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General Method for Preparation of Allenic Zinc Reagents by Three-Carbon Homologation of Triorganozincates: Convergent Three-Component Coupling of Propargylic Substrates, Triorganozincates, and Electrophilic Reagents

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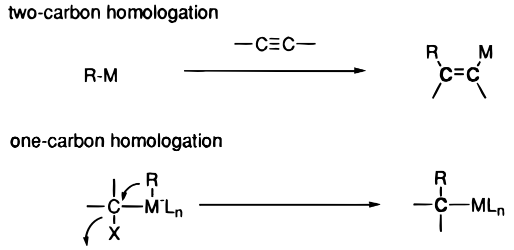
Abstract: Allenic zinc reagents ($R^1R^2C{=}C{=}C(R^3)ZnL$) are efficiently prepared by the reaction of propargylic substrates ($R^1R^2C(X)C{\equiv}CH$, X = $MeSO_2O$, Cl, R_2NCO_2) with a variety of triorganozincates ($(R^3)_3ZnM$; R^3 = alkyl, alkenyl, aryl, M = Li, MgCl). Treatment of the allenic zinc reagents with D_2O gives the corresponding deuteroallenes with high deuterium incorporation. The allenic zinc reagents thus prepared undergo a coupling reaction with a variety of electrophiles (aldehydes, acyl chlorides, I_2, NCS, and chlorosilanes) regioselectively at the γ position to afford the corresponding propargylic derivatives ($R^1R^2C(El)C{\equiv}CR^3$, El = RCH(OH), RCO, I, Cl, R_3Si) in high yields. Silicon containing allenic zinc reagents $R^1CH{=}C{=}C(CH_2SiMe_3)ZnL$ and $R^1CH{=}C{=}C(SiPhMe_2)ZnL$ are readily prepared by the reaction of propargylic carbamates ($R^1CH(OCONPh_2)C{\equiv}CH$) with $(TMSCH_2)_3ZnLi$ and by the reaction of bromopropargylic mesylates $R^1CH(OSO_2Me)C{\equiv}CBr$ with $(PhMe_2Si)_3ZnLi$, respectively. Successive treatment of these reagents with electrophiles affords functionalized organosilicon compounds of high synthetic utility.

Homologation of organometallics is of increasing importance in organic synthesis because subsequent bond formation of the resulting organometallics leads to a convergent construction of complex carbon frameworks by a one-pot procedure. The synthetic potential has been demonstrated, for example, in recent development of useful carbon−carbon bond forming reactions using carbometalation of alkynes[1] and in three-component coupling approaches to a prostaglandin synthesis via conjugate addition/alkylation sequence.[2] While carbometalation and conjugate addition lead to a two-carbon homologation of organometallics, one-carbon homologation or methylene insertion is achieved by 1,2-migration of ate-type carbenoids (Scheme 1). Recently, we have shown that homologation of triorganozincates via 1,2-migration of zincate carbenoids are utilized in preparation of alkenyl-,[3] cyclopropyl,[4] and alkylzinc reagents.[5] Numerous other examples of one-carbon homologation via ate-type carbenoids other than zincates have also been reported.[6]

Previously, Zweifel[7] and Midland[8] reported independently 1,2-migration of alkynylborates derived from propargyl acetates and chlorides (eq 1). In this reaction, 1,2-migration takes place with simultaneous liberation of the leaving groups at the γ position to generate allenic borons. We envisioned that a novel three-carbon homologation of triorganozincate could be developed by utilizing possible 1,2-migration of alkynylzincates **2** (Scheme 2). Indeed, we found that (1) such alkynylzincates can be generated simply by the reaction of propargylic substrates **1** with triorganozincate, (2) the resulting alkynylzincates **2** undergo facile 1,2-migration to give allenic zinc **3**, and (3) the allenic zinc **3** undergo coupling reaction with a variety of electrophiles regioselectively at the γ positions to give prop-

Scheme 1



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Scheme 2.

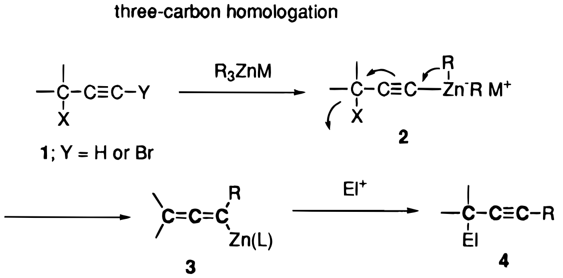


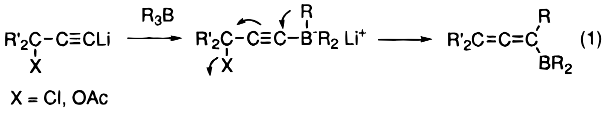
Table 1. Preparation of Allenic Zinc **3a** by the Reaction of Propargylic Derivatives **1a**−**g** with Bu$_3$ZnLi[a]

entry	substrate	equiv of Bu$_3$ZnLi	conditions	yield of **5a** (%)	*d*-content (%)	yield of **3a** (%)[b]
1	**1a**	2.0	A	97	92	89
2		1.3	A	72	52	37
3		2.0	B	88	91	80
4	**1b**	2.0	A	97	81	79
5		1.3	A	86	56	48
6	**1c**	2.0	A	81	89	72
7	**1d**	2.0	C	90	>95	86
8		1.3	C	71	>95	67
9	**1e**	2.0	C	55	64	26
10[c]	**1f**	2.0	A	0		
11[c]	**1g**	2.0	A	0		

[a] The substrate and the zincate were first mixed at −85 °C. Before the addition of D$_2$O, the mixture was stirred for 15 min at 0 °C (conditions A), allowed to warm slowly from −85 to 0 °C over 1−3 h (conditions B), or stirred at −15 °C for 15 min and then at rt for 1−2 h (conditions C). [b] The yield of allenic zinc **3a** estimated based on the yield and deuterium content of allene **5a**. [c] [1-^{2}H]-**1f**,**g** of >99% deuterium content were recovered in 94% and 91% yield, respectively, in entries 10 and 11.

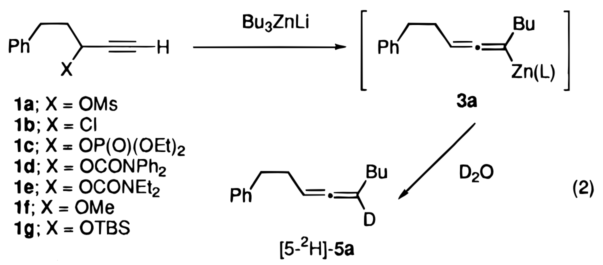
argylic derivatives **4**, providing an efficient one-pot method for introduction of a nucleophile (R^1) and an electrophile (El) to the propargylic substrates **1** at the 1,3-positions.

In this paper, we wish to report on the scope and limitation of the three-carbon homologation of triorganozincates and its application to the convergent three-component coupling synthesis of propargylic derivatives.[9]



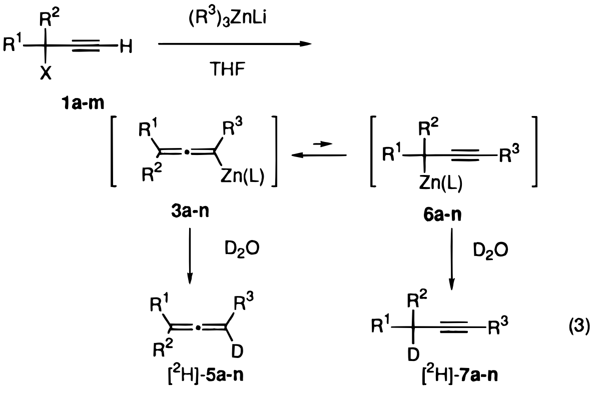
Results and Discussion

Preparation of Allenic Zinc Reagents. Reactions were carried out for a series of 5-phenyl-1-pentyne-3-ol derivatives **1a**−**g** and Bu$_3$ZnLi in THF at temperatures from −85 °C to 0 °C (or to rt) (eq 2, Table 1). The reaction was quenched with D$_2$O and the yield of allenic zinc **3a** was estimated based on the yield and deuterium content of allene [5-^{2}H]-**5a**.



The reaction of mesylate **1a** with 2.0 equiv of Bu$_3$ZnLi afforded [5-^{2}H]-**5a** with high deuterium incorporation in almost quantitative yield, demonstrating the high-yield formation of allenic zinc **3a** (entry 1). The level of deuterium incorporation was dropped considerably when 1.3 equiv of the zincate was used (entry 2). Control of the reaction temperatures was also influential; the rapid warming of the reaction mixture (conditions A) gave a better result in comparison with the slow warming (conditions B) (entries 1 vs 3). Other propargylic derivatives such as chloride **1b**, phosphate **1c**, and carbamates **1d**,**e** also afforded allenic zinc **3a** with varying efficiencies (entries 4−9). Of these, *N*,*N*-diphenylcarbamate **1d** exhibited notably high yield of allenic zinc **3a** comparable to mesylate **1a**. No allene formation was observed in the reaction of the methoxy and TBSO derivatives **1f**,**g** (entries 10 and 11).

The scope of the reaction with respect to the structures of organozincates was investigated by using mesylate **1a** as a substrate (eq 3 and Table 2). A series of lithium trialkylzincates (R^3 = Me, Bu, *s*-Bu, and *t*-Bu) was successfully used in the preparation of the corresponding homologated allenic zinc (entries 1−6). Three equiv of Me$_3$ZnLi were necessary for the successful preparation of **3b** (entries 3 and 4). Allenic zinc **3e** and **3f** bearing alkenyl and aryl groups, respectively, were also prepared by using the corresponding lithium zincates (entries 7 and 8). Chloromagnesium zincate obtained by the reaction of BuMgCl with ZnCl$_2$ reacted similarly with slightly lower efficiency than the lithium zincate (entry 2).



Allenic organometals often exists as equilibrating mixture with isomeric propargylic species.[10] Equilibration between allenic and propargylic zinc bromides has been studied previously.[11] Direct evidence for the formation of allenic zinc **3a** was provided by FTIR analysis of the reaction mixture of **1a** and Bu$_3$ZnLi (2.0 equiv). Thus, the mixture showed a strong band due to the vibration ν_{as} (C=C=C) at 1890 cm^{-1}.[10a,11] No band due to ν (C≡C) was observed in the region 2250−2100 cm^{-1}. The result supports our assumption that allene **5** is produced by protonation of allenic zinc **3** through an S$_E$2 pathway. In the reaction using simple triorganozincates, formation of alkyne **7** was negligible (<3%). On the other hand, the reactions using the sterically demanding *s*-Bu$_3$ZnLi and *t*-Bu$_3$ZnLi afforded alkynes **7c**,**d** as minor products (entries 5 and 6). The IR spectrum of the reaction mixture of **1a** and *t*-Bu$_3$ZnLi (2.0 equiv) showed a weak absorption (ν (C≡C)) at 2158

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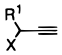
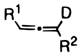
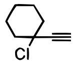
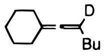
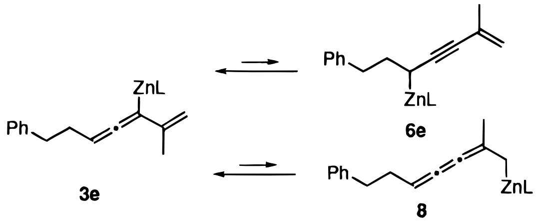
Table 2. Generation of Allenic Zinc **3** by the Reaction of Propargylic Derivatives **1** and Triorganozincates[a]

entry	substrates **1**  (R^1, X)	triorganozincates	products **5**  (R^2)	yield[b] (%)	*d* content (%)
1	**1a** ($PhCH_2CH_2$, MsO)	Bu_3ZnLi	**5a** (Bu)	97	92
2	**1a**	$Bu_3ZnMgCl$	**5a**	73[c]	86
3	**1a**	Me_3ZnLi	**5b** (Me)	92	56
4[d]	**1a**	Me_3ZnLi	**5b**	90	75
5	**1a**	*s*-Bu_3ZnLi	**5c** (*s*-Bu)	96[e]	94
6	**1a**	*t*-Bu_3ZnLi	**5d** (*t*-Bu) **11**[g] **12**[g] **13**[g]	76[f] 5 7 6	93
7	**1a**	$(CH_2{=}C(Me))_3ZnLi$	**5e** ($CH_2{=}C(Me)$)	77	72
8	**1a**	Ph_3ZnLi	**5f** (Ph)	77	81
9[h]	**1a**	Et_2(*s*-Bu)ZnLi	**5g** (Et) **5c**	40 56	- -
10		Et_2(Ph)ZnLi	**5g**	88	88
11		Et_2(2-Thienyl)ZnLi	**5g**	78	62
12		Et_2(*t*-BuO)ZnK	**5g**	90	37
13[i]	**1d** ($PhCH_2CH_2$, Ph_2NCO_2)	Bu_3ZnLi	**5a**	90	>95
14[i]	**1d**	$Bu_3ZnMgCl$	**5a**	83[j]	>95
15[i]	**1d**	Me_3ZnLi	**5b**	67	>95
16[d,i]	**1d**	Me_3ZnLi	**5b**	94	>95
17	**1h** (*n*-C_8H_{17}, MsO)	Bu_3ZnLi	**5h** (Bu)	97	92
18	**1i** (2,6-dimethyl-5-heptenyl, OMs)	Bu_3ZnLi	**5i** (Bu)	96	92
19	**1j** (*c*-C_6H_{11}, MsO)	Bu_3ZnLi	**5j** (Bu)	95	91
20	**1k** (TBSO$(CH_2)_5$, MsO)	Bu_3ZnLi	**5k** (Bu)	93	94
21	**1l** ((MeO)2CH(CH2)4, OMs)	Bu_3ZnLi	**5l** (Bu)	91	>95
	1m 	Bu_3ZnLi	**5m** 	95[l]	86
22[k]	**1m**	Bu_3ZnLi	**5m**	95[l]	86
23	**1m**	$Bu_3ZnMgCl$	**5m**	79[l]	81

[a] Unless otherwise noted, all reactions were performed using 2.0 equiv of zincates under conditions A in Table 1. [b] Unless otherwise noted, yields refer to isolated yields. [c] Combined yield of **5a** (66%) and 1-phenyl-4-nonyne (**7a**) (6%). [d] 3.0 Equiv of the zincate was used. [e] Combined yield of **5c** (86%) and 3-methyl-8-phenyl-4-octyne (**7c**) (6%). [f] Combined yield of **5d** (60%) and 2,2-dimethyl-7-phenyl-3-heptyne (**7d**) (16%).[g] For structures of **11**−**13**, see Scheme 3. [h] The reaction mixture was quenched by the addition of H_2O. [i] The reaction was perfumed under conditions C in Table 1. [j] Combined yield of **5a** (71%) and **7a** (11%). [k] The reaction was perfumed under conditions B in Table 1. [l] GC yield.

cm^{-1} together with a strong absorption (ν_{as} (C═C═C)) at 1892 cm^{-1},[10a,11] suggesting that allenic zinc **3d** is in equilibrium with its propargylic form **6d**. It is probable that alkyne **7d** was produced from **6d** through an S_E2 pathway. Interestingly, judging from the D_2O quench experiment (entry 7), organozinc species generated by the reaction of $(CH_2{=}C(Me))_3ZnLi$ appears to exist as allenic zinc **3e** in spite of a possible isomerization to propargylic zinc **6e** and butatrienylmethylzinc **8** (eq 4).



