text{HC}\equiv\text{CCPh}$), 68.3 (2C, $\text{HC}\equiv\text{CCH}_2$), 44.8 (CPh), 41.5 (2C, CH_2CPh), 14.9 (2C, $\text{CH}_2\text{C}\equiv\text{CH}$).

19b ($\text{R}' = \text{Pr}$, $\text{R}'' = \text{H}$), b.p. ca. 50°C (12 mmHg), n_{D}^{20} 1.4427; mass spectrum m/e (% of base peak) 134 (M^{+} , 0.3), 133 (2), 119 (13), 105 (80), 91 (100), 79 (41), 66 (19), 53 (14), 41 (15), 39 (11); ^1H NMR (60 MHz) δ 2.10–2.70 (3H, $\text{CHC}\equiv\text{C}$, m), 1.88 ($\text{HC}\equiv\text{CCH}$, d, 2.3 Hz), 1.74 ($\text{HC}\equiv\text{CCH}_2$, t, 2.5 Hz), 1.10–1.70 (6H, $\text{CH}_2\text{CHCH}_2\text{CH}_2$, m), 1.75–1.05 (CH_3 , m). **21b** + $\text{HC}\equiv\text{CCH}(\text{Pr})\text{CH}_2\text{CH}(\text{C}\equiv\text{CH})\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$, b.p. ca. 100°C (12 mmHg); mass spectrum m/e (% of base peak) (main isomer) 186 (M^{+} , 0.1), 185 (0.3), 171 (0.4), 157 (4), 142 (44), 129 (80), 128 (80), 119 (55), 105 (80), 91 (100), 79 (73), 65 (21), 53 (14), 41 (12), 39 (9).

19d ($\text{R}' = \text{SMe}$, $\text{R}'' = \text{H}$), b.p. 52°C (0.15 mmHg), n_{D}^{20} 1.5033; mass spectrum m/e (% of base peak) 138 (M^{+} , 37), 123 (88), 98 (34), 89 (100), 84 (61), 65 (45), 51 (20), 45 (42), 39 (32); ^1H NMR δ 3.50 (CHS, td, 7.2 Hz, 2.4 Hz), 2.27 ($\text{HC}\equiv\text{CCH}$, d, 2.4 Hz), 2.16 (SMe, s), 2.02 ($\text{HC}\equiv\text{CCH}_2$, t, 2.4 Hz), 1.90 (CH_2CH , dt, 7.2 Hz, 7 Hz), 1.85 ($\text{CH}_2\text{C}\equiv\text{C}$, td, 7 Hz, 2 Hz); ^{13}C NMR δ 82.4 ($\text{HC}\equiv\text{CCH}$), 82.0 ($\text{HC}\equiv\text{CCH}_2$), 71.9 ($\text{HC}\equiv\text{CCH}$), 69.1 ($\text{HC}\equiv\text{CCH}_2$), 33.9 (CHS), 32.9 (CH_2CH), 15.9 ($\text{CH}_2\text{C}\equiv\text{CH}$), 129 (SMe). **21d**, b.p. 95°C (0.15 mmHg), n_{D}^{20} 1.5209; mass spectrum m/e (% of base peak) 190 (M^{+} , 2), 175 (20), 141 (30), 128 (28), 123 (100), 115 (58), 102 (23), 91 (63), 85 (41), 77 (26), 65 (34), 51 (25), 45 (33), 39 (28); ^1H NMR δ 2.52 ($\text{HC}\equiv\text{CC}$, s), 2.30–2.45 (CH_2C , m), 2.14 (SMe, s), 1.83–2.05 ($\text{CH}_2\text{C}\equiv\text{C}$, m); ^{13}C NMR δ 83.1 (2C, $\text{HC}\equiv\text{CCH}_2$), 82.9 ($\text{HC}\equiv\text{CC}$), 74.2 ($\text{HC}\equiv\text{CC}$), 68.7 (2C, $\text{HC}\equiv\text{CCH}_2$), 45.2 (SC), 37.3 (2C, CH_2C), 14.12 (2C, $\text{CH}_2\text{C}\equiv\text{CH}$), 12.2 (SMe).

19e ($\text{R}' = \text{NMe}_2$, $\text{R}'' = \text{H}$); mass spectrum m/e (% of base peak) 136 ($M + \text{H}^{+}$, 0.5), 135 (M^{+} , 1), 134 (4), 120 (2), 110 (2), 107 (3), 94 (4), 91 (2), 82 (100), 42 (21).

