(3 mL) and heated under reflux for 3 h. The mixture was then poured into saturated aqueous $NaHCO_3$ and extracted with EtOAc, and the extract was chromatographed on silica. Elution with EtOAc/petroleum ether (1:10) gave methyl dibenzo[1,4]dioxin-1-carboxylate (**15**) (28 mg), mp and mixed mp 88 °C, and EtOAc/petroleum ether (1:4) gave dimethyl dibenzo[1,4]dioxin-1,9-dicarboxylate (**14**) (0.94 g, 58%), mp and mixed mp 145–146 °C. When MeI (2.2 equiv) was substituted for CO_2, only 1-methyldibenzo[1,4]dioxin (**7**) (76%) was isolated.

Metalation of Dibenzodioxin at Room Temperature. *n*-Butyllithium (80.5 mL of a 1.54 N solution in hexane, 0.12 mol) was added at room temperature to a solution of dibenzodioxin (10.0 g, 0.054 mol) in Et_2O (150 mL), and the mixture was stirred at this temperature for 48 h and then cooled to −70 °C. Dimethylformamide (12.0 mL, 0.15 mol) was added rapidly, and the mixture was stirred for a further 10 min and poured into EtOAc. The mixture was filtered to remove an insoluble, yellow polymeric material (4.55 g), and the filtrate was washed well with water and worked up to give an oil (12.7 g), which was chromatographed on silica. Elution with EtOAc/petroleum ether (1:10) gave dibenzo[1,4]dioxin-1-carboxaldehyde (**8**) (0.31 g) (identical with that obtained earlier). Elution with EtOAc/petroleum ether (3:20) gave dibenzo[1,4]dioxin-1,4-dicarboxaldehyde (**16**) (0.84 g) as a deep yellow waxy solid: ^1H NMR ($CDCl_3$) δ 10.44 (s, 2 H, CHO), 7.44 (s, 2 H, $ArH_{2,3}$), 7.04–6.95 (AA'BB' system, 4 H, $ArH_{6,7,8,9}$). Further elution with EtOAc/petroleum ether (3:20) gave a yellow solid (1.05 g), containing mostly dibenzo[1,4]dioxin-1,6-dicarboxaldehyde (**19**): ^1H NMR ($CDCl_3$) δ 10.43 (s, 2 H, CHO), 7.50 (dd, 2 H, J = 7.89 and 1.81 Hz, $ArH_{2,6}$), 7.11 (dd, 2 H, J = 7.99 and 1.81 Hz, $ArH_{4,9}$), 7.06 (dd, 2 H, J = 7.99 and 7.89 Hz, $ArH_{3,7}$). Later fractions of the same eluant contained mostly dibenzo[1,4]dioxin-1,9-dicarboxaldehyde (**18**) (0.49 g): ^1H NMR ($CDCl_3$) δ 10.39 (s, 2 H, CHO), 7.42 (dd, 2 H, J = 7.82 and 1.57 Hz, $ArH_{2,8}$), 7.06 (dd, 2 H, J = 7.92 and 1.60 Hz, $ArH_{4,6}$), 6.94 (dd, 2 H, J = 7.92 and 7.82 Hz, $ArH_{3,7}$).

Oxidation of the Aldehydes: Representative Procedure. Dimethyl Dibenzo[1,4]dioxin-1,4-dicarboxylate (17). Finely ground $KMnO_4$ (1.6 g, 10.4 mmol) was added in portions over 1 h to a stirred solution of the 1,4-dialdehyde **16** (0.84 g, 3.45 mmol) in Me_2CO (10 mL), after which time no starting material was evident by TLC analysis. The mixture was concentrated to dryness under reduced pressure, and the residue was triturated with 5 N NaOH and filtered. The filtrate was acidified with concentrated HCl to give the crude diacid as a yellow solid (0.81 g, 85%). This was dried under vacuum over silica gel and then esterified by heating under reflux in MeOH (30 mL) containing concentrated H_2SO_4 (2 mL). Workup gave a solid, which was chromatographed on silica. Elution with EtOAc/petroleum ether (3:20) gave dimethyl dibenzo[1,4]dioxin-1,4-dicarboxylate (**17**) (0.76 g, 85%), which crystallized from $CHCl_3$/petroleum ether as cubes: mp 119–120 °C; ^1H NMR ($CDCl_3$) δ 7.39 (s, 2 H, $ArH_{2,3}$), 6.95 (m, 4 H, $ArH_{6,7,8,9}$), 3.94 (s, 6 H, COOMe). Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found: C, 64.02; H, 3.98.

Similar oxidation of the crude 1,6-dialdehyde **19** gave dimethyl dibenzo[1,4]dioxin-1,6-dicarboxylate (**20**), which crystallized as rods from $CHCl_3$/petroleum ether: mp 204 °C; ^1H NMR ($CDCl_3$) δ 7.47 (dd, 2 H, J = 7.98 and 1.67 Hz, $ArH_{2,7}$), 7.11 (dd, 2 H, J = 8.04 and 1.67 Hz, $ArH_{4,9}$), 6.95 (dd, 2 H, J = 8.04 and 7.98 Hz, $ArH_{3,8}$), 3.93 (s, 6 H, COOMe). Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found: C, 63.90; H, 4.03.

Similar oxidation of the crude 1,9-dialdehyde 18 gave dimethyl dibenzo[1,4]dioxin-1,9-dicarboxylate (**14**), mp and mixed mp 147–150 °C, and with an ^1H NMR spectrum identical with that of authentic material.

X-ray Crystallography. Dimethyl dibenzo[1,4]dioxin-1,9-dicarboxylate (**14**) crystallized from Me_2CO as colorless orthorhombic crystals, $P2_1P2_1P2_1$; cell constants a = 5.8969$_4$, b = 13.8492$_7$, c = 16.6800$_2$ Å; z = 4; V = 1362.204 Å^3. Lattice constants and intensity data were measured using Ni-filtered Cu Kα radiation, λ = 1.5418 Å, on a Nonius CAD-4 diffractometer. The data set consisted of 1332 unique reflections, of which 750 were considered observed ($I > 3\sigma > (I)$). The structure was solved by direct methods using SHELX-S[17] and refined using SHELX-76.[18] The largest shift/esd values during the final refinement were < 0.1. Maximum and minimum peaks in the final difference map were +1.3 and −0.18 eÅ^{-3}, respectively. At convergence R and R_w were 0.0359 and 0.0361, respectively.

Acknowledgment. This work was supported by the Auckland Division of the Cancer Society of New Zealand and the Medical Research Council of New Zealand. We are grateful to the referees for their pertinent comments.

Registry No. **2**, 51689-36-2; **4**, 123701-15-5; **5**, 123701-16-6; **6**, 123701-17-7; **7**, 123701-18-8; **8**, 51689-41-9; **9**, 123701-19-9; **10**, 35051-82-2; **11**, 123701-20-2; **12**, 99420-27-6; **13**, 32578-12-4; **14**, 123701-21-3; **15**, 51689-37-3; **16**, 123701-22-4; **17**, 123701-23-5; **18**, 123701-24-6; **19**, 123701-25-7; **20**, 92965-43-0; *m*-$MeOC_6H_4CO_2H$, 586-38-9; dibenzo[1,4]dioxin, 262-12-4; dibenzo[1,4]dioxin-1,4-dicarboxylic acid, 123701-26-8.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond angles, and bond distances for **14** and a computer-drawn ORTEP diagram of **14** (8 pages). Ordering information is given on any current masthead page.

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Selective Propargylation of Carbonyl Compounds with Allenylstannane/Alkyllithium Mixed Reagents

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1-Substituted allenyltrialkylstannanes readily undergo transmetalation with an alkyllithium to generate a tetraalkylstannane and an equilibrating mixture of the allenyl- and propargyllithium compounds. The organolithium derivatives react with a variety of aldehydes and ketones at low temperature to give, after aqueous workup, the regioisomeric acetylenic and allenic carbinols in high yields. The degree of the regioselection is highly sensitive to the steric and electronic properties of the carbonyl substrates. Excellent acetylene selectivities are obtainable by combination of the bulky reagents and substrates or by using acylsilanes as carbonyl components. The origin of the regioselectivity is discussed.