(4)

We briefly investigated the reaction of mixed zincates Et_2(R)ZnM (entries 9−12).[12] The mixed zincates were prepared by treatment of Et_2Zn with an equivalent of RM and used in the reaction of **1a**. Although a mixture of [5-^{2}H]-**5g** (R^3 = Et) and [5-^{2}H]-**5c** (R^3 = *s*-Bu) was produced in the reaction of Et_2(*s*-Bu)ZnLi, the selective formation of [5-^{2}H]-**5g** was observed when Et_2(Ph)ZnLi and Et_2(2-thienyl)ZnLi was used. The reaction of Et_2(Ph)ZnLi, in particular, afforded the corresponding allenic zinc **3g** in satisfactory yield (77%) judging from 88% deuterium incorporation in **5g**. In spite of the low level of deuterium incorporation, the high-yield formation of **5g** by using Et_2(*t*-BuO)ZnK is also noteworthy.

As shown in entries 17−23, a variety of allenic zinc reagents including those bearing siloxy and acetal moieties were successfully prepared by the reaction of the corresponding propargylic substrates. The reaction of tertiary propargylic chloride **1m** yielded trisubstituted allenic zinc **5m** in an efficient manner. With the combination of propargylic substrates and organozincates, a wide range of allenic zinc reagents are available. It has been reported that allenic zinc reagents were prepared by lithiation of the corresponding allenes[13] or alkynes (R^1-$CH_2C{\equiv}CR^3$)[14] followed by transmetalation. Application of the method to the preparation of 1,3-disubstituted derivatives **3** (R^2 = H) would unavoidably result in nonselective formation of a mixture of the regioisomers. The present reaction allows such allenic zinc species to be prepared in a regiospecific manner.

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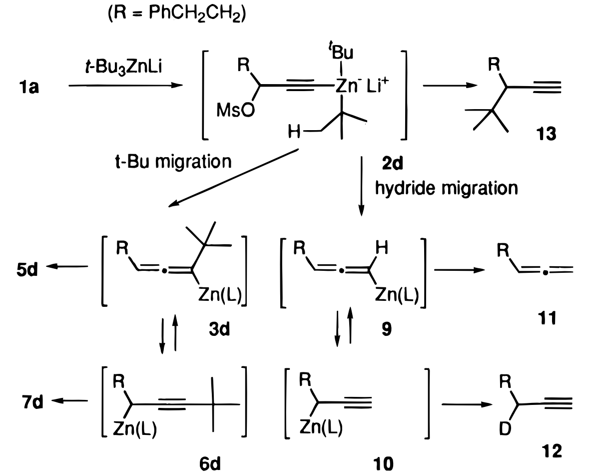
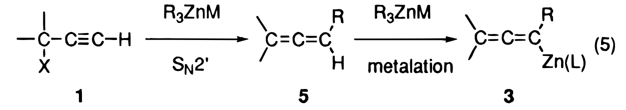
Table 3. Reaction of Propargylic Derivatives with Bu_3ZnLi (2.0 Equiv) at Low Temperatures

entry	substrate	temp (°C)	time (min)	yield (%) **1**	(*d*-content (%)) **5a**
1	**1d**	−15	15	99 (100)	
2	**1e**	−15	15	98 (100)	
3	**1a**	−60	30	5 (0)	90 (93)
4	**1b**	−40	30	33 (10)	66 (91)

Scheme 3. (R = $PhCH_2CH_2$)



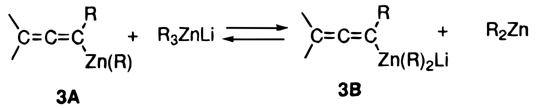
Internal alkyne $PhCH_2CH_2CH(OMs)C{\equiv}CCH_3$ (**1n**) did not react at all with Bu_3ZnLi under similar conditions. Treatment of allene **5a** with Bu_3ZnLi (2.0 equiv) at 0 °C for 1 h and D_2O quench of the reaction resulted in the recovery of **5a** (98%) without deuterium incorporation. These observations exclude the formation of allenic zinc **3** via a mechanism involving the initial formation of allene **5** via S_N2' pathway followed by regioselective metalation by a zincate (eq 5). Quantitative deuterium incorporation in the recovered starting material observed in the reaction of **1f**,**g** (Table 1, entries 10 and 11) shows that zincates are basic enough to abstract acetylenic protons. Therefore, the formation of allenic zinc **3** most probably proceeded through a mechanism involving initial metalation of propargylic derivatives by zincates and subsequent 1,2-alkyl migration of the resulting alkynylzincates **2** (Scheme 2).



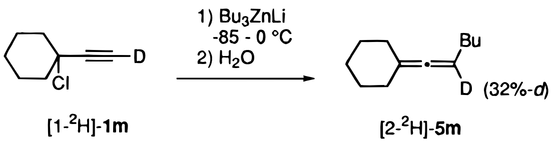
(5)

Evidence for the intermediacy of alkynylzincate **2** was provided by D_2O-quench experiments at low temperatures (Table 3). Treatment of diphenylcarbamate **1d** with Bu_3ZnLi at −15 °C for 15 min followed by the addition of D_2O afforded [1-^{2}H]-**1d** with >95% deuterium incorporation without formation of allene **5a** (entry 1). Upon warming up to rt, alkynylzincate **2d**, generated under these conditions, was converted to allenic zinc **3a** (Table 1, entry 7). A similar result was obtained for diethylcarbamate **1e** (Table 3, entry 2 and Table 1, entry 9). In contrast to the carbamates, mesylate **1a** afforded allenic zinc **3a** even at −60 °C and no deuterium was found in the recovered **1a** (entry 3). An intermediate result was obtained for chloride **1m** (entry 4). The 1,2-migration is a rate determining step for **1d**,**e** with less reactive carbamoyloxy groups. On the other hand, proton abstraction is a rate determining step for mesylate **1a** with a good leaving group. Both steps are of comparable rates in the reaction of chloride **1m**.[15]

In most instances, deuterium contents of allenes [^{2}H]-**5** were less than 100%, indicating formation of protonated allenes **5** as byproducts in the reaction mixture before treatment with D_2O. In the course of the reaction, initially formed allenic zinc **3A** reacts reversibly with a triorganozincate to form more basic allenic zincate **3B** (eq 6).[16] Protonation of allenic zincate **3B** by remaining substrate **1** may explain the formation of the protonated allene. This was confirmed by the reaction of the labeled chloride [1-^{2}H]-**1m** (eq 7); the reaction gave allene [2-^{2}H]-**5m** with 32% deuterium incorporation in 92% yield.



(6)



(7)

The undesirable protonation pathway via **3B** may compete significantly in the reaction using 1.3 equiv of zincates. Employment of 2.0 (or 3.0) equiv of zincates may effectively retard the pathway especially in the later phase of the reaction leading to the high-yield formation of allenic zinc **3**. It should be noted that in the reaction of carbamates **1d**,**e**, however, the substrates were completely converted to the alkynylzincates **2** before they undergo an 1,2-migration and, therefore, the intervention of such pathway is infeasible. Indeed, the reaction of **1d** using 1.3 equiv of Bu_3ZnLi gave **5a** with >95% deuterium incorporation (Table 1, entry 8). Use of excess amount of zincates is also advantageous for obtaining higher yields of allene **5**.

In the reaction of **1a** with *t*-Bu_3ZnLi, several minor products were obtained other than allene **5d** (Scheme 3). Allenic zinc **3d** with the sterically demanding *tert*-butyl group isomerized considerably to propargylic zinc **6d**, leading to the formation of **5d** and **7d** in 52% and 16% yield, respectively. The formation of reduction products **11** (5%) and **12** (7%) suggests the generation of allenic zinc **9** and propargylic zinc **10** in the reaction mixture. Their formation are most reasonably explained by a mechanism involving hydride migration from alkynylzincate intermediate **2d** with simultaneous elimination of isobutene. Hydride reduction has been often observed in the reaction of *tert*-butylmetals.[18] The present observation, however, is a first example of such reactivity for the zincates. Finally, alkyne **13** (6%), a formal 1,4-migration product of alkynylzincate **2d**, was also obtained in this reaction.

Reaction of Allenic Zinc 3 with Aldehydes: Stereoselective Synthesis of *anti*-Homopropargylic Alcohols. The reaction

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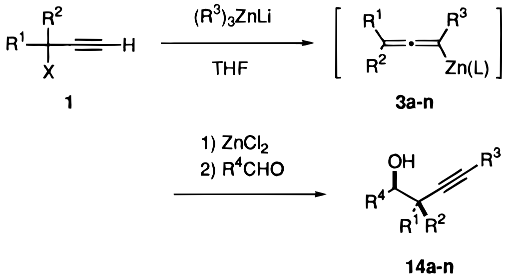
[15] The nature of leaving groups in **1** also influences to the acidity of acetylenic proton. Thus, deprotonation of mesylate **1a** proceeded even at −60 °C judging from 90% yield formation of allene **5a** (entry 3). On the other hand, deprotonation of carbamate **1d** did not proceed in appreciable rate at the same temperature.

[16] Assuming a rapid ligand transfer,[17] organozincates $[R^1(R^2)\text{-}C{=}C{=}C(R^3)]_n(R^3)_{3-n}ZnLi$ ($n = 2, 3$) as well as diorganozinc $[R^1(R^2)\text{-}C{=}C{=}C(R^3)]_2Zn$ ($n = 0-2$) should also be present in the reaction mixture. Although these organozinc species were neglected in order to simplify the discussion, the same conclusion are deduced by considering these species.

[17] (a) Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4140. (b) Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 1602. (c) Seitz, L. M.; Little, B. F. *J. Organomet. Chem.* **1969**, *18*, 227.

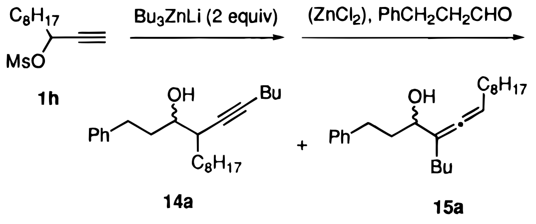
[18] (a) Harada, T. Maeda, H.; Oku, A. *Tetrahedron Lett.* **1985**, *26*, 6489. (b) Ritter, R. H.; Cohen, T. *J. Am. Chem. Soc.* **1986**, *108*, 3718. (c) Topolsk, M.; Duraisamy, M.; Rachon, J.; Gawronski, J.; Gawronska, K.; Geoedken, V.; Walborsky, H. M. *J. Org. Chem.* **1993**, *58*, 546.

of allenic metal reagents with aldehydes gives homopropargylic alcohols and/or α-allenic alcohols depending on the nature of the metal atoms.[10] Success in control of the regioselectivity reported recently made the reaction as an efficient and useful method for the extension of the carbon chains.[13] Zweifel et al. have previously reported the selective formation of homopropargylic alcohols in the reaction of aldehydes with 3-substituted allenic chlorozinc reagents.[14] The reaction is also stereoselective affording the *anti* isomer with high stereoselectivity. We found that a variety of *anti*-homopropargylic alcohols **14** were prepared convergently by a successive treatment of propargylic derivatives **1** with triorganozincates and aldehydes in one-pot (eq 8).



(8)

We first examined the direct reaction of allenic zinc **3h** ($R^1 = C_8H_{17}$, $R^2 = H$, $R^3 = Bu$), prepared by the reaction of mesylate **1h** and Bu_3ZnLi (2 equiv), with 3-phenylpropanal (eq 9). However, the reaction resulted in the nonselective formation of homopropargylic alcohol **14a** (*anti*:*syn* = 55:45) and α-allenic alcohol **15a**. Both regio- and stereoselectivity were improved dramatically when allenic zinc **3h** was treated with $ZnCl_2$ before the addition of the aldehyde. Thus, treatment of **3h** with $ZnCl_2$ (3.0 equiv) at −85 °C followed by the addition of 3-phenylpropanal (1.5 equiv) yielded stereoselectively *anti*-homopropargylic alcohols **14a** without formation of allenic alcohol **15a**. It should be noted that the formation of 3-phenyl-3-heptanol which would arise by butylation of the aldehyde was not observed in this reaction.

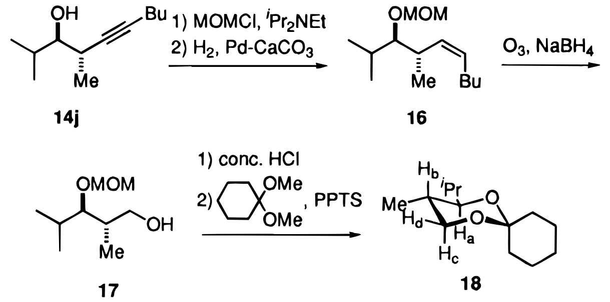


(9)

equiv of $ZnCl_2$	yiled of **14a**	*anti:syn*	yiled of **15a**
0	77%	55:45	12%
0.5	79%	89:11	0%
3.0	83%	96:4	0%

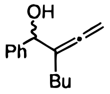
Reactions were examined for various combinations of propargylic substrates, organozincates, and aldehydes under similar conditions (Table 4). The reaction of aliphatic aldehydes exhibited high *anti*-selectivity (>94:6). Of these reactions, higher selectivities were observed in the reaction of bulky aldehydes (entries 1−5). Stereoselectivity was constantly high irrespective of the steric as well as the electronic nature of the substituent R^3 in allenic zinc reagents (entries 12−16). The reaction with benzaldehyde exhibited a notably low level of stereoselectivity (entry 5). A similar anomaly of benzaldehyde has been observed elsewhere.[13a,19] High synthetic utility of the present one-pot reactions is also exemplified in application to the synthesis of highly functionalized homopropargylic alcohols such as **14p**, **14s**, and **14t**.

Scheme 4

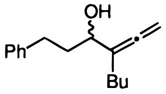


J a,b = 10.2 Hz, *J* b.c = 11.0 Hz

The reaction proceeded regioselectively not only for 1,3-disubstituted allenic zincs but also for trisubstituted allenic zincs (entries 21 and 22). A notable exception for the regioselectivity was observed in the reaction of parent propargyl mesylate (**1o**). The reaction of **1o** with Bu_3ZnLi and aldehydes resulted in the formation of α-allenic alcohols **15w**,**x** in preference to homopropargylic alcohols **14w**,**x** (entries 23 and 24).