19f ($\text{R}' = \text{Ph}$, $\text{R}'' = \text{Et}$), b.p. 87°C (0.15 mmHg), n_{D}^{20} 1.5288, 55% yield; (two diastereomers with a ratio of 58/42); mass spectrum m/e (% of base peak) 196 (M^{+} , 1), 195 (2), 181 (7), 167 (44), 156 (18), 141 (7), 128 (6), 115 (100), 89 (9), 79 (6), 65 (5), 53 (4), 41 (3), 39 (3); ^1H NMR δ 7.10–7.35 (5H, Ph), 2.16–2.34 ($\text{CH}_2\text{C}\equiv\text{C}$),

2.15/2.12 ($\text{HC}\equiv\text{CCH}$, s, 2.3 Hz), 1.90 ($\text{HC}\equiv\text{CCH}_2$, t, 2.5 Hz), 1.55–2.05 (CHCH_2 , m), 1.30–1.66 (CHCH_3 , m), 0.94/0.84 (CH_3 , t, 7 Hz); ^{13}C NMR δ 139.0/139.7 (C1, Ph), 128.1/128.0/127.9 (2C, *o*-, *m*-Ph), 126.7 (*p*-Ph), 83.56/83.64 ($\text{HC}\equiv\text{CCH}$), 82.4/82.1 ($\text{HC}\equiv\text{CCH}_2$), 72.1 ($\text{HC}\equiv\text{CCH}$), 69.6/70.1 ($\text{HC}\equiv\text{CCH}_2$), 45.1/45.4 (CHCH_2), 40.4/39.7 (CHPh), 23.2/22.2 (CH_2CH_3), 20.0/19.4 ($\text{CH}_2\text{C}\equiv\text{C}$), 11.3 (CH_3). The product was contaminated with 5% of the isomeric allenyne $\text{H}_2\text{C}=\text{C}=\text{C}(\text{Ph})\text{CH}(\text{Et})\text{CH}_2\text{C}\equiv\text{CH}$, characteristic signal: ^1H NMR δ 5.07 ($\text{H}_2\text{C}=\text{C}=\text{CCH}$, d, 2.0 Hz). A mixture of benzylacetylene and phenylallene with a ratio of 92/8 was obtained in 30% yield as a low boiling fraction, b.p. 40°C (0.15 mmHg).

e. Dimetalation of allylacetylene with BuLi and subsequent protonation and silylation

A solution of 0.110 mol of BuLi (in 68 mL of hexane) and 50 mL of THF was prepared at -50°C . (When protonation was to be subsequently carried out, the hexane of the commercially supplied BuLi solution was sucked off, and replaced by a high boiling (ca. 160°C) alkane mixture, prior to the addition of THF.) A solution of 0.050 mol of allylacetylene in 20 mL of THF was added during 2 min at 50°C and the mixture then stirred for an additional 45 min without external cooling, allowing the temperature to rise to room temperature. The mixture was then cooled to -60°C and 10 mL of a mixture of water/THF (1/1 v/v) or trimethylchlorosi-

Table 5

Dimetalation of enynes

Enyne ^a	Base ^b	Electrophile ^c	Yield (%)	Products (isomer ratio) ^d			
				Z/E ^e	Conjugated ^e	Skipped ^f	Allenes ^g
Allylacetylene	BuLi	H_2O (0°C) ^h	<i>i</i>	86/14	73	27 ^j	
Allylacetylene	BuLi	ClSiMe_3	60 ^k	54/46	100		
1a	BuK	oxirane	82 ^l	83/17	86	14	
Non-3-en-1-yne	BuK	H_2O	86	44/56	72	16	12
Non-3-en-1-yne	BuK (LiBr)	BuBr	100 ^m				
1c	BuK	H_2O	76	0/100	65		35
1d	BuK	H_2O	78	34/66	37		63
1d	BuK (LiBr)	H_2O	80	29/71	62	38 ⁿ	
1d	BuK (LiBr)	MeI	98 ^o	10/90	73		
1d	BuK (LiBr)	MeI (0°C) ^h	71 ^p	42/58	88	12 ^q	
1e	BuK	H_2O	90	0/100	100		
1e	BuK	ClSiMe_3	100 ^r				
$\text{HC}\equiv\text{CCH}=\text{CMe}_2$	BuK	ClSiMe_3	71 ^s	80/20	100		