Selective methods for nucleophilic allylation and propargylation of carbonyl compounds are still being explored.[1] Allenyl and propargyl metal derivatives are of particular interest since they equilibrate in solution in

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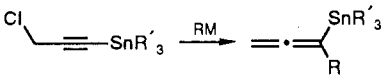
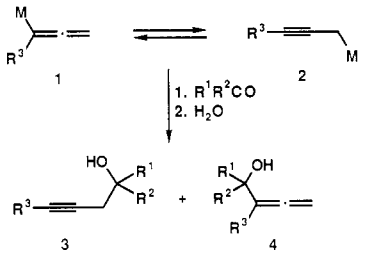
Table I. Synthesis of Allenylstannane Derivatives



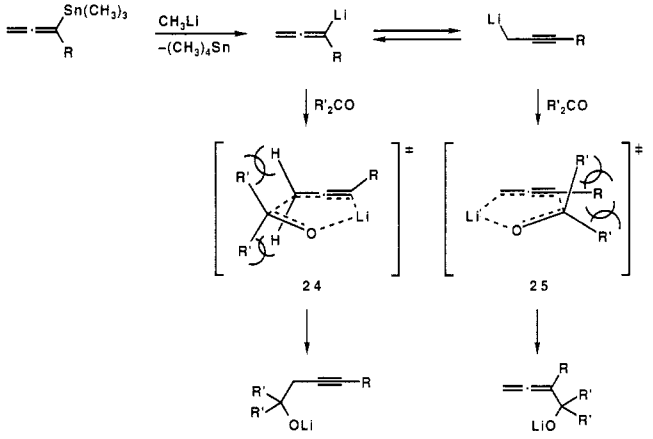
R′	RM	conditions: solvent	conditions: temp, °C	product	% yield[a]
n-C_4H_9	n-$C_5H_{11}Li$/CuI, 2.6 P(n-C_4H_9)$_3$	ether	−78	**12a**	37[b]
CH_3	n-$C_5H_{11}MgBr$, 3% CuCN	THF	−25	**12b**	74[b]
CH_3	i-C_3H_7MgCl, 3% CuCN	THF	−25	**13**	85
CH_3	t-C_4H_9MgCl, 3% CuCN	THF	−25	**14**	89

[a] Isolated yield. [b] See ref 6c.

Scheme I. Reaction of Allenyl or Propargyl Metals with Carbonyl Compounds



Scheme II. Mechanism of Selective Propargylation



many cases, and these isomers react differently with carbonyl compounds.[2] It is believed that allenyl metals (**1**) lead mainly to acetylenic adducts (**3**) and propargylic isomers (**2**) to allenic adducts (**4**) (Scheme I).[2] The overall selectivity, in principle, is determined by the equilibrium concentration, relative reactivity, and regioselectivity of these two isomeric species. The regiochemical outcome is subtly affected by steric and electronic properties of the reagents and substrates, as well as reaction conditions,[2] and thus is not easily predictable. Empirically, unsubstituted C_3H_3M systems of type **5** show moderate selectivity favoring acetylenic adducts,[2] but the terminally silylated compounds **6** exhibit very high acetylene selection.[3] In alkylated systems, the oxygen-functionalized compound **7** and organozinc **8** are known to afford a high level of acetylene selectivity.[4] The allenyl metalloids, **9** and **10**, act as propargyl anion equivalents and, with or without added Lewis acids, react with aldehydes to give the acetylenic alcohols.[5] Unfortunately, however, such nonequilibrating compounds have low reactivity toward ketones.[5] In connection with our project on the synthesis of antineoplastic punaglandins, where such existing methods were not applicable, we had an opportunity to search for an efficient propargylation procedure.[6]

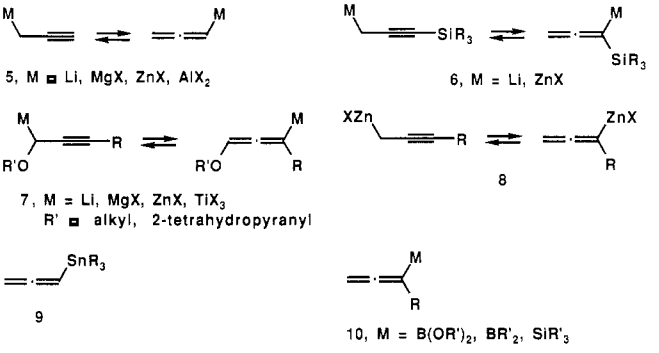


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Table II. Reaction of Aldehydes and Ketones with Allenylstannane/Alkyllithium Mixed Agents[a]

		11		12b		14	
entry	carbonyl compound	products (ratio)[b]	combined % yield[c]	products (ratio)[b]	combined % yield[c]	products (ratio)[b]	combined % yield[c]
1	octanal	**3a** + **4a** (6.6:1)	92	**3f** + **4f** (2.2:1)	88	**3s** + **4s** (5.3:1)	84
2	pivalaldehyde	**3b** + **4b** (7.0:1)	81	**3g** + **4g** (4.5:1)	83	**3t** + **4t**[d] (44:1)	90
3	benzaldehyde			**3h** + **4h** (1.5:1)	85	**3u** + **4u** (6.0:1)	94
4	(*E*)-cinnamaldehyde			**3i** + **4i** (1.7:1)	87		
5	diethyl ketone			**3j** + **4j** (4.7:1)	94		
6	diisopropyl ketone			**3k** + **4k** (7.1:1)	97		
7	pinacolone	**3c** + **4c** (5.9:1)	88	**3l** + **4l** (14:1)	95	**3v** only	95
8	*tert*-butyl heptyl ketone			**3m** + **4m** (3.9:1)	93		
9	isopropyl phenyl ketone			**3n** + **4n** (2.9:1)	83	**3w** + **4w**[d] (119:1)	98
10	cyclohexanone	**3d** + **4d** (5.2:1)	89	**3o** + **4o** (8.1:1)	84	**3x** only	97
11	2-cyclohexenone			**3p** + **4p** (2.9:1)	91		
12	(1*R*)-(+)-camphor			**3q** + **4q** (9.2:1)	93		
13	2-adamantanone	**3e** + **4e** (3.1:1)	98	**3r** + **4r** (21:1)	94	**3y** only	98
14	estrone 3-*O*-*tert*-butyldimethylsilyl ether					**3z** only	67[e]

[a] Reaction conditions are given in a standard procedure in the Experimental Section. [b] Determined by 270-MHz ^{1}H NMR analysis. [c] Unless otherwise stated, yield was determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane (δ 5.96) as an internal standard. [d] The structure was assigned by allenyl proton: δ 4.82 for **4t**; δ 4.90 for **4w**. [e] Isolated yield. The starting carbonyl compound was recovered in 31% yield.

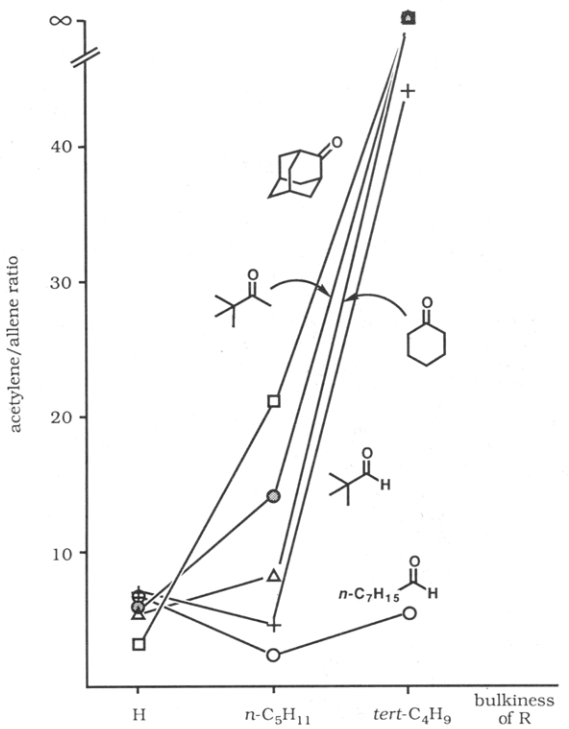

Figure 1. Substituent effects on the acetylene/allene selectivity.