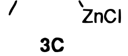


15w



15x

The nature of the coordination state of zinc atoms in allenic zinc species influences much to the mode of addition (S_E2' vs S_E2) and the stereoselectivity. The direct use of allenic zinc reagent **3h** without treatment with $ZnCl_2$ resulted in nonselective formation of **14a** and **15a** (eq 9). Because 2 equiv of Bu_3ZnLi were employed in generation of **3h**, the reagents most probably existed as a equilibrating mixture of diorganozinc **3A** and zincate **3B** (eq 6). By the addition of 3 equiv of $ZnCl_2$, the mixture was converted to allenic chlorozinc species **3C**, whose reaction with aldehydes proceeded regio- and stereoselectively. The addition of 0.5 equiv of $ZnCl_2$ may lead to the formation of diorganozinc **3A**. Interestingly, reaction using such organozinc species afforded homopropargylic alcohols **14a** regioselectively but with lower stereoselectivity (89:11) (eq 10). By comparing the result with that of the direct use of **3h** (a mixture of **3A** and **3B**), it can be deduced that zincates **3B** participated preferentially in the nonselective reaction with the aldehyde.[20] Of three types of allenic zinc species, chlorozinc **3C** and diorganozinc **3A** possess Lewis acidic nature at the zinc atoms, undergoing S_E2' type reaction with aldehydes through a six-membered cyclic transition state to give **14a** with high *anti*-selectivity.[13,14] On the other hand, allenic zincates without appreciable Lewis acidity coupled with aldehydes both via S_E2 and S_E2' pathways through linear transition states.



3C

The identity of the major product as the *anti* isomer was established for **14j** by chemical correlation with the previously reported acetal derivative **18**[21] (Scheme 4). In ^1H NMR analysis,

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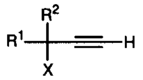
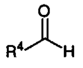
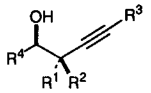
[19] (a) Favre, E.; Gaudemar, M. *J. Organomet. Chem.* **1975**, *92*, 17.

[20] It was reported that the reaction of allenic allanates with aldehydes gave homopropargylic alcohols regioselectively but with low diastereoselectivity; Zweifel, G.; Hahn, G. *J. Org. Chem.* **1984**, *49*, 4565.

[21] Harada, T.; Matsuda, Y.; Uchimura, J.; Oku, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1429.

Table 4. Preparation of Homopropargylic Alcohols **14** by the Reactions of Allenic Zinc Reagents **3** with Aldehydes[a]

entry	substrates **1**	zincates	aldehydes	homopropargylic alcohols **14**	isolated yield	stereoselectivity[b]
	 (R^1, R^2, X)	$(R^3)_3ZnLi$	 (R^4)	 (R^1, R^2, R^3, R^4)	(%)	*anti* : *syn*
1	**1h** (C_8H_{17}, H, OMs)	Bu_3ZnLi	$Ph(CH_2)_2$	**14a** (C_8H_{17}, H, Bu, $Ph(CH_2)_2$)	83	96 : 4[c]
2	**1h**		Et	**14b** (C_8H_{17}, H, Bu, Et)	83	95 : 5[c]
3	**1h**		*i*-Pr	**14c** (C_8H_{17}, H, Bu, *i*-Pr)	85	99 : 1[c]
4	**1h**		*t*-Bu	**14d** (C_8H_{17}, H, Bu, *t*-Bu)	84	99.7 : 0.3
5	**1h**		Ph	**14e** (C_8H_{17}, H, Bu, Ph)	82	52 : 48
6	**1j** (*c*-C_6H_{11}, H, OMs)	Bu_3ZnLi	Et	**14f** (*c*-C_6H_{11}, H, Bu, Et)	89	97 : 3
7	**1j**		*i*-Pr	**14g** (*c*-C_6H_{11}, H, Bu, *i*-Pr)	86	99.5 : 0.5
8	**1j**		Ph	**14h** (*c*-C_6H_{11}, H, Bu, Ph)	84	56 : 44
9	**1n** (Me, H, OMs)	Bu_3ZnLi	$Ph(CH_2)_2$	**14i** (Me, H, Bu, $Ph(CH_2)_2$)	98	94 : 6[c]
10	**1n**		*i*-Pr	**14j** (Me, H, Bu, *i*-Pr)	90	98.5 : 1.5[c]
11	**1n**		*t*-Bu	**14k** (Me, H, Bu, *t*-Bu)	85	99.7 : 0.3
12[d]	**1n**	Me_3ZnLi	*i*-Pr	**14l** (Me, H, Me, *i*-Pr)	66	99.3 : 0.7
13	**1n**	*s*-Bu_3ZnLi	*i*-Pr	**14m** (Me, H, ^{s}Bu, *i*-Pr)	92	98.2 : 1.8
14	**1n**	*t*-Bu_3ZnLi	*i*-Pr	**14n** (Me, H, *t*-Bu, *i*-Pr)	73	98.5 : 1.5
15	**1n**	Ph_3ZnLi	*i*-Pr	**14o** (Me, H, Ph, *i*-Pr)	51	98.2 : 1.8
16	**1n**	$(CH_2{=}CH(Me))_3$-ZnLi	*i*-Pr	**14p** (Me, H, $CH_2{=}CH(Me)$, *i*-Pr)	63	98.6 : 1.4
17[d]	**1a** ($Ph(CH_2)_2$, H, OMs)	Me_3ZnLi	*i*-Pr	**14q** ($Ph(CH_2)_2$, H, Me, *i*-Pr)	72	98.3 : 1.7
18	**1a**	Ph_3ZnLi	*i*-Pr	**14r** ($Ph(CH_2)_2$, H, Ph, *i*-Pr)	56	99.1 : 0.9
19	**1k** ($(MeO)_2CH(CH_2)_4$, H, OMs)	Bu_3ZnLi	Et	**14s** ($(MeO)_2CH(CH_2)_4$, H, Bu, Et)	84	95 : 5[c]
20	**1k**	Bu_3ZnLi	*i*-Pr	**14t** ($(MeO)_2CH(CH_2)_4$, H, Bu, *i*-Pr)	88	98 : 2[c]
21[e]	**1m** (-$(CH_2)_5$-, Cl)	Bu_3ZnLi	Ph	**14u** (-$(CH_2)_5$-, Bu, Ph)	84	-
22[e]	**1m**		$Ph(CH_2)_2$	**14v** (-$(CH_2)_5$-, Bu, $Ph(CH_2)_2$)	82	-
23	**1o** (H, H, OMs)	Bu_3ZnLi	Ph	**14w** (H, H, Bu, Ph)	18	-
				15w	52	
24	**1o**		$Ph(CH_2)_2$	**14x** (H, H, Bu, $Ph(CH_2)_2$)	8 (65)	-
				15x	65	

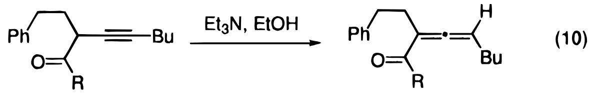
[a] Unless otherwise noted, allenic zinc reagents were prepared by using 2.0 equiv of zincates under conditions A in Table 1 and allowed to react with aldehydes (1.5 equiv) at the tempratures from −85 to 0 °C after treatment with $ZnCl_2$ (3.0 equiv). [b] Unless otherwise noted, the ratios were determined by GC analysis (30 m OV-1 capillary column). [c] The ratio was determined by ^1H NMR anlysis. [d] 3.0 Equiv of the zincate were used. The resulting allenic zinc was used after treatment with 5.0 equiv of $ZnCl_2$. [e] Allenic zinc reagent **3m** was prepared under conditions B in Table 1.

18 showed a typical axial−axial coupling between H_a and H_b (J_{ab} = 10.2 Hz).

Coupling Reactions of Allenic Zinc Species 3 with Other Electrophiles. Allenic zinc reagents **3** also underwent coupling reaction with other electrophiles such as acyl chlorides, chlorosilanes, iodine, and NCS affording the corresponding propargylic derivatives regioselectively (Table 5).

Treatment of disubstituted allenic zinc **3a**, prepared from **1a** and Bu_3ZnLi (2 equiv), with 1.5 equiv of acyl chlorides at −75 °C for 3 h gave regioselectively alkynones **19a**−**d** with minor formation of allenyl ketones **20a**−**d** (entries 1−5). As in the reaction with aldehydes, butyl addition to the acyl halide was not detected. The higher level of the regioselectivity was observed in the reaction of sterically demanding pivaloyl chloride (entry 5). In the acylation, the addition of $ZnCl_2$ (3 equiv) did not improve the regioselectivity (entry 4). For ethoxycarbonylation of **3a**, 3.0 equiv of ethyl chloroformate was necessary to obtain the satisfactory yield of **19e** (entries 6 and 7). Trisubstituted allenic zinc **3m**, generated by the reaction of chloride **1m** with $(Bu)_3ZnLi$ (2.0 equiv), reacted with acetyl chloride in a nonregioselective manner affording a 1:1 mixture of alkynone **19f** and allenyl ketone **20f** (entry 8).

Alkynones **19a**−**d** were prone to isomerization to allenyl ketones **23a**−**d** under non-neutral conditions. Precautions were required in their isolation by silica gel column chromatography. Treatment of alkynones **19a**−**d** with triethylamine in methanol yielded quantitatively ketones **23a**−**d** (eq 10), which has previously been used as intermediates for the synthesis of 2,3,5-trisubstituted furan derivatives.[22]



(10)

191a-d

21a; R = CH_3, 97%, **21b**; R = Bu, 95%
21c ;R = ^{i}Pr, 95%, **21d**; R = ^{t}Bu, 100%

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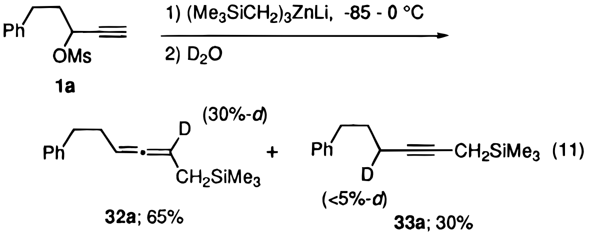
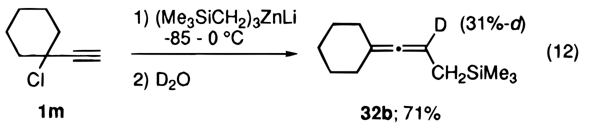
(22) (a) Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990**, *55*, 3450. (b) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1991**, *56*, 960. (c) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1992**, *57*, 3387.

Treatment of allenic zinc **3a** with iodine (6 equiv) at −85 °C gave 3-iodo-1-phenyl-4-nonyne (**22a**) in 81% yield together with a small amount of 5-iodo-1-phenyl-3,4-nonadiene (**23a**) (entry 9). Chlorination of **3a** with NCS also proceeded regioselectively to give propargylic chloride **22b** (entry 10), while, on the other hand, attempted bromination either with Br_2 or NBS resulted in the formation of complex mixtures. Reaction of allenic zinc **3a** with chlorotrimethylsilane and chorodimetylphenylsilane afforded regioselectively propargylic silanes **24a** and **24b**, respectively, in high yields (entries 11 and 12). The selectivity was decreased when chloro(chloromethyl)dimethylsilane and chlorotriethylsilane were used (entries 13 and 14). No coupling reaction took place with *tert*-butylchlorodimethylsilane.

Preparation and Reaction of Silicon Containing Organozinc Reagents. In past few decades, advances have been made in the use of organosilicon compounds in organic synthesis.[23] Of these, propargyl- and ethynylsilanes have been established to be synthetic equivalents of allenic and acetylenic anions, respectively. The intramolecular reactions of functionalized propargyl- and ethynylsilanes has been often utilized for the construction of polycyclic carbon frameworks.[24] As described in the previous section, propargyl silanes **24** were obtained in high yields by the reaction of propargylic substrates with triorganozincates followed by silylation of the resulting allenic zinc reagents. α-(Trimethylsilylmethyl)allenic zincs **26** and α-silylallenic zincs **29** would be prepared by the three-carbon homologation of $(Me_3SiCH_2)_3ZnLi$ and $(R_3Si)_3ZnLi$, respectively. These silicon containing allenic zincs may serve as versatile reagents for the synthesis of functionalized propargylsilanes **28** and ethynylsilanes **31**, respectively (Scheme 5).

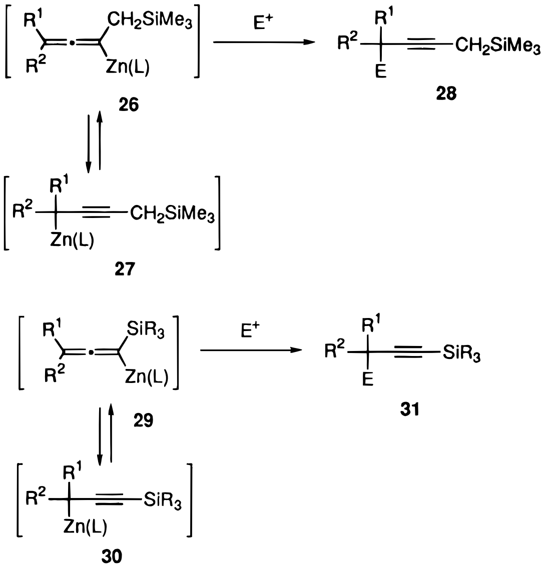
For the preparation of α-(trimethylsilylmethyl)allenic zincs **26**, we first examined the reaction of mesylate **1a** with $(Me_3SiCH_2)_3ZnLi$ (eq 11). Although the reaction afforded silylallene **32a** with minor formation of silylalkyne **33a**, the low level of deuterium incorporation in the products indicated the poor yields of the desired zinc reagents **26a** and **27a**. The reaction of chloride **1m** afforded silylmethylallene **32b** exclusively but again with low deuterium incorporation (eq 12).



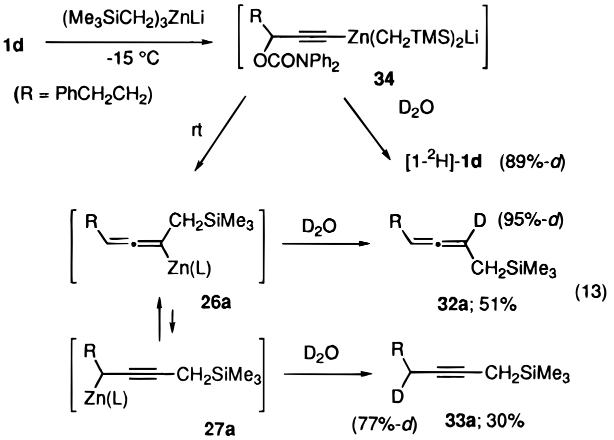


The basicity of $(TMSCH_2)_3ZnLi$ is considered to be lower than that of simple trialkylzincates because of the anion stabilizing ability of the α-silicon atom.[25] This may cause retardation of the rate of the initial deprotonation step to form the alkynylzincate intermediate. As discussed in the previous section, when the deprotonation step is slower than the subsequent 1,2-migration step, deprotonation of **1** by allenic zincate **3** (ZnL = $Zn(R)_2Li$), formed reversibly, may well compete with the reaction by the triorganozincate resulting in the less efficient generation of allenic zinc reagents. The problem was anticipated to be solved by using a substrate with a less reactive leaving group which reduces the rate of 1,2-migration.