^a Z/E ratios of the starting enynes: **1a** and non-3-en-1-yne 40/60, **1c–e** 0/100. ^b BuK refers to BuLi. ^c BuOK; the Li/K exchange prior to the functionalization is indicated with (LiBr). ^d The electrophile was added at about -60°C , unless indicated otherwise. ^e The structures of the compounds obtained were in accordance with spectroscopic data: ^1H and ^{13}C NMR, and GLC-MS. ^f Z/E ratio of the conjugated enyne $\text{HC}\equiv\text{CCH}=\text{CHCHRR}'$ ($\text{R}' = \text{H}$, $\text{CH}_2\text{CH}_2\text{OH}$; R as in Scheme 1). ^g Skipped enynes: E- and Z- $\text{HC}\equiv\text{CCH}_2\text{CH}=\text{CHR}$. ^h Allenes: E- and Z- $\text{H}_2\text{C}=\text{C}=\text{CHCH}=\text{CHR}$. ⁱ The electrophile was added at 0°C . ^j The volatility of the products did not allow removal of the solvent. Thus, the yield could not be determined. ^k Isomerized products: $\text{HC}\equiv\text{CC}(\text{CH}_2\text{CH}_2\text{OH})=\text{CHMe}$, Z/E = 50/50. ^l B.p. 90°C (12 mmHg); n_D^{20} 1.4643. ^m B.p. 68°C (0.05 mmHg). ⁿ Undistilled product; mixture of 21% non-3-en-1-yne (Z/E = 39/61), 14% monoalkylated products (4 isomers) and 55% bisalkylated products (2 isomers). ^o Z/E = 42/58. ^p Undistilled product; contained for 27% polymethylated material ($M^+ = 168$ m/e). ^q B.p. 27°C (0.1 mmHg). ^r Z/E $\approx 1/1$. ^s Undistilled product; mixture of bistrimethylsilylated products (4 isomers with $M^+ = 253$ m/e). ^t B.p. 98°C (12 mmHg); n_D^{20} 1.4671.

lane (0.15 mol) was added in one portion without external cooling. When silylation had been carried out, work-up was carried out as described in section b and the product was subjected to GLC-MS, ^1H and ^{13}C NMR analysis. When quenching with water had been carried out the organic solution was washed ten times with cold (0°C) water, and dried over magnesium sulfate. The volatile products and some remaining THF were distilled from the high boiling alkanes under reduced pressure (12 mmHg) through a 30 cm Vigreux column. A mixture of *E*-, *Z*-pent-3-en-1-yn, allylacetylene, butane and THF was collected in a receiver cooled at -80°C . The results are summarized in Table 5.

f. Dimetalation of enynes 1a, 1c-e, and $\text{HC}\equiv\text{CCH}=\text{CH}(\text{CH}_2)_4\text{CH}_3$ with $\text{BuLi}\cdot^t\text{BuOK}$ and subsequent protonation or functionalization

A solution of 0.110 mol of $^t\text{BuOK}$ in 60 mL of THF was cooled to -100°C , after which a solution of 0.110 mol of BuLi in 68 mL of hexane was added from a syringe during 2 min. During this addition the mixture was efficiently stirred and the temperature kept between -100 and -90°C . A solution of 0.050 mol of the enyne in 10 mL of THF was then added during 5 min, with the temperature kept below -80°C . Stirring at -80°C was continued for 1.5 h, after which the temperature was allowed to rise to 0°C . After 10 min stirring at this temperature the electrophile (an excess of water in THF, 0.050 mol of oxirane in THF, or an excess of trimethylchlorosilane) was added at -60°C , or the K/Li exchange was carried out by addition of a solution of 0.110 mol of anhydrous lithium bromide in 50 mL of THF at -20°C , and the electrophile then added (water/THF mixture of 0.050 mol of butyl bromide). Work-up was carried out as described in section b. The product mixtures were subjected to GLC-MS, ^1H and ^{13}C NMR analysis. The results are summarized in Table 5.

g. Determination of butyllithium

From the methods reported in literature [55–76] the rapid procedure described by Watson [69] and Ellison et al. [71] was chosen (but slightly modified), involving titration at room temperature of the BuLi–hexane solution (commercially available, ca. 1.6 *M*) with a 1.000 *M* solution of sec-butanol in xylene, and 2,2'-dipyridyl as indicator.

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