Results and Discussion

We used highly reactive, equilibrating organometallics generated in situ by mixing allenylstannanes and alkyllithiums and observed a unique regioselectivity in the reaction with carbonyl compounds. This method is particularly useful for selective propargylation of ketonic substrates, especially those possessing bulky substituents. The use of acylsilanes leads solely to the acetylene products.

Reaction of Carbonyl Compounds and the Allenylstannane/Alkyllithium Mixed Reagents. Prior to this work, only a limited number of methods were known for the preparation of the 1-alkylated allenylstannane compounds.[7] We found that various 1-alkylallenylstannanes, **12**–**14**, are obtainable by the reaction of readily available (3-chloropropynyl)stannanes **15**[8] and tributylphosphine-complexed organocopper reagents[9] or,

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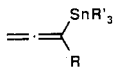
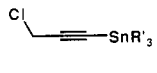
more conveniently, Grignard reagents in the presence of a catalytic amount of copper(I) cyanide.[10] Some examples are given in Table I.



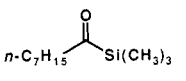
11, R = H; R' = n-C_4H_9
12a, R = n-C_5H_{11}; R' = n-C_4H_9
12b, R = n-C_5H_{11}; R' = CH_3
13, R = i-C_3H_7; R' = CH_3
14, R = $tert$-C_4H_9; R' = CH_3



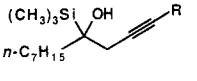
15a, R' = n-C_4H_9
15b, R' = CH_3

Reaction of the allenylstannanes, **11–14**, and alkyllithiums generates highly reactive reagents. An allenyltrialkylstannane was treated first with 1 equiv of halide-free methyl- or butyllithium in THF at −95 °C for 10 min and then with 1 equiv of a carbonyl substrate at the same temperature for 20 min. Subsequent aqueous workup afforded a mixture of the corresponding acetylenic and allenic alcohols, **3** and **4**. Table II summarizes the results. The reactive organometallics act as ambident nucleophiles and the acetylene/allene distribution appears to be highly influenced by the nature of the carbonyl substrates. For a given allenylstannane/alkyllithium reagent, ketones tend to exhibit a higher **3**/**4** ratio than aldehydes, and the reaction of sterically congested ketones consistently gives high acetylene selectivity. A bulky substituent in the organometallic compounds also enhances the formation of acetylene. The typical coopertive effects of increased regioselectivity are seen in the reaction of a **14**/methyllithium mixed reagent with pinacolone, isopropyl phenyl ketone, cyclohexanone, or 2-adamantanone which results in the nearly exclusive formation of acetylenic carbinols (>95%).

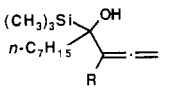
The selective propargylation of aldehydes using 1-substituted allenylstannane compounds has remained difficult. This limitation, however, has been overcome synthetically by replacing the aldehydic hydrogen by a trimethylsilyl group.[6a] Thus when acylsilane **16**[11] was condensed with a **12b**/methyllithium reagent, a 39:1 mixture of the acetylenic and allenic products, **17** and **20**, was produced in 90% yield. In like manner, reactions of the bulkier reagents, **13** and **14**, gave solely the acetylenic products, **18** and **19**, in 91 and 96% yields, respectively. Protodesilylation of **17–19** with tetrabutylammonium fluoride in wet THF[12] gave the corresponding secondary alcohols, **3f**, **21**, and **3s**, in 98, 91, and 97% yields, respectively, which are seen as formal aldehyde propargylation products. Partial hydrogenation of the acetylenic bond in **3f** over Lindlar catalyst afforded the (*Z*)-homoallylic alcohol **22** (98%), whereas its lithium bronze reduction in liquid ammonia gave the *E* isomer **23** (99%).[13,14]



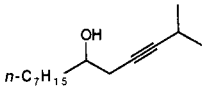
16



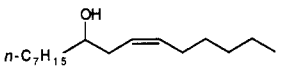
17, R = n-C_5H_{11}
18, R = i-C_3H_7
19, R = $tert$-C_4H_9



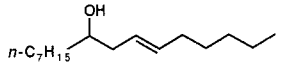
20, R = n-C_5H_{11}



21



22



23

Nature of the Organometallic Nucleophiles and Origin of the Regioselectivity. We consider the reactive species formed from the allenylstannanes and alkyllithiums in THF to be an equilibrating mixture of the allenyl- and propargyllithium compounds. Indeed ^{13}C NMR monitoring of the reaction of **13** and methyllithium in THF-d_8 at −78 °C revealed that tin to lithium transmetalation occurred almost instantaneously to give tetramethylstannane (δ −9.3 ppm) quantitatively. Other carbons gave broad signals at δ 26.0 and 26.4 (isopropyl methyls), 33, 43, and 111 ppm, suggesting the fluxional nature of the newly generated organolithium compounds.[17] The chemical behavior of such species, however, is different from that of organolithium compounds[18] formed from 2-alkynes and *tert*-butyllithium, perhaps owing to differences in the aggregation states.[18] The allenylstannane/methyllithium reagents appear to exhibit higher reactivity and better acetylene/allene selectivity.[19]

As outlined in Scheme II, the reaction proceeds via a cyclic transition state, **24** or **25**, giving the acetylenic and allenic products, respectively.[2] The regioselectivity of the addition of equilibrating ambident organolithium compounds is determined kinetically by the relative stabilities of transition states **24** and **25**, which are affected by electronic and steric factors.[2] Since the reaction is highly exothermic, these transition structures reflect the nature

(10) Review: Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954.

(11) Miller, J. A.; Zweifel, G. *Synthesis* **1981**, 288.

(12) Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1988**, *110*, 4826.

(13) (a) Mueller, R. H.; Gillick, J. G. *J. Org. Chem.* **1978**, *43*, 4647. (b) Doolittle, R. E. *Org. Prep. Proced. Int.* **1981**, *13*, 179.

(14) In this connection, we found that high propargyl selectivity is obtainable by using organozinc compounds generated from 1-bromo-2-octyne or 1-bromo-4,4-dimethyl-2-pentyne, zinc dust, and a catalytic amount of mercury(II) chloride in THF under ultrasonic irradiation.[15] This method is useful for reaction with acylsilane **16**, giving **17** (86%, acetylene/allene = 25:1) and **19** (90%, acetylene only), respectively. In reaction with aldehydes and ketones the product yields were slightly lowered and some byproducts were formed.[16]

(15) For the use of ultrasonication in organic synthesis, see a review: Suslick, K. S. *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: New York, 1986; Vol. 4, p 1.

(16) Reactions of diisopropyl ketone and 2-adamantanone with 1-bromo-2-octyne/zinc gave a mixture of **3k** + **4k** and **3r** + **4r** in 82% (7.4:1) and 85% (76:1) yields, respectively. Reactions of benzaldehyde, pinacolone, and cyclohexanone with 1-bromo-4,4-dimethyl-2-pentyne/zinc gave solely the acetylenic products **3u**, **3v**, and **3x** in 80, 63, and 68% yields, respectively. For the reaction using relevant zinc reagent prepared by mixing $ZnBr_2$ and potassium metal, see: (a) Kosugi, H.; Konta, H.; Uda, H. 52nd Annu. Meet. Jpn. Chem. Soc. (Kyoto), 1986, Abstr. II 1073. (b) Watanabe, Y.; Kosugi, H.; Uda, H. 54th Annu. Meet. Jpn. Chem. Soc. (Tokyo), 1987, Abstr. II 1122. (c) Kosugi, H.; Watanabe, Y.; Konta, H.; Uda, H. 29th Symp. Chem. Natural Products (Sapporo, Jpn.), 1987, Abstr. 417.