Scheme 5



Treatment of diphenylcarbamate **1d** with $(TMSCH_2)_3ZnLi$ at −15 °C for 1 h followed by the addition of D_2O lead to clean generation of alkynylzincate **34** as demonstrated by 89% deuterium incorporation in [1-^{2}H]-**1d** obtained in 86% yield (eq 13). While either silylallene **32a** or silylalkyne **33a** was not formed at this temperature, further treatment of the mixture at rt for 2 h followed by the addition of D_2O gave [2-^{2}H]-**32a** with 95% deuterium incorporation and [4-^{2}H]-**33a** with 77% deuterium incorporation in 51% and 30% yields, respectively. The combined yield of an equilibrating mixture of allenic zinc **26a** and propargylic zinc **27a** is thus estimated to be 72%.



Having established the method for the preparation of α-(trimethylsilylmethyl)allenic zincs **26**, we then examined their reactions with electrophiles (Scheme 6). Although the result of D_2O-quench experiment indicated that considerable amount of the reagents existed as propargylic zinc **27** under these conditions, the reactions gave propargylic adducts **35**−**38** regioselectively. Thus, iodides **35a**,**b**, disilylalkynes **36a**,**b**, and alkynones **39a**,**b** were obtained exclusively in the reaction of

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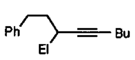
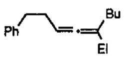
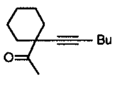
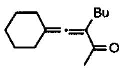
(23) (a) Fleming, I. In *Comprehensive Organic Synthesis*; Heathcock, C. H., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, p 563. (b) Schinzer, D. *Synthesis* **1988**, 263.

(24) Mulzer, J.; Altenbach, H.-J.; Braun, M.; Krohn, K.; Ressig, H.-U. *Organic Synthesis Highlights*; VCH Publishers: Weinheim, 1991; p 131.

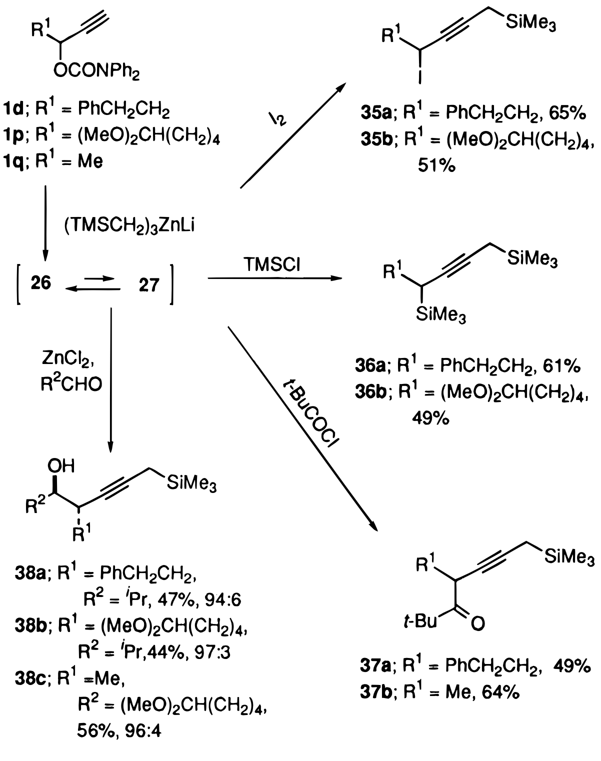
(25) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 809.

Table 5. Coupling Reactions of Allenic Zinc Reagents **3a**,**m** with Electrophiles[a]

entry	electrophile (equiv)	conditions[b]	products  (El)	yield (%)	 (El)	yield (%)
1	MeCOCl (1.5)	D	**19a** (MeCO)	71	**20a** (MeCO)	9
2	^{n}BuCOCl (1.5)	D	**19b** (^{n}BuCO)	79	**20b** (^{n}BuCO)	11
3	^{i}PrCOCl (1.5)	D	**19c** (^{i}PrCO)	63	**20c** (^{i}PrCO)	9
4[c]	^{i}PrCOCl (1.5)	D	**19c**	18	**20c**	2
5	^{t}BuCOCl (1.5)	D	**19d** (^{t}BuCO)	86	**20d** (^{t}BuCO)	5
6	EtOCOCl (1.5)	D	**19e** (EtOCO)	39	**20e** (EtOCO)	8
7	EtOCOCl (3.0)	D	**19e**	57	**20e**	11
8	MeCOCl (1.5)	D	 **19f**	43	 **20f**	39
9	I_2 (6.0)	E	**22a** (I)	81	**23a** (I)	6
10	NCS (6.0)	E	**22b** (Cl)	82	**23b** (Cl)	4
11	Me_3SiCl (1.5)	F	**24a** (Me_3Si)	81	**25a** (Me_3Si)	9
12	$Ph(Me)_2SiCl$ (1.5)	F	**24b** ($Ph(Me_2)Si$)	85	**25b** ($Ph(Me_2)Si$)	3
13	$ClCH_2(Me)_2SiCl$ (1.5)	F	**24c** (Me_2SiCH_2Cl)	68	**25c** (Me_2SiCH_2Cl)	13
14	Et_3SiCl (1.5)	F	**24d** (Et_3Si)	48	**25d** (Et_3Si)	28

[a] Allenic zinc reagents **3a** and **3m** were prepared by using 2 equiv of Bu_3ZnLi under conditions A and B in Table 1, respectively. [b] Conditions for the reaction with electrophiles; D (−75 °C for 3 h), E (at −85 to 0 °C over 1 h), and F (at −85 °C to rt over 2 h). [c] The allenic zinc reagent was used after treatment with $ZnCl_2$ (3 equiv).

Scheme 6



I_2, TMSCl, and pivaloyl chloride, respectively. The reactions of aldehydes proceeded stereoselectively as well to furnish *anti*-alcohols **38a**−**c**.

For the preparation of α-silylallenic zinc **29**, reactions were examined by using silylzincates $(PhMe_2Si)_3ZnLi$ and $(PhMe_2Si)_2BuZnLi$, which were prepared by the reaction of $ZnCl_2$ with $PhMe_2SiLi$ (3.0 equiv) and by the reaction of $ZnCl_2$ with $PhMe_2SiLi$ (2.0 equiv) and BuLi (1.0 equiv), respectively (Table 6).[12a] Although the reactions of mesylate **1a** and phosphate **1c** lead to the regioselective and high-yield formation of silylallene **42a** with minor formation of silylalkyne **43a** (entries 1−4), no deuterium was found in the products in the D_2O-quench experiments even when carbamate **1d** was employed (entry 5). The reaction of mixed zincate $(PhMe_2Si)_2BuZnLi$ gave silylation products **42a** and **43a** without formation of the butylation product **5a**. The yield of **42a** did not drop significantly even when 1.2 equiv of the mixed zincate were used. Previously, Fleming et al. have reported the preparation of silylallenes by the reaction of propargylic substrates with silylcuprates $[(R_3Si)_2CuLi]$.[26] As illustrated in entries 6 and 7, the reaction with the silylzincates is also applicable to other substrates and, therefore, serves as an alternative method for the preparation of silylallenes.

The relatively less basic nature of arylsilylmetals[27] may rationalize the absence of deuterium in the products. Alternatively, silylallene **42** would be produced through a direct S_N2'-type displacement by the silylzincates (eq 5) although such mechanism alone can not explain the formation of silylalkyne **43** as a minor product.[28] Irrespective to these mechanistic possibilities, it seemed that rapid generation of the intermediate alkynylzincate **41** is crucial for the successful generation of allenic zinc reagents **29**. It is well known that the rate of halogen/metal exchange is generally very fast even at low temperatures. Previously, we showed that *gem*-dibromo compounds undergo bromine/zinc exchange reaction rapidly with organozincates at low temperatures to give the corresponding zincate carbenoids.[3−5,29] More recently, the preparation of arylzincates by iodine/zinc exchange reaction of iodoarenes with organozincates have been reported.[30] These results prompted

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[26] (a) Fleming, I.; Terrett, N. K. *J. Organomet. Chem.* **1984**, *264*, 99. (b) Fleming, I.; Takai, K.; Thomas, A. P. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2269.

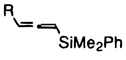
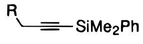
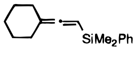
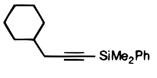
[27] Lambert, J. B.; Scultz, W. J., Jr. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1007.

[28] Treatment of $PhMe_2SiH$ with Bu_3ZnLi in THF at rt followed by addition of D_2O resulted in the recovery of $PhMe_2SiH$ without deuterium incorporation. Judging from the observation, it is less likely that silylallene **42** is formed through a mechanism involving a metathesis of the intermediate allenic zinc species and $PhMe_2SiH$ that would be produced initially in the reaction of the silylzincates with the terminal alkyne.

[29] Harada, T.; Katsuhira, T.; Hattori, K.; Oku, A. *Tetrahedron* **1994**, *50*, 7987.

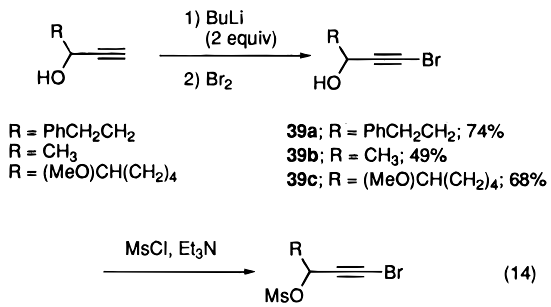
[30] Kondo, Y.; Takezawa, N.; Yamazaki, C.; Sakamoto, T. *J. Org. Chem.* **1994** *59*, 4717.

Table 6. Reaction of Propargylic Derivative **1** with Silylzincates[a]

entry	substrate	silylzincate	products			
			 **42** (R)	yield (%)[c]	 **43** (R)	ield (%)[c]
1	**1a**	$(PhMe_2Si)_3ZnLi$	**42a** ($PhCH_2CH_2$)	85	**43a** ($PhCH_2CH_2$)	14
2	**1a**	$(PhMe_2Si)_2(Bu)ZnLi$	**42a**	83	**43a**	14
3[b]	**1a**	$(PhMe_2Si)_2(Bu)ZnLi$	**42a**	72	**43a**	11
4	**1c**	$(PhMe_2Si)_3ZnLi$	**42a**	83	**43a**	15
5	**1d**	$(PhMe_2Si)_2(Bu)ZnLi$	**42a**	48	**1d**	49
6	**1l**	$(PhMe_2Si)_2(Bu)ZnLi$	**42b** ($(MeO)_2CH(CH_2)_4$)	89	**43b** ($(MeO)_2CH(CH_2)_4$)	5
7	**1m**	$(PhMe_2Si)_3ZnLi$	**42c** 	72	**43c** 	6

[a] Unless otherwise noted reactions were performed by using 2.0 equiv of silylzincates under conditions A in Table 1. [b] 1.2 Equiv of the silylzincate was used.

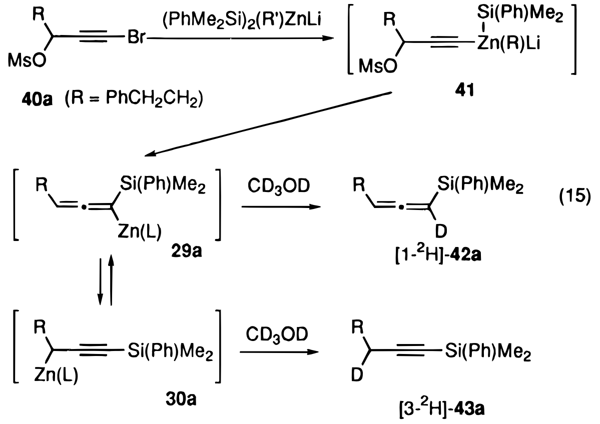
us to examine the reaction of bromopropargyl mesylates **40** and silylzincates (eq 15).



R = $PhCH_2CH_2$
R = CH_3
R = $(MeO)CH(CH_2)_4$

39a; R = $PhCH_2CH_2$; 74%
39b; R = CH_3; 49%
39c; R = $(MeO)CH(CH_2)_4$; 68%

40a; R = $PhCH_2CH_2$; 84%
40b; R = CH_3; 64%
40c; R = $(MeO)CH(CH_2)_4$; 84%



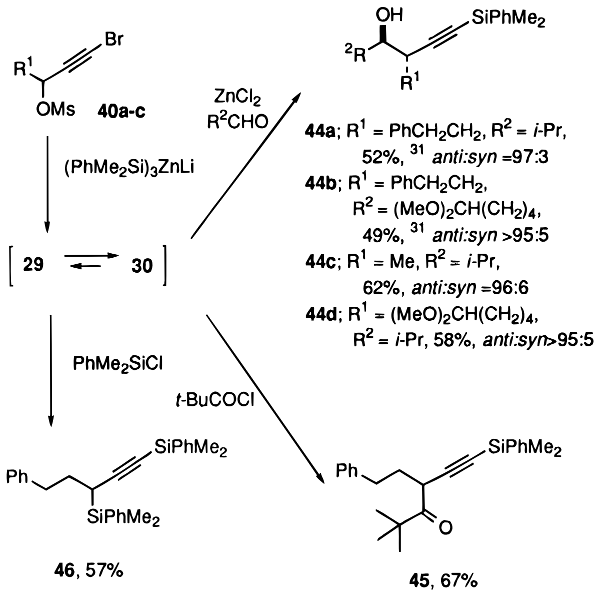
The requisite bromopropargyl mesylates **40a**−**c** were prepared readily by the reaction of dianion of the corresponding propargylic alcohols with Br_2 and subsequent mesylation of the resulting bromoalcohols **39a**−**c** (eq 14). The reaction of **40a** with $(PhMe_2Si)_3ZnLi$ (2 equiv) completed within 15 min at −85 °C. Treatment of the reaction mixture with CD_3OD at this temperature afforded silylalkyne [3-^{2}H]-**43a** and silylallene [1-^{2}H]-**42a** with high deuterium incorporation in 74% and 16% yield, respectively (Table 7, entry 1). The combined yield of propargylic zinc **30a** and allenic zinc **29a** which are in equilibrium under these conditions is estimated to be 82%. The efficient preparation of the organozinc reagents (77% yield) was also obtained even when 1.2 equiv of the silylzincate was used (entry 2). The use of mixed zincate $(PhMe_2Si)_2BuZnLi$ resulted in the less efficient generation of the **30a** and **29a** (entry 3). Disilylialkyne **46** (27%) (Scheme 7) and butylation product **5a** (17%) were produced as byproducts in this reaction. We, therefore, chose the reaction using a 1.2 equiv of $(PhMe_2Si)_3ZnLi$ (entry 2) as an optimal method and the silicon containing organozinc species **30** and **29** prepared by this method was used in the reaction with electrophiles.

Table 7. Reaction of Bromopropargyl Mesylate **40a** with Silylzincates[a]

entry	silylzincate	equiv	products	yield (%)	deuterium content (%)
1	$(PhMe_2Si)_3ZnLi$	2.0	**43a**	74	93
			42a	16	91
2	$(PhMe_2Si)_3ZnLi$	1.2	**43a**	75	93
			42a	9	82
3	$(PhMe_2Si)_2(Bu)ZnLi$	1.2	**43a**	34	88
			42a	4	78
			46	27	
4	Bu_3ZnLi	1.2	**5a**	37	>95
			48	41	

[a] Reactions were performed at −85 °C in THF for 15 min and quenched by the addition of CD_3OD.

Scheme 7



44a; R^1 = $PhCH_2CH_2$, R^2 = *i*-Pr, 52%,[31] *anti:syn* =97:3
44b; R^1 = $PhCH_2CH_2$, R^2 = $(MeO)_2CH(CH_2)_4$, 49%,[31] *anti:syn* >95:5
44c; R^1 = Me, R^2 = *i*-Pr, 62%, *anti:syn* =96:6
44d; R^1 = $(MeO)_2CH(CH_2)_4$, R^2 = *i*-Pr, 58%, *anti:syn*>95:5

As demonstrated in Scheme 7, silylzinc reagents **30** and **29** generated under these conditions underwent regioselective coupling reaction with electrophiles to give the corresponding functionalized silylalkynes **44**−**46**.[31] Although the result of CD_3OD-quench experiment showed that propargylic zinc **30** is a predominant species in the equilibrium,[32] the coupling reactions most probably took place from a minor but more reactive allenic zincs judging from regioselective formation of propargylic adducts as well as high *anti*-selectivity in the reaction with aldehydes. The results also indicates relatively fast rate of equilibration between **29** and **30**.

It should be noted that, upon warming up the reaction mixture of **40a** and $(PhMe_2Si)_3ZnLi$ silylzinc reagents to rt without addition of $PhMe_2SiCl$, disilylalkyne **46** was obtained in 31%. The result supports the formation of $PhMe_2SiBr$ by the bromine/zinc exchange with the silylzincate. The sililylation by $PhMe_2SiBr$ was almost negligible at −85 °C judging from a minor formation of **46** (<5%) in CD_3OD-quench experiment (Table 7, entries 1 and 2).[33] The reaction of **40a** with Bu_3ZnLi (1.2 equiv) gave not only allene [5-^{2}H]-**5a** with high deuterium incorporation (37%) but also bromoallene $PhCH_2CH_2CH{=}C{=}C(Br)Bu$ (**48**) (41%), which might be formed by bromine/zinc exchange reaction of unreacted substrate **40a** with zinc reagents **29a** and/or **30a** (entry 5). The result, therefore, suggests that silylzincates are more reactive in bromine/zinc exchange reaction than trialkylzincates.

In summary, we have developed a general method for the three-carbon homologation of triorganozincates by the reaction of propargylic substrates **1** (Scheme 2). With the combination of the propargylic substrates and organozincates, a wide range of allenic zinc reagents **3**, including the silyl derivatives **26** and **29**, are available. The allenic zinc reagents underwent coupling reaction with a variety of electrophiles regioselectively at the γ positions to give the corresponding propargylic derivatives **4**, providing an efficient one-pot method for introduction of a nucleophile (R^1) and an electrophile (El) to the propargylic substrates at the 1,3-positions. Of these, the reaction with aldehydes proceeded with high stereoselectivity as well to give *anti*-homopropargyl alcohols.

Experimental Section

General Methods. Unless otherwise noted ^{1}H- and ^{13}C-NMR spectra were recorded at 300 MHz and 75.6 MHz, respectively, in $CDCl_3$. All commercially available reagents were used without further purification unless otherwise noted. Triethylamine, *N*,*N*-diisopropylethylamine, chlorotrimethylsilane, and dichloromethane were distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. All reactions were performed under argon. Unless otherwise noted, organic extracts were dried over $MgSO_4$. Flash chromatography was conducted on silica gel (Wakogel C-300). For the preparation of starting materials **1a**−**q** and **40a**−**c**, see Supporting Information.

General Procedure for the Preparation of Triorganozincates R_3ZnM (M = Li or MgCl). To a solution of $ZnCl_2$ (191 mg, 1.4 mmol) in THF (4.2 mL) at 0 °C was added a solution of RM (4.2 mmol) (BuLi; 1.6 M in hexane; BuMgBr; 1 M in THF, MeLi; 1.4 M in ether, *s*-BuLi, 1.3 M in cyclohexane; *t*-BuLi; 1.5 M in pentane, PhLi; 1 M in cyclohexane-ether, $TMSCH_2Li$; 1 M in pentane, $PhMe_2SiLi$;[34] 1 M in THF). The mixture was stirred for 15 min at 0 °C. Mixed zincates $Et_2(R)ZnLi$ were prepared as follows: To a solution of Et_2Zn (2 mmol, 1 M in hexane) in THF (6 mL) at 0 °C was added RM (2 mmol), and the mixture was stirred for 15 min at this temperature.

General Procedure for the Preparation of Allenic Zincs 3a−m (D_2O-Quench Experiment, Table 2). To a solution of triorganozincates (1.4 mmol) in THF at −85 °C was added a solution of propargylic derivative **1** (0.7 mmol) in THF (1 mL) and the mixture was stirred for 15 min. The cooling bath was exchanged to the one at 0 °C and the mixture was stirred further for 15 min. After addition of D_2O (ca. 0.5 mL), the mixture was poured into 1 N HCl and extracted three times with ether. The combined organic layers were washed with $NaHCO_3$ (5%), dried, and concentrated. The residue was purified by flash chromatography (pentane or hexane) to afford deuterio allenes **5a**−**m**. The deuterium contents were analyzed by ^{1}H NMR. Spectral data of non-deuterio allenes **5a**,**b**, prepared separately by quenching **3** with H_2O, are as follows.

1-Phenyl-3,4-nonadiene (5a): ^{1}H-NMR δ 0.90 (3H, m), 1.27−1.42 (4H, m), 1.96 (2H, m), 2.31 (2H, m), 2.73 (2H, br t, J = *ca.* 8 Hz), 5.05−5.18 (2H, m), 7.16−7.32 (5H, m); ^{13}C-NMR δ 203.9, 141.9, 128.5, 128.2, 125.8, 91.5, 90.2, 35.5, 31.3, 30.7, 28.6, 22.2, 13.9; IR (liquid film) 1960, 1600, 1495, 1450, 870, 740, 695 cm^{-1}; MS, *m*/*z* (relative intensity) 200 (M^+,4), 157 (20), 144 (32), 129 (50), 91 (100); HRMS calcd for $C_{15}H_{20}$; 200.1566, found; 200.1562. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found C, 90.18; H, 10.30.

5-Phenyl-2,3-hexadiene (5b): ^{1}H-NMR δ 1.62 (3H, dd, J = 3.5 and 6.7 Hz), 2.27−2.36 (2H, m), 2.74 (2H, br t, J = *ca.* 8 Hz), 5.02−5.16 (2H, m), 7.17−7.33 (5H, m); IR (liquid film) 1965, 1605, 1495, 1450, 870, 745, 700 cm^{-1}; MS, *m*/*z* (relative intensity) 158 (M^+, 7), 143 (36), 129 (81), 91 (100); HRMS calcd for $C_{12}H_{14}$; 158.1096, found; 158.1092. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found C, 90.95; H, 9.04.

General Procedure for the Preparation of Homopropargyl Alcohols 14a−x. Allenic zinc intermediate **3** was prepared from propargylic mesylate **1** (1.0 mmol) by a procedure described above. To a solution of the allenic zinc **3** at −85 °C was added a solution of $ZnCl_2$ (1.0 M in THF) (3.0 mL, 3.0 mmol) over 15 min by using a syringe-pump. The mixture was stirred for additional 1 h at the same temperature. An aldehyde (1.5 mmol) was then added, and the mixture was allowed to warm to 0 °C during 2 h. The mixture was poured into 1 N HCl (20 mL) and extracted three times with ether. The combined organic layers were washed with 5% $NaHCO_3$, dried, and concentrated in vacuo. Purification of the residue by flash chromatography (5−20% ethyl acetate in hexane or 10−20% ether in pentane) afforded homopropargyl alcohols **14a**−**x**.

(3*R,4*S**)-4-Octyl-1-phenyl-5-decyn-3-ol (*anti*-14a):** bp 170−180 °C/0.15 mmHg (Kugelrohr); ^{1}H-NMR δ 0.88 (3H, t, J = 6.8 Hz), 0.91 (3H, t, J = 7.2 Hz), 1.22−1.54 (18H, m), 1.70−1.93 (3H, m, including OH), 2.19 (2H, dt, J = 2.1 and 6.8 Hz), 2.39 (1H, m), 2.68 (1H, td, J = 8.2 and 14.0 Hz), 2.82 (1H, ddd, J = 6.7, 8.6, and 14.0 Hz), 3.44 (1H, br q), 7.15−7.31 (5H, m); ^{13}C-NMR δ 142.2, 128.4, 128.3, 125.7, 84.7, 79.0, 72.6, 39.4, 37.5, 32.14, 32.12, 31.9, 31.1, 29.5, 29.4, 29.2, 27.6, 22.7, 21.9, 18.4, 14.1, 13.6; IR (liquid film) 3550 (br), 3430 (br), 1465, 1450, 745, 725, 695 cm^{-1}; MS (CI), *m*/*z* (relative intensity) 343 (MH^+, 2), 325 (11), 238 (9), 110 (100), 91 (88); HRMS (CI) calcd for $C_{24}H_{39}O$ (MH^+); 343.3003, found; 343.3004. Anal. Calcd for $C_{24}H_{38}O$: C, 84.15; H, 11.18. Found C, 84.12; H, 11.03.

(3*S,4*S**)-4-Octyl-1-phenyl-5-decyn-3-ol (*syn*-14a):** ^{1}H-NMR δ 0.88 (3H, t, J = 7.0 Hz), 0.91 (3H, t, J = 7.1 Hz), 1.20−1.54 (18H, m), 1.74 (1H (OH), br d, J = 6.7 Hz), 1.76−1.97 (2H, m), 2.18 (2H, dt, J = 2.2 and 6.8 Hz), 2.50 (1H, m), 2.67 (1H, ddd, J = 7.0, 9.6, and 13.7 Hz), 2.90 (1H, ddd, J = 5.4, 9.8, and 13.7 Hz), 3.55 (1H, m), 7.16−7.32 (5H, m); ^{13}C-NMR δ 142.3, 128.5, 128.3, 125.7, 83.9, 80.0, 73.0, 39.4, 35.4, 32.2, 31.9, 31.2, 30.5, 29.5, 29.4, 29.3, 27.6, 22.7, 21.9, 18.4, 14.1, 13.6; IR (liquid film) 3550 (sh), 3390 (br), 1465, 1455, 750, 725, 700 cm^{-1}; MS (CI), *m*/*z* (relative intensity) 343 (MH^+, 1.2), 325 (7), 238 (10), 138 (76), 110 (94), 91 (100); HRMS (CI) calcd for $C_{24}H_{39}O$ (MH^+); 343.3003, found; 343.3006.

(3*R,4*S**)-4-Octyl-5-decyn-3-ol (*anti*-14b):** bp 80−85 °C/0.15 mmHg (Kugelrohr); ^{1}H-NMR δ 0.87 (3H, t, J = 7.0 Hz), 0.90 (3H, t, J = 7.3 Hz), 0.95 (3H, t, J = 7.4 Hz), 1.20−1.62 (20H, m), 1.73 (1H (OH), br d, J = 5 Hz), 2.18 (2H, dt, J = 2.2 and 6.9 Hz), 2.38 (1H, m), 3.32 (1H, br s); ^{13}C-NMR δ 84.5, 79.2, 74.7, 38.8, 32.2, 31.9, 31.2,

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(31) The byproduct formation of isomeric allenic alcohols was observed in the reaction of silylzinc reagents **30a** and **29a**: the reactions with 2-methylpropanal and 6,6-dimethoxyhexanal gave 7-methyl-1-phenyl-5-(dimethylphenylsilyl)-3,4-octadien-6-ol (**47a**) (14%) and 11,11-dimethoxy-1-phenyl-5-(dimethylphenylsilyl)-3,4-undecadien-6-ol (**47b**) (11%), respectively.

(32) When the reaction of **40a** and (PhMe2Si)3ZnLi (1.2 equiv) was quenched with CD_3OD after treatment with $ZnCl_2$ (1.6 equiv), silylalkyne [3-^{2}H]-**43a** (89%-*d*) and silylallene [1-^{2}H]-**42a** (58%-*d*) were obtained in 77% and 7.8% yield, respectively.

(33) On the other hand, nonnegligible amount of **46** (27%) was produced in the reaction of $(PhMe_2Si)_2BuZnLi$. The difference in reactivity might be derived from the differences of ligands.

(34) Gilman, H.; Lichtenwalter, G. D. *J. Am. Chem. Soc.* **1958**, *80*, 607.

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29.51, 29.44, 29.3, 28.5, 27.6, 22.7, 21.9, 18.4, 14.1, 13.6, 10.2; IR (liquid film) 3570 (br), 3425 (br), 1465, 1460, 1105, 975 cm^{-1}; MS (CI), *m/z* (relative intensity) 267 (MH$^+$, 3), 249 (9), 237 (3), 166 (7), 137 (10), 123 (13), 110 (100); HRMS (CI) calcd for $C_{18}H_{35}O$ (MH$^+$); 267.2690, found; 267.2689. Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found C, 80.99; H, 12.86.