(17) For ^{13}C NMR data of allenyllithium generated from allene and n-butyllithium, see: van Dongen, J. P. C. M.; van Dijkman, H. W. D.; de Bie, M. J. A. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29. Reaction of vinylstannane and methyllithium did not give lithium stannate complexes: (a) Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1987**, *322*, 141. (b) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868. And see also: Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842.

(18) When aldehydes are condensed with the alkyne-derived lithium compounds in the presence of triisobutylaluminum or tri-*sec*-butylborane, high allenyl selectivities are emerged. Use of titanium tetraisopropoxide diminishes the allenyl selectivity. These Lewis acid mixed reagents are inert to ketonic substrates. See: (a) Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Org. Chem.* **1982**, *47*, 2225. (b) Furuta, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768. (c) Pearson, N. R.; Hahn, G.; Zweifel, G. *J. Org. Chem.* **1982**, *47*, 3364.

(19) Reactions of pivalaldehyde, pinacolone, cyclohexanone, and 2-cyclohexenone with 2-octyne/*tert*-butyllithium gave a mixture of the corresponding **3** and **4**. Combined yield and ratio were: **3g** + **4g**, 70%, 3.2:1; **3l** + **4l**, 84%, 9.0:1; **3o** + **4o**, 77%, 2.7:1; **3p** + **4p**, 78%, 2.1:1.

of the starting organolithium and carbonyl compounds.[20] The Li–C(sp^2) bond polarity in the allenyllithium is higher than that of the Li–C(sp^3) in the propargyl isomer,[21] providing electronic preference of **24** to **25**. The introduction of an electron-donating R group, enhancing the nucleophilicity of the organolithiums, would stabilize both transition states to some extent.[22] Sterically, **24** suffers from H/R′ eclipsed nonbonding repulsion, whereas **25** is destabilized by a gauche type R/R′ interaction. These steric effects become important with bulky R and R′ groups.

Throughout 26 experiments tried so far using substituted organometallics and carbonyl substrates, acetylenic carbinols were the major regioisomers without exception. The reactions using the allenylstannane **11** also consistently gave acetylene products. Since in these cases structure **24** is less favorable than **25** from steric grounds, this general trend indicates the electronic control of the regiochemistry. In addition, steric factors significantly affect the degree of the acetylene/allene selectivity as shown in Figure 1. Notably, the acetylene/allene ratio in the reaction of the simple allenyl compound **11** decreases with increasing bulkiness of the carbonyl substituents; octanal, cyclohexanone, and 2-adamantanone gave 6.6:1, 5.2:1, and 3.1:1 ratios, respectively. This is due to the increase of H/R′ eclipsed interaction in **24**. On the other hand, gauche repulsion, which destabilizes **25**, increases the regioselectivity substantially. Thus reactions using the alkylated allenyl compound **12b** and diethyl ketone, cyclohexanone, pinacolone, and 2-adamantanone gave the acetylene/allene ratios of 4.7:1, 8.1:1, 14:1, and 21:1, respectively. This repulsive interaction is predominant when R is *tert*-butyl, and perfect acetylene selection is seen in the reaction of **14** and cyclohexanone, pinacolone, or 2-adamantanone.

In certain cases, electronic factors also affect the extent of the regioselection. The acetylene/allene ratio decreases from the reaction of octanal with simple allenylstannane **11** to that of octanal with **12b** (6.6:1 to 2.2:1). Electron release from the pentyl group activates the propargyl structure to a greater extent than the allenyl isomer, offsetting the acetylene preference in the nonalkylated compound.[22] Consistent with this view, competitive experiments using octanal as the substrate revealed the following relative reactivities: (1-pentylallenyl)lithium 7.7, allenyllithium 4.7, 2-octyn-1-yllithium 2.7, and propargyllithium 1.0. Unsaturated carbonyl substrates such as benzaldehyde, (*E*)-cinnamaldehyde, or 2-cyclohexenone exhibit rather low acetylene selectivity (1.5–2.9:1). This is unexpected from the simple steric model and may be interpreted in terms of electron delocalization, resulting in a loose transition state which mitigates the R/R′ gauche interaction in **25**. Further, the trimethylsilyl group in the acylsilane substrate plays a striking role in enhancing acetylene selectivity. Reaction of the **12b**/methyllithium reagent with **16** exhibited a 10-fold higher selectivity than with the carbon analogue, *tert*-butyl heptyl ketone (39:1 vs 3.9:1). Since trimethylsilyl is larger but sterically less demanding than *tert*-butyl,[23] the enhanced selectivity originates from differences in the electronic properties of these two groups.[24] The electropositive silyl group could shift the transition state to a late (productlike) position, and, then the allene-generating transition state **25** would become highly disfavored because of the serious R/R′ repulsion caused by increased steric congestion.

Experimental Section

General Remarks. (a) Instruments. Capillary GLC analyses were performed with following column and conditions: Condition 1: PEG-20M bonded capillary column (df = 0.15 μm, 0.25 mmϕ × 25 m, Gasukuro Kogyo Inc.) using helium carrier gas (0.7 kg/cm^2). Split ratio was 1/117. Column and injection temperatures were 180 and 200 °C, respectively. Condition 2: OV-1 bonded capillary column (df = 0.30 μm, 0.25 mmϕ × 50 m, Gasukuro Kogyo Inc.) using helium carrier gas (0.7 kg/cm^2). Split ratio was 1/110. Column and injection temperatures were 210 and 240 °C, respectively. Melting points were uncorrected. Bulb-to-bulb short-path distillation was performed by using a Büchi Kugelrohrofen. The cited temperatures for these distillations refer to the oven temperature and therefore are not true boiling points. Sonications were run in a Sharp Ultrasonic Cleaner UTB-152 (150W, 28 KHz).

(b) Chromatography. R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. The plates were sprayed with a solution of 2% *p*-anisaldehyde in 5% ethanolic sulfuric acid and then heated until the spots became clearly visible. Liquid chromatography was conducted using Silica gel 60 (E. Merck, 7734 70–230 mesh; or Fuji Devison, BW-80, 80–200 mesh). Flash liquid chromatography was conducted using a Kiriyama ILC PB column system (a glass column and a pump). Recycling preparative high-performance liquid chromatography was conducted using a Japan Analytical Industry Model LC-908 chromatograph.

(c) Solvent. Dry ether, THF, DME, pentane, and benzene were distilled over sodium benzophenone ketyl under argon atmosphere. Dry CH_2Cl_2 was distilled over P_4O_{10}. Dry DMF and CH_3CN were distilled over CaH_2. Dry t-C_4H_9OH was distilled over Mg.