(3*S,4*S**)-4-Octyl-5-decyn-3-ol (*syn*-14b):** ^{1}H-NMR δ 0.88 (3H, t, $J = 7.0$ Hz), 0.91 (3H, t, $J = 7.1$ Hz), 0.99 (3H, t, $J = 7.4$ Hz), 1.20−1.69 (21H, m, including OH (br d, $J = 6.4$ Hz) at 1.65), 2.18 (2H, dt, $J = 2.2$ and 6.9 Hz), 2.47 (1H, m), 3.44 (1H, m); ^{13}C-NMR δ 83.7, 80.3, 75.2, 39.0, 31.9, 31.2, 30.3, 29.53, 29.50, 29.3, 27.6, 26.5, 22.7, 21.9, 18.4, 14.1, 13.6, 10.3; IR (liquid film) 3360 (br), 1465, 1460, 1110, 975 cm^{-1}; MS (CI), *m/z* (relative intensity) 267 (MH$^+$, 5), 265 (5), 249 (16), 123 (23), 110 (100); HRMS (CI) calcd for $C_{18}H_{35}O$ (MH$^+$); 267.2690, found; 267.2682.

General Procedure for Acylation Allenic Zinc 3a. Allenic zinc **3a** was prepared from propargylic mesylate **1a** (167 mg, 0.7 mmol) by a procedure described previously. To a solution of **3a** at −75 °C was added an acylchloride (1.05 mmol) or ethyl chloroformate (2.1 mmol), and the resulting mixture was then stirred at −75 °C temperature for 3 h. The mixture was poured into 1 N HCl (20 mL) and extracted three times with ethyl acetate (15 mL). The combined organic extracts were washed with 5% $NaHCO_3$, dried, and concentrated in vacuo. Purification of the residue by flash chromatography using cooled (*ca.* 5 °C) 5−10% ether in hexane as an eluent afforded a mixture of the propargylic ketone **19** and the allenic ketone **20**. The spectral data of the propargylic products **19a**,**f** and the allenic ketone **20f** are as follows.

3-(2-Phenylethyl)-4-nonyn-2-one (19a): bp 120−130 °C/0.05 mmHg (Kugelrohr); ^{1}H-NMR δ 0.93 (3H, t, $J = 7.2$ Hz), 1.37−1.57 (4H, m), 1.85−2.08 (2H, m), 2.24 (2H, dt, $J = 2.4$ and 6.9 Hz), 2.27 (3H, s), 2.68 (1H, ddd, $J = 7.4$, 8.8, and 13.7 Hz), 2.80 (1H, ddd, $J = 5.7$, 9.0, and 13.7 Hz), 3.14 (1H, tdd, $J = 2.4$, 5.2, and 8.8 Hz), 7.15−7.31 (5H, m) [a minor product **20a** resonated at 2.10 (3H, s) and 5.57 (1H, tt, $J = 2.5$ and 7.0 Hz)]; ^{13}C-NMR δ 205.9, 141.2, 128.5, 128.4, 126.0, 85.7, 76.8, 45.0, 33.0, 32.8, 30.8, 27.6, 21.9, 18.4, 13.5; IR (liquid film) 1720, 1495, 1450, 1355, 750, 695 cm^{-1}; MS, *m/z* (relative intensity) 242 (M$^+$, 4), 241 (9), 199 (3), 185 (6), 138 (23), 91 (74), 43 (100); HRMS calcd for $C_{17}H_{22}O$; 242.1671, found; 242.1666. Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found C, 84.07; H, 9.05.

1-Acetyl-1-(1-hexynyl)cyclohexane (19f): bp 80−90 °C/0.07 mmHg (Kugelrohr); ^{1}H-NMR δ 0.90 (3H, t, $J = 7.2$ Hz), 1.15 (1H, m), 1.34−1.80 (13H, m), 2.21 (2H, t, $J = 6.8$ Hz), 2.29 (3H, s); ^{13}C-NMR δ 209.0, 85.9, 80.8, 49.7, 33.8, 31.0, 25.7, 25.6, 22.4, 21.9, 18.5, 13.6; IR (liquid film) 2230 (m), 1715, 1450, 1350, 1210, 1170 cm^{-1}; MS, *m/z* (relative intensity) 206 (M$^+$, 2), 191 (4), 177 (4), 163 (46), 121 (37), 93 (46), 79 (65), 67 (87), 43 (100); HRMS calcd for $C_{14}H_{22}O$; 206.1672, found; 206.1684. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found C, 81.24; H, 10.67.

3-(Cyclohexylidene)methyleneheptan-2-one (20f): bp 90−95 °C/0.06 mmHg (Kugelrohr); ^{1}H-NMR δ 0.87 (3H, m), 1.22−1.39 (4H, m), 1.52−1.70 (6H, m), 2.10−2.15 (2H, m), 2.18−2.26 (7H, m, including s (3H) at 2.22); ^{13}C-NMR δ 206.9, 200.0, 107.6, 106.4, 30.6, 30.1, 27.1, 26.8, 26.2, 25.8, 22.1, 13.9; IR (liquid film) 1945, 1675, 1445, 1350, 1260, 1245, 1230, 1215 cm^{-1}; MS, *m/z* (relative intensity) 206 (M$^+$, 6), 191 (3), 177 (3), 164 (22), 163 (23), 121 (28), 93 (29), 79 (44), 67 (57), 43 (100); HRMS calcd for $C_{14}H_{22}O$; 206.1672, found; 206.1659. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found C, 81.24; H, 10.99.

General Procedure for the Transformation of Alkynones 19a−d to Allenic Ketones 23a−d. To a solution of alkynone **19** (0.25 mmol) in ethanol (2.0 mL) at rt was added Et_3N (0.053 mL, 0.38 mmol), and the mixture was stirred for 15 h at rt. Concentration of the mixture in vacuo and purification of the residue by flash chromatography (5% ether in hexane) gave allenic ketone **23**. The spectral data of **23a**,**b** are as follows.

3-(2-Phenylethyl)-3,4-nonadien-2-one (23a): bp 120−130 °C/0.05 mmHg (Kugelrohr); ^{1}H-NMR δ 0.90 (3H, m), 1.25−1.42 (4H, m), 2.00−2.07 (2H, m), 2.25 (3H, s), 2.39−2.58 (2H, m), 2.7 (2H, br t, J = *ca. 8* Hz), 5.50(1H, tt, $J = 2.6$ and 7.0 Hz), 7.13−7.29 (5H, m); ^{13}C-NMR δ 212.4, 199.2, 141.6, 128.5, 128.2, 125.8, 108.7, 95.7, 34.0, 31.1, 28.3, 27.8, 26.9, 22.2, 13.8; IR (liquid film) 1950, 1680, 1355, 1230, 750, 700 cm^{-1}; MS, *m/z* (relative intensity) 242 (M$^+$, 9), 241 (21), 199 (6), 185 (10), 151 (10), 91 (51), 43 (100); HRMS calcd for $C_{17}H_{22}O$; 242.1672, found; 242.1664. Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found C, 84.13; H, 9.28.

6-(2-Phenylethyl)-6,7-dodecadien-5-one (23b): ^{1}H-NMR δ 0.89 (3H, t, $J = 7.3$ Hz), 0.90 (3H, t, $J = 7.0$ Hz), 1.23−1.42 (6H, m), 1.49−1.59 (2H, m), 1.99−2.07 (2H, m), 2.39−2.62 (4H, m, including dtd (1H, $J = 2.5$, 8.0, and 14.6 Hz) at 2.45 and br t (2H) at 2.59), 2.70 (2H, br t), 5.48 (1H, tt, $J = 2.5$ and 7.0 Hz), 7.13−7.29 (5H, m); ^{13}C-NMR δ 211.8, 202.0, 141.7, 128.5, 128.2, 125.7, 108.1, 95.7, 38.9, 34.1, 31.2, 28.5, 27.9, 27.3, 22.4, 22.2, 13.85, 13.79; IR (liquid film) 1945, 1675, 1455, 745, 695 cm^{-1}; MS, *m/z* (relative intensity) 284 (M$^+$, 14), 283 (22), 227 (11), 193 (6), 91 (54), 85 (73), 57 (100); HRMS calcd for $C_{20}H_{28}O$; 284.2141, found; 284.2143.

3-Iodo-1-phenyl-4-nonyne (22a). To a solution of allenic zinc **3a**, prepared from **1a** (0.7 mmol) as described previously, at −85 °C, was added a solution of I_2 (1.07 g, 4.2 mmol) in THF (1 mL) over a period of 15 min by using a syringe-pump. The mixture was allowed to warm to 0 °C over 1 h, then poured into 1 N HCl (20 mL), and extracted three times with ether (15 mL). The combined organic extracts were washed successively with saturated $NaHSO_3$ and 5% $NaHCO_3$, dried, and concentrated in vacuo. Purification of the residue by flash chromatography (hexane) gave 185 mg (81%) of **22a** and 13.7 mg (6%) of 5-iodo-1-phenyl-3,4-nonadiene (**23a**). **22a:** bp 120−140 °C/0.05 mmHg (Kugelrohr); ^{1}H-NMR δ 0.92 (3H, t, $J = 7.2$ Hz), 1.36−1.56 (4H, m), 2.13−2.33 (4H, m), 2.70−2.88 (2H, m), 4.52 (1H, tt, $J = 2.3$ and 6.8 Hz), 7.18−7.33 (5H, m); ^{13}C-NMR δ 140.2, 128.6, 128.5, 126.2, 88.2, 81.5, 43.2, 35.3, 30.5, 21.9, 18.8, 13.6, 11.8; IR (liquid film) 2225, 1495, 1450, 745, 700 cm^{-1}; MS, *m/z* (relative intensity) 199 (M$^+$ − I, 5), 143 (18), 129 (9), 117 (11), 91 (100). Anal. Calcd for $C_{15}H_{19}I$: C, 55.23; H, 5.87. Found C, 55.39; H, 5.90. **23a:** ^{1}H-NMR δ 0.90 (3H, br t, J = *ca.* 7 Hz), 1.25−1.44 (4H, m), 2.25−2.32 (2H, m), 2.32−2.49 (2H, m), 2.76 (2H, br t, J = *ca.* 7.6 Hz), 5.04 (1H, tt, $J = 2.9$ and 6.5 Hz), 7.17−7.33 (5H, m); ^{13}C-NMR δ 202.3, 141.2, 128.42, 128.36, 126.0, 93.4, 63.9, 40.6, 34.6, 31.2, 29.9, 21.4, 13.8; IR (liquid film) 1950, 1600, 1495, 1450, 1105, 740, 695 cm^{-1}; MS, *m/z* (relative intensity) 199 (M$^+$ − I, 4), 143 (21), 129 (12), 117 (12), 91 (100).

3-Chloro-1-phenyl-4-nonyne (22b). To a stirred solution of allenic zinc **3a**, prepared from **1a** (0.7 mmol) as described previously, at −85 °C, was added *N*-chlorosuccinimide (0.56 g, 4.2 mmol) in one portion. The resulting suspension was then allowed to warm to 0 °C over 1 h. The mixture was poured into 1 N HCl (20 mL), and it was extracted three times with ether (15 mL). The combined extracts were washed with 5% $NaHCO_3$, dried, and concentrated in vacuo. Purification of the residue by flash chromatography (hexane) gave 135 mg (82%) of **22b** and 6.6 mg (4%) of 5-chloro-1-phenyl-3,4-nonadiene (**23b**). **22b:** bp 105−115 °C/0.06 mmHg (Kugelrohr); ^{1}H-NMR δ 0.92 (3H, t, J = 7.2 Hz), 1.35−1.56 (4H, m), 2.17−2.28 (4H, m), 2.84 (2H, br t, J = *ca.* 7 Hz), 4.52 (1H, tt, $J = 2.1$ and 6.7 Hz), 7.17−7.33 (5H, m); ^{13}C-NMR δ 140.4, 128.51, 128.48, 126.2, 87.7, 78.3, 48.8, 41.1, 32.3, 30.5, 21.9, 18.5, 13.6; IR (liquid film) 2240, 1605, 1495, 1465, 1455, 1330, 750, 700 cm^{-1}; MS, *m/z* (relative intensity) 234 (M$^+$, 0.3), 199 (M$^+$ − Cl, 9), 198 (6), 155 (26), 141 (22), 129 (22), 91 (100); HRMS calcd for $C_{15}H_{19}Cl$; 234.1177, found; 234.1200. Anal. Calcd for $C_{15}H_{19}Cl$: C, 76.74; H, 8.16. Found C, 76.89; H, 8.14. **23b:** ^{1}H-NMR δ 0.89 (3H, t, $J = 7.2$ Hz), 1.24−1.47 (4H, m), 2.26 (2H, dt, $J = 2.9$ and 7.2 Hz), 2.32−2.50 (2H, m), 2.75 (2H, m), 5.52 (1H, tt, $J = 2.9$ and 6.4 Hz), 7.15−7.31 (5H, m); ^{13}C-NMR δ 199.2, 141.2, 128.4, 128.3, 126.0, 106.2, 99.1, 36.1, 34.7, 30.9, 29.2, 21.7, 13.8; IR (liquid film) 1970, 745, 700 cm^{-1}; MS, *m/z* (relative intensity) 234 (M$^+$, 0.3), 199 (3), 178 (9), 155 (14), 91 (100); HRMS calcd for $C_{15}H_{19}Cl$; 234.1177, found; 234.1180.

General Procedure for the Silylation of Allenic Zinc 3a. To a stirred THF solution of allenic zinc **3a**, prepared from **1a** (0.7 mmol), at −85 °C was added a chlorotriorganosilane (1.5 mmol). The mixture was then allowed to warm to 0 °C over 2 h. The mixture was poured into 1 N HCl (20 mL) and extracted three times with ether (15 mL). The combined extracts were washed with 5% $NaHCO_3$, dried, and concentrated in vacuo. Purification of the residue by flash chromatography (1−6% ether in hexane) gave propargylic silane **24** and allenic silane **25**. The spectral data of **24a**,**b** and **25a**,**b** are as follows.

1-Phenyl-3-trimethylsilyl-4-nonyne (24a): ^{1}H-NMR δ 0.04 (9H, s), 0.92 (3H, t, $J = 7.1$ Hz), 1.38−1.73 (7H, m), 2.22 (2H, dt, $J = 2.2$ and 6.7 Hz), 2.65 (1H, ddd, $J = 7.4$, 8.7, and 13.5 Hz), 2.98 (1H, ddd, $J = 5.3$, 8.2, and 13.5 Hz), 7.14−7.31 (5H, m); ^{13}C-NMR δ 142.5, 128.6, 128.2, 125.6, 81.2, 81.3, 35.8, 31.7, 31.6, 21.9, 19.4, 18.7, 13.6, −3.2; IR (liquid film) 2220 (m), 1250, 865, 840, 745, 695 cm^{-1}; MS, *m/z* (relative intensity) 257 ($M^+ - CH_3$, 0.1), 198 (5), 91 (16), 73 (100). Anal. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36. Found C, 79.23; H, 10.24.

1-Phenyl-5-trimethylsilyl-3,4-nonadiene (25a): ^{1}H-NMR δ 0.07 (9H, s), 0.89 (3H, t, $J = 7.1$ Hz), 1.25−1.43 (4H, m), 1.91 (2H, m), 2.27 (2H, m), 2.69 (2H, m), 4.84 (1H, tt, $J = 3.0$ and 6.5 Hz), 7.14−7.31 (5H, m); ^{13}C-NMR δ 205.2, 142.2, 128.5, 128.2, 125.7, 96.9, 84.9, 36.2, 31.3, 30.5, 29.1, 22.4, 14.0, −1.4; IR (liquid film) 1935, 1245, 835, 745, 695 cm^{-1}; MS, *m/z* (relative intensity) 257 ($M^+ - CH_3$, 0.1), 198 (7), 91 (11), 73 (100).

1-Phenyl-3-(dimethylphenylsilyl)-4-nonyne (24b): bp 150−160 °C/1.9 mmHg (Kugelrohr); ^{1}H-NMR δ 0.340 (3H, s), 0.348 (3H, s), 0.92 (3H, t, $J = 7.1$ Hz), 1.36−1.56 (4H, m), 1.58−1.70 (2H, m), 1.81 (1H, m), 2.22 (2H, dt, $J = 2.5$ and 6.8 Hz), 2.61 (1H, td, $J = 8.4$ and 13.5 Hz), 2.94 (1H, ddd, $J = 6.0$, 7.5, and 13.5 Hz), 7.12−7.39 (8H, m), 7.51−7.55 (2H, m); ^{13}C-NMR δ 142.3, 137.2, 134.0, 129.1, 128.6, 128.2, 127.6, 125.6, 81.9, 80.9, 35.6, 31.54, 31.45, 21.9, 19.0, 18.7, 13.7, −4.3, −5.1; IR (liquid film) 2220 (m), 1245, 1110, 830, 815, 775, 745, 730, 695 cm^{-1}. Anal. Calcd for $C_{23}H_{30}Si$: C, 82.57; H, 9.04. Found C, 82.40; H, 9.09.

1-Phenyl-5-(dimethylphenylsilyl)-3,4-nonadiene (25b): ^{1}H-NMR δ 0.33 (6H, s), 0.82 (3H, t, $J = 7.1$ Hz), 1.18−1.37 (4H, m), 1.87 (2H, br dt, $J =$ *ca.* 3.0 and 7.3 Hz), 2.27 (2H, br td, $J =$ *ca.* 6.5 and 8.9 Hz), 2.65 (2H, m), 4.88 (1H, tt, $J = 3.2$ and 6.6 Hz), 7.14−7.37 (8H, m), 7.49−7.55 (2H, m); ^{13}C-NMR δ 206.4, 142.1, 138.5, 133.8, 128.9, 128.4, 128.2, 127.7, 125.7, 95.6, 85.6, 36.1, 31.2, 30.5, 29.2, 22.3, 13.9, −2.85, −2.92; IR (liquid film) 1930, 1250, 1110, 830, 810, 775, 730, 695 cm^{-1}.

6-Phenyl-1-(trimethylsilyl)-2,3-hexadiene (32a) and 1-(Trimethylsilyl)-6-phenyl-2-hexyne (33a). The reaction of mesylate **1a** and $(TMSCH_2)_3ZnLi$ (2 equiv) was carried out by a procedure similar to that described in a general procedure for the preparation of allenic zinc **3a**−**m**. The D_2O-quench of the reaction and purification of the crude products by flash chromatography (1−5% benzene in hexane) gave [2-^{2}H]-**32a** (65%, 30%-*d*) and **33b** (30%, <5%-*d*). **32a:** ^{1}H-NMR δ 0.02 (9H, s), 1.24−1.30 (2H, m), 2.23−2.34 (2H, m), 2.71 (2H, t, $J = 7.8$ Hz), 5.50−5.15 (2H, m), 7.13−7.32 (5H, m); IR (liquid film) 1955, 1245, 850, 840, 695 cm^{-1}; MS, *m/z* (relative intensity) 230 (M^+, 3), 156 (28), 91 (29), 73 (100), 59 (20); HRMS calcd for $C_{15}H_{22}Si$; 230.1491, found; 230.1509. **33a:** ^{1}H-NMR δ 0.10 (9H, s), 1.44 (2H, t, $J = 2.7$ Hz), 1.77 (2H, tt, $J = 6.9$ and 7.7 Hz), 2.17 (2H, tt, $J = 2.7$ and 6.9 Hz), 2.71 (2H, t, $J = 7.7$ Hz), 7.15−7.3 (5H, m); IR (liquid film) 2210, 1245, 850, 740, 695 cm^{-1}; MS, *m/z* (relative intensity) 230 (M^+, <1), 215 (2), 156 (7), 104 (25), 91 (9), 73 (100); HRMS calcd for $C_{15}H_{22}Si$; 230.1491, found; 230.1478.

1-Cyclohexylidene-3-(trimethylsilyl)-1-propene (32b). The reaction of chloride **1m** and $(TMSCH_2)_3ZnLi$ (2 equiv) was carried out by a procedure similar to that described in a general procedure for the preparation of allenic zinc **3a**−**m**. The D_2O-quench of the reaction and purification of the crude products by flash chromatography (pentane) gave [2-^{2}H]-**32b** (71%, 31%-*d*). **32b:** ^{1}H-NMR δ 0.01 (9H, s), 1.26 (2H, d, $J = 8.1$ Hz), 1.54 (6H, m), 2.08 (4H, m), 4.93 (1H, quintet of t, J = 2.1 and 8.1 Hz); ^{13}C-NMR δ 198.6, 101.5, 84.7, 32.1, 27.5, 26.2, 18.5, −2.0; IR (liquid film) 1960, 1245, 850, 810 cm^{-1}; MS, *m/z* (relative intensity) 194 (M^+, 10), 179 (10), 120 (8), 73 (100); HRMS calcd for $C_{12}H_{22}Si$; 194.1492, found; 194.1491. Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found C, 73.99; H, 11.35.

Preparation of α-(Trimethylsilylmethyl)allenic Zinc 26a. To a solution of $(TMSCH_2)_3ZnLi$ (1.4 mmol) in THF at −85 °C was added a solution of diphenylcarbamate **1d** (0.7 mmol) in THF (1 mL). The mixture was stirred at −15 °C for 1 h and then at rt for 2 h. After addition of D_2O (ca. 0.5 mL), the mixture was poured into 1 N HCl and extracted three times with ether. The combined organic layers were washed with $NaHCO_3$ (5%), dried, and concentrated. The residue was purified by flash chromatography (1−5% benzene in hexane) to give allenes [2-^{2}H]-**32a** (51%, 95%-*d*) and alkyne [4-^{2}H]-**33b** (30%, 77%-*d*).

4-Iodo-1-trimethylsilyl-6-phenyl-2-hexyne (35a). The reaction of allenic zinc **26a** with iodine (6 equiv) was carried out by a procedure similar to that described in the preparation of **22a**. Purification of the crude products by flash chromatography (hexane) gave **35a** (65%): ^{1}H-NMR δ 0.14 (9H, s), 1.53 (2H, d, $J = 2.7$ Hz), 2.23 (2H, m), 2.81 (2H, m), 4.59 (1H, tt, $J = 2.7$ and 6.8 Hz), 7.2−7.3 (5H, m); IR (liquid film) 2220, 1250, 750, 700 cm^{-1}; MS, *m/z* (relative intensity) 229 ($M^+ - I$, 5), 213 (11), 155 (10), 91 (71), 73 (100); HRMS calcd for $C_{15}H_{21}Si$ ($M^+ - I$); 229.1413, found; 229.1415.

4-Iodo-9,9-dimethoxy-1-trimethylsilyl-2-nonyne (35b). The reaction of allenic zinc **26** (R = $(MeO)_2CH(CH_2)_4$), prepared by the reaction of carbamate **1p** with $(TMSCH_2)_3ZnLi$, with iodine (6 equiv) was carried out by a procedure similar to that described in the preparation of **22a**. Purification of the crude products by flash chromatography (2% ethyl acetate in hexane) gave **35b** (51%): ^{1}H-NMR δ 0.11 (9H, s), 1.3−1.7 (8H, m, including d ($J = 2.7$ Hz, 2H) at 1.49), 1.92 (2H, m), 4.36 (1H, t, $J = 5.7$ Hz), 4.63 (1H, m); IR (liquid film) 2220, 1250, 1130, 850 cm^{-1}; MS(CI), *m/z* (relative intensity) 351 ($MH^+ -$ MeOH, <1), 223 (14), 119 (86), 73 (100); HRMS calcd for $C_{13}H_{24}IOSi$ ($MH^+ -$ MeOH); 351.0643, found; 351.0651.

1,4-Bis(trimethylsilyl)-6-phenyl-2-hexyne (36a). The reaction of allenic zinc **26a** with chlorotrimethylsilane (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the silylation of allenic zinc **3a**. Purification of the crude products by flash chromatography (1% ethyl acetate in hexane) gave **36a** (61%): ^{1}H-NMR δ 0.03 (9H, s), 0.11 (9H, s), 1.50 (2H, d, $J = 2.2$ Hz), 1.5−1.7 (3H, m), 2.63 (1H, m), 2.99 (1H, m), 7.2−7.3 (5H, m); IR (liquid film) 1250 (s), 1170, 840, 745, 695 cm^{-1} (s); MS, *m/z* (relative intensity) 302 (M^+, 2), 271 (4), 229 (30), 123 (47), 73 (100); HRMS calcd for $C_{18}H_{30}Si_2$; 302.1886, found; 302.1881.

9,9-Dimethoxy-1,4-bis(trimethylsilyl)-2-nonyne (36b). The reaction of allenic zinc **26** (R = $(MeO)_2CH(CH_2)_4$), prepared by the reaction of carbamate **1p** with $(TMSCH_2)_3ZnLi$, with chlorotrimethylsilane (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the silylation of allenic zinc **3a**. Purification of the crude products by flash chromatography (10% benzene in hexane) gave **36b** (49%): ^{1}H-NMR δ 0.03 (9H, s), 0.07 (9H, s), 1.2−1.7 (11H, m, including d (2H, $J = 2.8$ Hz) at 1.44), 3.31 (6H, s), 4.36 (1H, t, $J = 5.7$ Hz); ^{13}C-NMR δ −3.09, −2.00, 7.28, 19.95, 24.34, 29.49, 29.67, 32.52, 52.60, 80.03, 104.64; IR (liquid film) 1930, 1250, 1125, 840 cm^{-1}; MS, *m/z* (relative intensity) 328 (M^+, <1), 177 (3), 89 (28), 73 (100); HRMS calcd for $C_{17}H_{36}Si_2O_2$; 328.2254, found; 328.2259. Anal. Calcd for $C_{17}H_{36}Si_2O_2$: C, 62.13; H, 11.04. Found C, 62.15; H, 11.19.

2,2-Dimethyl-4-(2-phenylethyl)-7-trimethylsilyl-5-heptyn-3-one (37a). The reaction of allenic zinc **26a** with pivaloyl chloride (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the acylation of allenic zinc **3a**. Purification of the crude products by flash chromatography (10−50% benzene in hexane) gave **37a** (49%): ^{1}H-NMR (200 MHz) δ 0.08 (9H, s), 1.16 (9H, s), 1.46 (2H, d, $J = 2.6$ Hz), 1.95 (2H, m), 2.5−2.8 (2H, m), 3.60 (1H, m), 7.2−7.3 (5H, m); IR (liquid film) 2220, 1710, 1250, 850, 745, 700 cm^{-1}; MS, *m/z* (relative intensity) 314 (M^+, 6), 313 (20), 299 (9), 257 (25), 91 (50), 73 (100); HRMS (CI) calcd for $C_{20}H_{31}SiO$ (MH^+); 315.2144, found; 315.2150.

2,2,4-Trimethyl-7-trimethylsilyl-5-heptyn-3-one (37b). The reaction of allenic zinc **26** (R = Me), prepared by the reaction of carbamate **1q** with $(TMSCH_2)_3ZnLi$, with pivaloyl chloride (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the acylation of allenic zinc **3a**. Purification of the crude products by flash chromatography (7% ethyl acetate in hexane) gave **37c** (64%): ^{1}H-NMR (200 MHz) δ 0.05 (9H, s), 1.20 (9H, s), 1.24 (3H, d, $J = 6.9$ Hz), 1.41 (2H, d, $J = 2.6$ Hz), 3.72 (1H, tq, J = 2.6 and 6.9 Hz); IR (liquid film) 2240, 1720, 1250, 1045, 850 cm^{-1}; MS, *m/z* (relative intensity) 224 (M^+, 4), 209 (12), 147 (20), 73 (80), 57 (100); HRMS calcd for $C_{13}H_{24}SiO$; 224.1596, found; 224.1594.

(3*R,4*S**)-2-Methyl-4-(2-phenylethyl)-7-trimethylsilyl-5-heptyn-3-ol (38a).** The reaction of allenic zinc **26a** with 2-methylpropanal (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the preparation of homopropargyl alcohols.

Purification of the crude products by flash chromatography (5−15% ethyl acetate in hexane) gave **38a** (47%): ^{1}H-NMR δ 0.12 (9H, s), 0.87 (3H, d, *J* = 6.7 Hz), 0.95 (3H, d, *J* = 6.7 Hz), 1.50 (2H, d, *J* = 2.5 Hz), 1.65−1.9 (4H, m), 2.50−2.94 (3H, m), 3.03 (1H, m), 7.15−7.3 (5H, m); IR (liquid film) 3500 (br), 2225, 1250, 850, 750, 700 cm^{-1}; MS, *m/z* (relative intensity) 259 (M+ − C$_3$H$_7$, 1), 230 (M$^+$ − Si(CH$_2$)Me$_2$, 10), 197 (8), 156 (34), 91 (42), 73 (100).

(3*R,4*S**)-(5,5-Dimethoxypentyl)-2-methyl-7-trimethylsilyl-5-heptyn-3-ol (38b).** The reaction of allenic zinc **26** (R = (MeO)$_2$CH(CH$_2$)$_4$), prepared by the reaction of carbamate **1p** with (TMSCH$_2$)$_3$ZnLi, with 2-methylpropanal (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the preparation of homopropargyl alcohols. Purification of the crude products by flash chromatography (10−30% ether in hexane) gave **38b** (44%): ^{1}H-NMR δ 0.08 (9H, s), 0.89 (3H, d, *J* = 6.6 Hz), 0.97 (3H, d, J = 6.6 Hz), 1.2−1.8 (12H, m, including d (2H, *J* = 2.5 Hz) at 1.45), 2.53 (1H, m), 2.99 (1H, dt, *J* = 3.5 and 8.0 Hz), 3.30 (6H, s), 4.35 (1H, t, *J* = 5.7 Hz); IR (liquid film) 3450 (br), 2220, 1130, 850 cm^{-1}; MS (CI), *m/z* (relative intensity) 297 (MH$^+$ − MeOH, 8), 265 (28), 249 (6), 209 (25), 73 (100); HRMS (CI) calcd for C$_{17}$H$_{33}$O$_2$Si (MH$^+$ − MeOH); 297.2250, found; 297.2252.