(d) Substrates and Reagents. Trimethyl(3-chloropropynyl)stannane (**15b**),[6c,8] tributyl(1,2-propadienyl)stannane (**11**),[5c] tributyl(1,2-octadien-3-yl)stannane (**12a**),[6b,c] and trimethyl(1,2-octadien-3-yl)stannane (**12b**)[6c] were synthesized according to the procedure reported in the literature. Isopropylmagnesium chloride (2.00 M ether solution), *tert*-butylmagnesium chloride (2.00 M ether solution), methyllithium (1.08 or 1.26 M ether solution), and *tert*-butyllithium (1.90 or 1.77 M pentane solution) were purchased from Aldrich. Molarity of alkyllithiums was determined by titration.[27] Lithium wire (sodium content 0.01%) and tetrabutylammonium fluoride (1.0 M THF solution) were purchased from Aldrich. Zinc powder (purity 99.9%) was purchased from Rare Metallic Co., Ltd. Lindlar catalyst (Nippon Engelhard, Lot No. 29) was used for hydrogenation. The following carbonyl compounds were obtained from commercial sources and used after distillation before use: octanal, pivalaldehyde, benzaldehyde, (E)-cinnamaldehyde, diethyl ketone, diisopropyl ketone, pinacolone, isopropyl phenyl ketone, cyclohexanone, 2-cyclohexenone. 2-Adamantanone (Aldrich) and (1*R*)-(+)-camphor (Wako Chemical) were used in commercial grade. *tert*-Butyl heptyl ketone[28] was synthesized from octanal and *tert*-butyllithium followed by pyridinium chlorochromate oxidation. Estrone 3-*O*-*tert*-butyldimethylsilyl ether was prepared according to the

(20) Hammond's postulate: Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.
(21) Hopkinson, A. C.; Lien, M. H. *J. Chem. Phys.* **1977**, *67*, 517.
(22) See: (a) Mesnard, D.; Charpentier, J.-P.; Miginiac, L. *J. Organomet. Chem.* **1981**, *214*, 15. (b) Mesnard, D.; Charpentier, J.-P.; Miginiac, L. *Ibid.* **1981**, *214*, 23.
(23) C–C bond length 1.54 Å; C–Si bond length 1.86 Å.
(24) The electronic structure is reflected in both of the observed bathochromic shift of the n-π* transition (382 nm for compound **16**) and in the long-wavelength shift of the C=O stretching frequencies (1635 cm^{-1} for **16**).[25] These characteristics are well explained by the positive inductive effect of the silyl group and a co-interacting Si(3d)–C(π*) electron withdrawal (back donation).[26]
(25) (a) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95. (b) Agolini, F.; Klemenko, S.; Csizmadia, I. G.; Yates, K. *Spectrochim. Acta* **1968**, *24A*, 169. (c) Dexheimer, E. M.; Buell, G. R.; Le Croix, C. *Spectrosc. Lett.* **1978**, *11*, 751. (d) Armitage, D. A. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, p 71.
(26) Bock, H.; Alt, H.; Seidl, H. *J. Am. Chem. Soc.* **1969**, *91*, 355.
(27) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.
(28) Cahiez, G.; Bernard, D.; Normant, J. F. *Synthesis* **1977**, 130.

procedure reported in the literature.[29] Trimethyl(octanoyl)silane (**16**) was synthesized according to the procedure reported in the literature.[11] A pH 7.4 phosphate buffer solution (0.1 M, Nakarai) was used in workup procedures. Reactions with organometallic reagents were conducted under argon atmosphere. The apparatus (ampule, test tube, and flask) for such reactions were evacuated by heating with a heat gun under high vacuum and then filled with argon.

Trimethyl(4-methyl-1,2-pentadien-3-yl)stannane (13). This compound was prepared by a similar procedure[6c] to the synthesis of **12b** using **15b** (1025 mg, 4.32×10^{-3} mol), isopropylmagnesium chloride in ether (2.16 mL, 4.32×10^{-3} mol), and copper(I) cyanide (11.6 mg, 1.30×10^{-4} mol). After workup, bulb-to-bulb short-path distillation (45–50 °C (7 mmHg) gave **13** (85%): TLC R_f 0.63 (hexane); IR ($CHCl_3$) 1930 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.20 (s, 9, $^2J(^{117}Sn-^1H)$ = 52.4 Hz, $^2J(^{119}Sn-^1H)$ = 54.7 Hz, Sn-$(CH_3)_3$), 1.05 (d, 6, J = 6.6 Hz, 2 CH_3), 2.25–2.50 (m, 1 CH), 4.22 (d, 2 J = 2.64 Hz, $^4J(^{117}Sn-^1H)$ = 39.9 Hz, $^4J(^{119}Sn-^1H)$ = 41.6 Hz, allenyl); HRMS, m/z calcd for $C_9H_{18}Sn$ 246.0431 (Sn = 119.9022), found 246.0410. Anal. Calcd for $C_9H_{18}Sn$: C, 44.13; H, 7.41. Found: C, 44.10; H, 7.60.

Trimethyl(4,4-dimethyl-1,2-pentadien-3-yl)stannane (14). This compound was prepared by a similar procedure[6c] to the synthesis of **12b** using **15b** (1655.0 mg, 6.97×10^{-3} mol), *tert*-butylmagnesium chloride in ether (3.49 mL, 6.97×10^{-3} mol), and copper(I) cyanide (19.9 mg, 2.22×10^{-4} mol). After workup, bulb-to-bulb short-path distillation (40–46 °C (2 mmHg)) gave **14** (89%) as a colorless oil: TLC R_f 0.64 (hexane); IR ($CHCl_3$) 1920 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.21 (s, 9, $^2J(^{117}Sn-^1H)$ = 52.1 Hz, $^2J(^{119}Sn-^1H)$ = 54.1 Hz, $Sn(CH_3)_3$), 1.08 (s, 9, t-C_4H_9), 4.22 (s, 2, $^4J(^{117}Sn-^1H)$ = 40.2 Hz, $^4J(^{119}Sn-^1H)$ = 41.5 Hz, allenyl). Anal. Calcd for $C_{10}H_{20}Sn$: C, 46.37; H, 7.78. Found: C, 46.36; H, 7.76.

Standard Procedure for Propargylation Using Allenylstannane/Alkyllithium Mixed Agents (Table II, Entry 7). Trimethyl(4,4-dimethyl-1,2-pentadien-3-yl)stannane (**14**, 94.7 mg, 3.66×10^{-4} mol) was placed in a 10-mL test tube and dissolved in dry THF (2 mL) under argon atmosphere. After the solution was cooled to −95 °C, methyllithium (0.290 mL, 3.66×10^{-4} mol) was added at this temperature, and the mixture was stirred at −95 °C for 10 min. Pinacolone (0.0416 mL, 3.33×10^{-4} mol) was added to this at −95 °C. The mixture was stirred at −95 °C for 20 min, poured into a pH 7.4 phosphate buffer solution (2 mL), and then extracted with ether (5 mL × 2). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residual oil, after being mixed with 1,1,2,2-tetrachloroethane (δ 5.96, 8.0 μL), was subjected to a 270-MHz NMR analysis. Product yield and isomer ratio were determined by comparing integrals of hydrogens on hydroxylated carbons for secondary alcohols and propargylic and allenic hydrogens for tertiary alcohols.

Standard Procedure for Propargylation Using 2-Alkyne/*tert*-Butyllithium Mixed Agents. 2-Octyne (0.29 mL, 2.00 × 10^{-3} mol) was placed in a 10-mL test tube and dissolved in dry THF (3 mL) under argon atmosphere. After the solution was cooled to −78 °C, *tert*-butyllithium (1.13 mL, 2.00×10^{-3} mol) was added at this temperature, and then the mixture was stirred at −78 °C for 10 min. The mixture was warmed up to 0 °C and stirred for 60 min at this temperature,[18] and then the mixture was cooled again to −95 °C. To this pinacolone (0.228 mL, 1.82 × 10^{-3} mol) was added at this temperature and further stirred for 20 min. Then the mixture was poured into a pH 7.4 phosphate buffer solution (5 mL) and extracted with ether (4 mL × 2). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residual oil, after being mixed with 1,1,2,2-tetrachloroethane (8.0 μL), was subjected to a 270-MHz NMR analysis.

Standard Procedure for Propargylation Using 1-Bromo-2-alkyne/Zinc Mixed Agents. 1-Bromo-4,4-dimethyl-2-pentyne[30] (109.5 mg, 6.25×10^{-4} mol) was placed in a 10-mL Schlenk tube and dissolved in dry THF (1.0 mL) under argon atmosphere. Zinc (40.9 mg, 6.25×10^{-4} mol) and mercury(II) chloride (3.4 mg, 1.3×10^{-5} mol) were added to this, and then the mixture was ultrasonicated on a water bath at 20–22 °C for 10 h. After the mixture was cooled to 0 °C, pinacolone (0.071 mL, 5.68×10^{-4} mol) was added. The mixture was stirred at 0 °C for 30 min, warmed up to 30 °C, and stirred further for 3 h at this temperature. The reaction mixture was poured into saturated aqueous NH_4Cl solution (3 mL) and extracted with ether (3 mL × 2). The organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residual oil, after being mixed with 1,1,2,2-tetrachloroethane (8.0 μL), was subjected to a 270-MHz NMR analysis.