(4*S,5*R**)-10,10-Dimethoxy-4-methyl-1-trimethylsilyl-2-decyn-5-ol (38c).** The reaction of allenic zinc **26** (R = Me), prepared by the reaction of carbamate **1q** with (TMSCH$_2$)$_3$ZnLi, with 6.6-dimethoxyhexanal (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the preparation of homopropargyl alcohols. Purification of the crude products by flash chromatography (5−15% ethyl acetate in hexane) gave **38c** (56%): Isolated by flash chromatography (5−15% ethyl acetate in hexane); ^{1}H-NMR δ 0.09 (9H, s), 1.17 (3H, d, *J* = 7.0 Hz), 1.34−1.64 (10H, m, including d (2H, *J* = 2.5 Hz) at 1.45), 1.78 (1H, brd, *J* = ca. 7 Hz), 2.48 (1H, m), 3.3−3.4 (7H, m, including s (6H) at 3.31), 4.36 (1H, t, *J* = 5.7 Hz); IR (liquid film) 3470 (br), 2220, 1250, 1130, 850 cm^{-1}; MS(CI), *m/z* (relative intensity) 269 (MH$^+$ − MeOH, 24), 237 (6), 147 (17), 129 (42), 115 (25), 73 (100); HRMS (CI) calcd for C$_{15}$H$_{29}$O$_2$Si (MH$^+$ − MeOH); 269.1937, found; 269.1929.

1-(Dimethylphenylsilyl)-5-phenyl-1,2-pentadiene (42a) and 1-(Dimethylphenylsilyl)-5-phenyl-1-pentyne (43a). The reaction of mesylate **1a** with (PhMe$_2$Si)$_3$ZnLi (2 equiv) was carried out by a procedure similar to that described in a general procedure for the preparation of allenic zinc **3a**−**m**. Purification of the crude products by flash chromatography (1−5% benzene in hexane) gave **42a** (85%) and **43a** (14%). **42a:** ^{1}H-NMR δ 0.26 (6H, s), 2.24−2.33 (2H, m). 2.66 (t, *J* = 7.9 Hz), 4.87 (1H, q, *J* = 6.7 Hz), 5.07 (1H, td, *J* = 3.5 and 6.8 Hz), 7.15−7.4 (8H, m), 7.77 (2H, m); ^{13}C-NMR δ 211.0, 141.8, 138.6, 133.7, 129.1, 128.4, 128.2, 127.7, 125.8, 83.4, 81.5, 36.0, 29.7, −2.27, −2.32; IR (liquid film) 1935, 1245, 1110, 830, 810, 780, 730, 695 cm^{-1}; MS, *m/z* (relative intensity) 278 (M$^+$, 1), 200 (29), 185 (10), 135 (100); HRMS calcd for C$_{19}$H$_{22}$Si; 278.1492, found; 278.1486. **43a:** ^{1}H-NMR δ 0.40 (6H, s), 1.86 (2H, quintet, *J* = 7.2 Hz), 2.28 (2H, t, J = 7.1 Hz), 2.74 (2H, t, J = 7.8 Hz) 7.15−7.3 (8H, m), 7.65 (2H, m); IR (liquid film) 2170, 1245, 1110, 835, 815, 775, 730, 695 cm^{-1}; MS (CI), *m/z* (relative intensity) 279 (MH$^+$, 7), 263 (22), 200 (13), 185 (4), 125 (100), 91 (16), 65 (4); HRMS calcd for C$_{19}$H$_{22}$Si; 278.1492, found; 278.1487.

8,8-Dimethoxy-1-(dimethylphenylsilyl)-1,2-octadiene (42b) and 8,8-Dimethoxy-1-(dimethylphenylsilyl)-1-octyne (43b). The reaction of mesylate **1l** with (PhMe$_2$Si)$_3$ZnLi (2 equiv) was carried out by a procedure similar to that described in a general procedure for the preparation of allenic zinc **3a**−**m**. Purification of the crude products by flash chromatography (0.5−5% ethyl acetate in hexane) gave **42b** (89%) and **43b** (5%). **42b:** ^{1}H-NMR δ 0.36 (6H, s), 1.38 (4H, m), 1.60 (2H, m), 1.98 (2H, m), 3.31 (6H, s), 4.34 (1H, t, *J* = 5.7 Hz), 4.82 (1H, q, *J* = 6.8 Hz), 5.04 (1H, td, *J* = 3.6 and 6.8 Hz), 7.35 (3H, m), 7.53 (2H, m); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 211.1, 138.7, 133.6, 129.0, 127.7, 104.5, 83.7, 81.1, 52.61, 52.54, 32.3, 29.5, 27.7, 24.2, −2.26, −2.30; IR (liquid film) 1940, 1250, 1130, 1115, 840, 820 785, 730, 700 cm^{-1}; MS, *m/z* (relative intensity) 273 (M$^+$ − MeO, <1), 182 (6), 135 (89), 89 (41), 75 (100). Anal. Calcd for C$_{18}$H$_{28}$SiO$_2$: C, 71.00; H, 9.27. Found C, 70.85; H, 9.21. **43b:** ^{1}H-NMR δ 0.38 (6H, s), 1.3−1.7 (8H, m), 2.28 (2H, t, *J* = 7.0 Hz), 3.31 (6H, s), 4.35 (1H, t, *J* = 5.8 Hz), 7.36 (3H, m), 7.62 (2H, m); ^{13}C-NMR δ −0.60, 19.88, 24.11, 28.48, 28.64, 32.44, 52.69, 82.41, 104.55, 109.40, 127.78, 129.21, 133.65, 137.82; MS, *m/z* (relative intensity) 304 (M$^+$, <1), 273 (<1), 151 (62), 135 (64), 75 (100); HRMS calcd for C$_{18}$H$_{28}$SiO$_2$; 304.1859, found; 304.1858.

[2-(Dimethylphenylsilyl)ethenylidene]cyclohexane (42c) and 2-Cyclohexyl-1-(dimethylphenylsilyl)ethyne (43c). The reaction of chloride **1m** with (PhMe$_2$Si)$_3$ZnLi (2 equiv) was carried out by a procedure similar to that described in a general procedure for the preparation of allenic zinc **3a**−**m**. Purification of the crude products by flash chromatography (0.5−5% ethyl acetate in hexane) gave **42c**[35] (72%) and **43c**[36] (6%).

Preparation of α-(Phenyldimethylsilyl)allenic Zinc 29a. To a solution of (PhMe$_2$Si)$_3$ZnLi (0.6 mmol) in THF at −85 °C was added a solution of mesylate **40a** (159 mg, 0.5 mmol) in THF (2 mL) and the mixture was stirred for 15 min. After addition of CD$_3$OD (ca. 0.5 mL), the mixture was poured into 1 N HCl and extracted three times with ether. The combined organic layers were washed with NaHCO$_3$ (5%), dried, and concentrated. The residue was purified by flash chromatography (1−20% benzene in hexane) to give allene [1-^{2}H]-**42a** (9%, 82%-*d*) and alkyne [1-^{2}H]-**43a** (75%, 93%-*d*).

(3*R,4*S**)-6-(Dimethylphenylsilyl)-2-methyl-4-(2-phenylethyl)-5-hexyn-3-ol (44a) and 7-Methyl-1-phenyl-5-(dimethylphenylsilyl)-3,4-octadien-6-ol (47a).** The reaction of allenic zinc **29a** with 2-methylpropanal (1.5 equiv) was carried out using 1.6 equiv of ZnCl$_2$ by a procedure similar to that described in a general procedure for the preparation of homopropargyl alcohols. Purification of the crude products by flash chromatography (2.5−5% ethyl acetate in hexane) gave **44a** (52%) and **47a** (14%). **44a:** ^{1}H-NMR δ 0.43 (6H, s), 0.90 (3H, d, *J* = 6.7 Hz), 0.96 (3H, d, *J* = 6.6 Hz), 1.67 (1H, d, *J* = 8.6 Hz), 1.81 (1H, m), 1.97 (1H, m), 2.65−2.85 (4H, m), 3.13 (1H, ddd, *J* = 3.8, 7.3, and 8.6 Hz), 7.15−7.45 (8H, m), 7.64 (2H, m); IR (liquid film) 3560 (br), 3460 (br), 2160, 1250, 1115, 780, 730, 700 cm^{-1}; MS (CI), *m/z* (relative intensity) 351 (MH+, <1), 333 (2), 200 (60), 135 (100); HRMS (CI) calcd for C$_{23}$H$_{31}$SiO (MH$^+$); 351.2144, found; 351.2142. Anal. Calcd for C$_{23}$H$_{30}$SiO: C, 78.80; H, 8.62. Found C, 78.87; H, 8.83. **47a:** ^{1}H-NMR δ 0.37 (3H, s), 0.39 (3H, s), 0.73 (3H, d, *J* = 6.7 Hz), 0.83 (3H, d, *J* = 6.8 Hz), 1.36 (1H, d, *J* = 6.8 Hz), 1.59 (1H, m), 2.33 (2H, m), 2.67 (2H, m), 3.78 (1H, ddd, *J* = 2.4, 4.8, and 6.8 Hz), 5.10 (3H, dt, *J* = 2.4, and 6.9 Hz), 7.15−7.40 (8H, m), 7.52 (2H, m); IR (liquid film) 3550 (br), 3460 (br), 1935, 1250, 1110, 780, 700 cm^{-1}; MS (CI), *m/z* (relative intensity) 333 (MH$^+$ − H$_2$O, 1), 297 (2), 200 (60), 135 (100); HRMS (CI) calcd for C$_{23}$H$_{29}$Si (MH$^+$ − H$_2$O); 333.2038, found; 333.2036.

(3*S,4*R**)-3-(2-Phenylethyl)-10,10-dimethoxy-1-(dimethylphenylsilyl)-1-decyn-4-ol (44b) and 11,11-Dimethoxy-1-phenyl-5-(dimethylphenylsilyl)-3,4-undecadien-6-ol (47b).** The reaction of allenic zinc **29a** with 6,6-dimethoxyhexanal (1.5 equiv) was carried out using 1.6 equiv of ZnCl$_2$ by a procedure similar to that described in a general procedure for the preparation of homopropargyl alcohols. Purification of the crude products by flash chromatography (2.5−5% ethyl acetate in hexane) gave **44b** (49%) and **47b** (11%). **44b:** ^{1}H-NMR δ 0.43 (6H, s), 1.2−1.65 (8H, m), 1.69 (1H, d, *J* = 7.8 Hz), 1.75−2.0 (2H, m), 2.48 (1H, td, *J* = 4.5, 5.2, and 9.7 Hz), 2.65−3.95 (2H, m), 3.30 (6H, m), 3.50 (1H, m), 4.34 (1H, t, *J* = 5.7 Hz), 7.15−7.4 (m, 8H), 7.64 (2H, m); IR (liquid film) 3460 (br), 2170, 1250, 1125, 1120, 1055, 780, 725, 700 cm^{-1}; MS (CI), *m/z* (relative intensity) 407 (MH$^+$ − CH$_3$OH, 3), 375 (8), 223 (52), 129 (100); HRMS (CI) calcd for C$_{26}$H$_{35}$O$_2$Si (MH$^+$ − CH$_3$OH); 407.2406, found; 407.2414. **47b:** ^{1}H-NMR δ 0.38 (3H, s), 0.39 (3H, s), 1.15−1.7 (9H, m), 2.33 (2H, m), 2.67 (2H, m), 3.29 (6H, s), 4.02 (1H, m), 4.30 (1H, t, *J* = 5.7 Hz), 5.09 (1H, ddd, *J* = 2.2, 6.7, and 8.7 Hz), 7.15−7.4 (m, 8H), 7.53 (2H, m); IR (liquid film) 3450 (br), 1935, 1245, 1130, 775, 700 cm^{-1}; MS (CI), *m/z* (relative intensity) 407 (MH$^+$ − CH$_3$OH, <1), 389 (12), 223 (100), 135 (96); HRMS (CI) calcd for C$_{26}$H$_{33}$SiO (MH$^+$ − CH$_3$OH and H$_2$O); 389.2301, found; 389.2292.

6-(Dimethylphenylsilyl)-2,2-dimethyl-4-(2-phenylethyl)-5-hexyn-3-one (45). The reaction of allenic zinc **29a** with pivaloyl chloride (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the acylation of allenic zinc **3a**. Purification of the crude products by flash chromatography (2−10% ethyl acetate in hexane) gave **45** (65%): ^{1}H-NMR δ 0.39 (6H, s), 1.19 (9H, s), 2.05 (2H, m), 2.60−2.82 (2H, m), 3.71 (1H, dd, *J* = 6.8 and 7.7 Hz), 7.15−

7.4 (8H, m), 7.60 (2H, m); IR (liquid film) 2175, 1715, 1115, 820, 880, 700 cm^{-1}; MS (CI), *m/z* (relative intensity) 363 (MH$^+$, 28), 271 (71), 211 (94), 135 (100); HRMS (CI) calcd for $C_{24}H_{30}SiO$ (MH$^+$); 363.2144, found; 363.2140.

1,3-Bis(dimethylphenylsilyl)-5-phenyl-1-pentyne (46). The reaction of allenic zinc **29a** with chlorodimethylphenylsilane (1.5 equiv) was carried out by a procedure similar to that described in a general procedure for the silylation of allenic zinc **3a**. Purification of the crude products by flash chromatography (10−20% benzene in hexane) gave **46** (57%) and **43a** (13%). **46:** ^{1}H-NMR δ 0.37 (3H, s), 0.39 (3H, s), 0.41 (6H, s), 1.65−1.75 (2H, m), 1.96 (1H, dd, $J = 6.8$ and 7.7 Hz), 2.66 (1H, td, $J = 8.3$ and 13.7 Hz), 2.96 (1H, td, $J = 7.1$ and 13.7 Hz), 7.1−7.4 (6H, m), 7.52 (2H, m), 7.64 (2H, m); IR (liquid film) 2160, 1250, 1115, 815, 775, 700 cm^{-1}; MS (CI), *m/z* (relative intensity) 413 (MH$^+$, 2), 335 (8), 321 (10), 135 (100); HRMS (EI) calcd for $C_{27}H_{32}Si2$ (M$^+$); 412.2043, found; 412.2043. Anal. Calcd for $C_{27}H_{32}Si2$: C, 78.58; H, 7.81. Found C, 78.61; H, 7.94.

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Supporting Information Available: Additional information on the synthesis and characterization of compounds (35 pages). See any current masthead page for ordering and Internet instructions.

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