Procedure for Isolation of Acetylenic and Allenic Products. Unless otherwise noted, isolation of acetylenic or allenic products was conducted by flash column chromatography (Silica gel 60, E. Merck, 9385, 230–400 mesh; column size, 25 mmϕ × 12 cm) using a 500:1 to 20:1 mixture (gradient) of hexane and ethyl acetate as eluant. Isolated yields were 62 and 22% for **3m** and **4m**, respectively (Table II, entry 8); 60 and 20% for **3n** and **4n** (entry 9); 67% for **3z** (entry 14).

The separation of acetylenic and allenic compounds having close R_f values on TLC was performed using recycling preparative high-performance liquid chromatography (column, Japan Analytical Industry, JAIGEL AJ1H and AJ2H, 20 mmϕ × 60 cm; solvent, $CHCl_3$; pressure, 20–30 kg/cm^2; flow rate, 3.5 mL/min; detection, UV (254 nm) and RI two-pen system). Four to ten recycles were required. Isolated yields thus obtained were 58 and 9% for **3u** (earlier fraction) and **4u** (later fraction), respectively (Table II, entry 3); 64 and 5% for **31** (earlier) and **41** (later) (entry 7); 61 and 22% for **3e** (earlier) and **4e** (later) (entry 13). The acetylenic derivatives have shorter retention times than the allenic compounds under these HPLC conditions.

Compounds **3a**,[31] **4a**,[31b,c] **3b**,[5b,d,32] **4b**,[5b,d] **3c**,[33] **4c**,[33c,34] **3d**,[5o,31a,b,33a,b,35] **4d**,[31b,36] **3f**,[37] **4f**,[37] **3h**,[4g] **4h**,[4g] **3k**,[4e] **4k**,[4e] **3o**,[37] **4o**,[31b,37] **4p**,[31b] and **3t**[38] are known.

Unless otherwise stated, the high purity of the new compounds was certified by combustion analysis or their sharp melting point, GLC analysis, or ^1H and ^{13}C NMR assays.

2-(2-Propynyl)adamantan-2-ol (3e): mp 51–52 °C; TLC R_f 0.29 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3200, 3300 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.50–1.90 (m, 12, 5 CH_2 and 2 CH), 2.02 (s, 1, OH), 2.08 (t, 1, J = 2.6 Hz, CH), 2.20–2.30 (br d, 2, 2 CH), 2.62 (d, 2, J = 2.6 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 27.1, 27.2, 29.5, 32.8 (2 C), 34.5 (2 C), 36.6 (2 C), 38.1, 71.7, 73.8, 80.6. HRMS m/z calcd for $C_{13}H_{16}$ ($M^+ - H_2O$) 172.1253, found 172.1252.

2-Propadienyladamantan-2-ol (4e): mp 42–43 °C; TLC R_f 0.29 (5:1 hexane/ethylacetate); IR ($CHCl_3$) 3600–3200, 1950 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.50–1.95 (m, 13, 5 CH_2, 2 CH, and OH), 2.20–2.30 (br d, 2, 2 CH), 4.87 (d, 2, J = 6.6 Hz, allenyl), 5.47 (t, 1, J = 6.6 Hz, allenyl); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 27.1, 27.3, 32.7 (2 C), 34.9 (2 C), 37.9, 38.0 (2 C), 74.4, 78.0, 98.7, 206.8. HRMS m/z calcd for $C_{13}H_{18}O$ (M^+) 190.1358, found 190.1377.

2,2-Dimethyl-5-undecyn-3-ol (3g): TLC R_f 0.39 (10:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3400 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.90 (t, 3, J = 7.3 Hz, CH_3), 0.91 (s, 9, t-C_4H_9), 1.1–1.7 (m, 6, 3 CH_2), 2.1–2.5 (m, 5, 2 CH_2 and OH), 3.36 (dd, 1, J =3.0 and 9.9 Hz, CHO); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.0, 18.8, 22.3, 23.0, 25.7 (3 C), 28.8, 31.2, 34.5, 77.3, 77.6, 83.3; HRMS m/z calcd for $C_{13}H_{22}$ ($M^+ - H_2O$) 178.1723, found 178.1695. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.32; H, 12.56.

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2,2-Dimethyl-4-pentyl-4,5-hexadien-3-ol (4g): TLC R_f 0.30 (10:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3400, 1950 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.89 (t, 3, J = 7.0 Hz, CH_3), 0.94 (s, 9, t-C_4H_9), 1.20–1.60 (m, 7, 3 CH_2 and OH), 1.86–2.14 (m, 2, CH_2), 3.55–3.68 (br, 1, CHO), 4.75–4.96 (m, 2, allenyl); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.1, 22.6, 26.2 (3 C), 27.8, 30.9, 31.6, 37.2, 79.0, 79.8, 107.0, 205.9; HRMS m/z calcd for $C_{13}H_{24}O$ (M^+) 196.1828, found 196.1856. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.40; H, 12.59.

(*E*)-1-Phenyl-1-undecen-5-yn-3-ol (3i): TLC R_f 0.27 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3300 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.88 (t, 3, J = 7.1 Hz, CH_3), 1.20–1.60 (m, 6, 3 CH_2), 2.10–2.24 (m, 3, CH_2 and OH), 2.42–2.62 (m, 2, CH_2), 4.35–4.45 (m, 1, CHO), 6.27 (dd, 1 J = 6.3 and 15.5 Hz, vinyl), 6.65 (d, 1, J = 15.5 Hz, vinyl), 7.20–7.45 (m, 5, aromatic); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.0, 18.8, 22.3, 28.3, 28.7, 31.2, 71.1, 75.5, 83.8, 126.6 (2 C), 127.8, 128.6 (2 C), 130.6, 131.0, 136.7; HRMS m/z calcd for $C_{17}H_{22}O$ (M^+) 242.1672, found 242.1649.

(*E*)-4-Pentyl-1-phenyl-1,4,5-hexatrien-3-ol (4i): TLC R_f 0.35 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3300, 1960 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.88 (t, 3, J = 6.9 Hz, CH_3), 1.20–1.55 (m, 6, 3 CH_2), 1.90 (d, 1, J = 5.0 Hz, OH), 1.95–2.10 (m, 2, CH_2), 4.60–4.70 (br, 1, CHO), 4.90–5.00 (m, 2, allenyl), 6.21 (dd, 1, J = 6.9 and 15.8 Hz, vinyl), 6.63 (d, 1, J = 15.8 Hz, vinyl), 7.20–7.45 (m, 5, aromatic); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.1, 22.6, 27.4, 28.3, 31.6, 72.8, 79.8, 107.4, 126.7 (2 C), 127.8, 128.6 (2 C), 130.2, 131.2, 136.7, 204.2; HRMS m/z calcd for $C_{17}H_{22}O$ (M^+) 242.1672, found 242.1684.

3-Ethyl-5-undecyn-3-ol (3j): TLC R_f 0.38 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3300 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.89 (t, 6, J = 7.6 Hz, 2 CH_3), 0.90 (t, 3, J = 6.9 Hz, CH_3), 1.20–1.70 (m, 11, 5 CH_2 and OH), 2.17 (tt, 2, J = 7.1 and 2.5 Hz, CH_2), 2.31 (t, 2, J = 2.5 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 8.0, 14.1, 18.8 (2 C), 22.3, 28.8, 29.8, 30.7 (2 C), 31.2, 73.8, 76.0, 83.6; HRMS m/z calcd for $C_{11}H_{19}O$ ($M^+ - C_2H_5$) 167.1437, found 167.1432. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.26; H, 12.57.

3-Ethyl-4-pentyl-4,5-hexadien-3-ol (4j): TLC R_f 0.46 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3300, 1950 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.75–0.95 (m, 9, 3 CH_3), 1.15–1.85 (m, 11, 5 CH_2 and OH), 2.10–2.25 (m, 2, CH_2), 4.93 (t, 2, J = 3.8 Hz, allenyl); HRMS m/z calcd for $C_{13}H_{24}O$ (M^+) 196.1828, found 196.1816. This minor component decomposed on GLC, giving a major peak (t_R 9.1 min, PEG-20M on Chromosorb WAW, 3 mmϕ × 2 m, 1.2 kg/cm^2, 100 °C). The structure **4j** was assigned by allenyl protons at δ 4.93.

2,2,3-Trimethyl-5-undecyn-3-ol (3l): TLC R_f 0.53 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3400 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.90 (t, 3, J = 7.1 Hz, CH_3), 0.96 (s, 9, t-C_4H_9), 1.26 (s, 3, CH_3), 1.30–1.55 (m, 6, 3 CH_2), 1.90 (s, 1, OH), 2.18 (tt, 2, J = 2.3 and 6.9 Hz, CH_2), 2.28 (dt, 1, J = 16.5 and 2.3 Hz, a proton of CH_2), 2.53 (br. d, 1, J = 16.5 Hz, a proton of CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 13.9, 18.7, 22.1, 22.3, 25.4 (3 C), 28.3, 28.7, 31.1, 37.1, 74.8, 76.8, 83.9; HRMS m/z calcd for $C_{10}H_{17}O$ (M^+ – t-C_4H_9) 153.1280, found 153.1304.

2,2,3-Trimethyl-4-pentyl-4,5-hexadien-3-ol (4l): TLC R_f 0.53 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3300, 1950 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.89 (t, 3, J = 6.6 Hz, CH_3), 0.96 (s, 9, t-C_4H_9), 1.20–1.60 (m, 6, 3 CH_2), 1.32 (s, 3, CH_3), 1.76 (s, 1, OH), 1.90–2.10 (m, 2, CH_2), 4.86 (dt, 2, J = 3.6 and 3.6 Hz, allenyl); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.2, 22.7, 23.2, 25.2, 26.0 (3C), 28.4, 29.0, 31.8, 76.6, 79.4, 113.3, 205.8. HRMS m/z calcd for $C_{13}H_{23}O$ (M^+ – CH_3) 195.1750, found 195.1765. Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 79.88; H, 12.65.

8-*tert*-Butyl-10-hexadecyn-8-ol (3m): TLC R_f 0.33 (10:1 hexane/ethyl acetate); IR ($CHCl_3$) 3650–3450 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.89 (t, 3, J = 7.0 Hz, CH_3), 0.90 (t, 3, J = 7.0 Hz, CH_3), 0.98 (s, 9, t-C_4H_9), 1.20–1.70 (m, 18, 9 CH_2), 1.84 (s, 1, OH), 2.15 (tt, 2, J = 7.2 and 2.4 Hz, CH_2), 2.40 (dt, 1, J = 16.8 and 2.4 Hz, a proton of CH_2), 2.46 (dt, 1, J = 16.8 and 2.4 Hz, a proton of CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.0, 14.1, 18.8, 22.3, 22.7, 24.5, 25.9 (3 C), 26.0, 28.7, 29.4, 30.7, 31.2, 32.0, 35.8, 38.7, 76.1, 77.4, 83.8; HRMS m/z calcd for $C_{16}H_{29}O$ (M^+ – t-C_4H_9) 237.2220, found 237.2191.

4-*tert*-Butyl-3-pentyl-1,2-undecadien-4-ol (4m): TLC R_f 0.45 (10:1 hexane/ethyl acetate); IR ($CHCl_3$) 3650–3400, 1950 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, 3, J = 7.0 Hz, CH_3), 0.89 (t, 3, J = 6.7 Hz, CH_3), 0.95 (s, 9, t-C_4H_9), 1.20–1.73 (m, 19, 9 CH_2 and OH), 1.83–2.03 (m, 2, CH_2), 4.78–4.90 (m, 2, allenyl); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.2 (2 C), 22.7, 22.8, 24.1, 26.2 (3 C), 26.5, 28.3, 29.2, 29.5, 30.3, 31.9, 32.0, 33.8, 77.6, 79.1, 109.4, 205.9; HRMS, m/z calcd for $C_{19}H_{35}O$ (M^+ – CH_3) 279.2690, found 279.2667. Anal. Calcd for $C_{20}H_{38}O$: C, 81.56; H, 13.01. Found: C, 81.27; H, 13.34.

2-Methyl-3-phenyl-5-undecyn-3-ol (3n): TLC R_f 0.50 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3400 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.80 (d, 3, J = 6.9 Hz, CH_3), 0.84 (t, 3, J = 6.8 Hz, CH_3), 0.89 (d, 3, J = 6.9 Hz, CH_3), 1.10–1.40 (m, 6, 3 CH_2), 2.00–2.20 (m, 3, CH_2 and CH), 2.37 (s, 1, OH), 2.70–2.88 (m, 2, CH_2), 7.20–7.50 (m, 5, aromatic); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.0, 17.0, 17.7, 18.6, 22.2, 28.5, 30.5, 30.9, 37.3, 75.9, 77.8, 84.4, 126.1 (2 C), 126.6, 127.6 (2 C), 144.7; HRMS m/z calcd for $C_{15}H_{19}O$ (M^+ – i-C_3H_7) 215.1437, found 215.1455.

2-Methyl-4-pentyl-3-phenyl-4,5-hexadien-3-ol (4n): TLC R_f 0.55 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3450, 1950 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.70 (d, 3, J = 6.6 Hz, CH_3), 0.80 (t, 3, J = 6.6 Hz, CH_3), 1.01 (d, 3, J = 6.9 Hz, CH_3), 1.06–1.35 (m, 6, 3 CH_2), 1.60–1.90 (m, 2, CH_2), 2.06 (s, 1, OH), 2.40–2.53 (m, 1, CH), 4.93–5.07 (m, 2, allenyl), 7.20–7.50 (m, 5, aromatic); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.1, 17.2, 17.4, 22.6, 26.8, 27.5, 31.5, 34.3, 79.2, 80.0, 111.2, 126.0 (2 C), 126.5, 127.8 (2 C), 145.0, 204.1; HRMS m/z calcd for $C_{18}H_{26}O$ (M^+) 258.1985, found 258.2002.

Spectral data (IR, ^1H and ^{13}C NMR) of the new compounds, **3p**, **3q**, **4q**, **3r**, **4r**, **3s**, **4s**, **3u**, **4u**, **3v**, **3w**, **3x**, **3y**, are given in supplementary material.

1-(2-Octynyl)-2-cyclohexen-1-ol (3p): TLC R_f 0.32 (5:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{14}H_{20}$ (M^+ – H_2O) 188.1566, found 188.1576.

2-(2-Octynyl)borneol (3q): TLC R_f 0.48 (10:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{18}H_{30}O$ (M^+) 262.2298, found 262.2280. Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.36; H, 11.79. The stereochemistry is not defined.

2-(1-Pentylpropadienyl)borneol (4q): TLC R_f (10:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{18}H_{30}O$ (M^+) 262.2298, found 262.2288. Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.39; H, 11.82. The stereochemistry is not defined.

2-(2-Octynyl)adamantan-2-ol (3r): TLC R_f 0.31 (10:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{18}H_{26}$ (M^+ – H_2O) 242.2036, found 242.2028. Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.83; H, 11.07.

2-(1-Pentylpropadienyl)adamantan-2-ol (4r): mp 60–62 °C; TLC R_f 0.29 (10:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{18}H_{28}O$ (M^+) 260.2141, found 260.2127. Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 83.07; H, 11.03.

2,2-Dimethyl-3-tridecyn-6-ol (3s). No impurities were detected by GLC analysis (t_R 55 min, PEG-20M on Chromosorb WAW, 3 mmϕ × 2 m, 1.2 Kg/cm^2, 180 °C): TLC R_f 0.32 (8:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{15}H_{28}O$ (M^+) 224.2141, found 224.2108. Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.15; H, 12.74.

3-*tert*-Butyl-1,2-undecadien-4-ol (4s): TLC R_f 0.32 (8:1 hexane/ethyl acetate); a 87:13 mixture of **4s** (t_R 52 min) and **3s** analyzed by GLC under same conditions described above. The allenyl structure **4s** was assigned by major spectral peaks: HRMS m/z calcd for $C_{15}H_{28}O$ (M^+) 224.2141, found 224.2123.

5,5-Dimethyl-1-phenyl-3-hexyn-1-ol (3u): TLC R_f 0.30 (5:1 hexane/ethyl acetate). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.13; H, 9.04.

2-*tert*-Butyl-1-phenyl-2,3-butadien-1-ol (4u). No impurities were detected by GLC analysis (t_R 70 min, PEG-20M on Chromosorb WAW, 3 mmϕ × 2 m, 1.2 Kg/cm^2,m 200 °C): TLC R_f 0.30 (5:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{13}H_{15}O$ (M^+ – CH_3) 187.1124, found 187.1135.

2,2,3,7,7-Pentamethyl-5-octyn-3-ol (3v): TLC R_f 0.54 (5:1 hexane/ethyl acetate). Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.57; H, 12.13.

2,7,7-Trimethyl-3-phenyl-5-octyn-3-ol (3w): TLC R_f 0.47 (5:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{17}H_{23}$ (M^+ – OH) 227.1801, found 227.1808.

1-(4,4-Dimethyl-2-pentynyl)cyclohexanol (3x): mp 65–66 °C; TLC R_f 0.38 (5:1 hexane/ethyl acetate). Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.35; H, 11.52.

2-(4,4-Dimethyl-2-pentynyl)adamantanol (3y): TLC R_f 0.50 (5:1 hexane/ethyl acetate); HRMS m/z calcd for $C_{17}H_{24}$ ($M^+ - H_2O$) 228.1879, found 228.1864.

17-(4,4-Dimethyl-2-pentynyl)-3-[(*tert*-butyldimethylsilyl)oxy]estra-1,3,5(10)-trien-17-ol (3z): mp 98–100 °C; TLC R_f 0.40 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3400 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.18 (s, 6, $Si(CH_3)_2$), 0.94 (s, 3, CH_3), 0.97 (s, 9, Si-*t*-C_4H_9), 1.22 (s, 9, *t*-C_4H_9), 1.1–2.9 (m, 16, 6 CH_2, 3 CH, and OH), 2.36 (d, 1, J = 16.2 Hz, a proton of CH_2), 2.54 (d, 1, J = 16.2 Hz, a proton of CH_2), 6.5–6.7 (m, 2, aromatic), 7.12 (d, 1, J = 8.2 Hz, aromatic). Anal. Calcd for $C_{31}H_{48}O_2Si$: C, 77.44; H, 10.06. Found: C, 77.42; H, 10.09. The stereochemistry at C(17) is not defined.

8-(Trimethylsilyl)-10-hexadecyn-8-ol (17): TLC R_f 0.49 (8:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3200 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.09 (s, 9, $Si(CH_3)_3$), 0.82–0.94 (m, 6, 2 CH_2), 1.17–1.70 (m, 19, 9 CH_2 and OH), 2.16 (tt, 2, J = 6.9 and 2.3 Hz, CH_2), 2.35 (dt, 1, J = 16.3 and 2.3 Hz, a proton of CH_2), 2.44 (dt, 1, J = 16.3 and 2.3 Hz, a proton of CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ −3.0 (3 C), 14.0, 14.1, 18.8, 22.2, 22.7, 23.9, 28.1, 28.7, 29.2, 30.5, 31.1, 31.9, 38.4, 67.0, 75.9, 83.8; HRMS m/z calcd for $C_{19}H_{38}OSi$ (M^+) 310.2693, found 310.2719.

2-Methyl-6-(trimethylsilyl)-3-tridecyn-6-ol (18): TLC R_f 0.50 (8:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3200 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.09 (s, 9, $Si(CH_3)_3$), 0.88 (t, 3, J = 6.8 Hz, CH_3), 1.15 (d, 6, J = 6.9 Hz, 2 CH_3), 1.20–1.70 (m, 13, 6 CH_2 and OH), 2.35 (dd, 1, J = 16.5 and 2.3 Hz, a proton of CH_2), 2.43 (dd, 1, J = 16.5 and 2.3 Hz, a proton of CH_2), 2.45–2.63 (m, 1, CH); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ −2.9 (3 C), 14.1, 20.7, 22.7, 23.2 (2 C), 23.8, 28.1, 29.2, 30.5, 31.9, 38.3, 66.9, 75.1, 89.6; HRMS m/z calcd for $C_{17}H_{34}OSi$ (M^+) 282.2380, found 282.2346. Anal. Calcd for $C_{17}H_{34}OSi$: C, 72.27; H, 12.13. Found: C, 72.18; H, 12.33.

2,2-Dimethyl-6-(trimethylsilyl)-3-tridecyn-6-ol (19): TLC R_f 0.35 (10:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3300 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.09 (s, 9, $Si(CH_3)_3$), 0.89 (t, 3, J = 7.3 Hz, CH_3), 1.21 (s, 9, *t*-C_4H_9), 1.1–1.7 (m, 13, 6 CH_2 and OH), 2.35 (d, 1, J = 16.3 Hz, a proton of CH_2), 2.43 (d, 1, J = 16.3 Hz, a proton of CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ −2.9 (3 C), 14.0, 22.8, 23.8, 27.6, 28.1, 29.3, 30.5, 31.3 (3 C), 31.9, 38.4, 66.9, 74.4, 92.6; HRMS m/z calcd for $C_{18}H_{36}OSi$ (M^+) 296.2536, found 296.2558.

10-Hexadecyn-8-ol (3f).[37] 8-(Trimethylsilyl)-10-hexadecyn-8-ol (**17**, 51.8 mg, 1.65×10^{-4} mol) was placed in a 10-mL test tube and dissolved in DMF (1.5 mL). After the solution was cooled to 0 °C, tetrabutylammonium fluoride (1.00 mL, 1.00×10^{-3} mol) was added. The mixture was stirred for 15 min at this temperature, warmed up to 27 °C, and stirred further for 24 h. After the mixture was cooled again to 0 °C, ether (2 mL) and saturated aqueous NaCl solution (2 mL) were added, and the mixture was extracted with ether (4 mL × 2). The organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residual oil was subjected to silica gel column chromatography (0.6 g) using a 40:1 mixture of hexane and ethyl acetate as eluant, yielding **3f** (38.6 mg, 98%) as a colorless oil: TLC R_f 0.32 (8:1 hexane/ethyl acetate); IR ($CHCl_3$) 3650–3100 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.82–0.94 (m, 6, 2 CH_3), 1.15–1.60 (m, 18, 9 CH_2), 1.80–2.05 (br, 1, OH), 2.10–2.20 (m, 2, CH_2), 2.26 (ddt, 1, J = 16.5, 6.9, and 2.3 Hz, a proton of CH_2), 2.40 (ddt, 1, J = 16.5, 4.6, and 2.3 Hz, a proton of CH_2), 3.58–3.76 (m, 1, CHO).

2-Methyl-3-tridecyn-6-ol (21) and 2,2-Dimethyl-3-tridecyn-6-ol (3s). These secondary alcohols were prepared by a similar procedure to the synthesis of **3f** using **18**, **19**, and tetrabutylammonium fluoride, yielding **21** (91%), **3s** (97%) as colorless oils, respectively, after liquid chromatography on silica gel using a 60:1 mixture of hexane and ethyl acetate as eluant. **21**: TLC R_f 0.42 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3650–3300 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.88 (t, 3, J = 6.8 Hz, CH_3), 1.1–1.9 (m, 13, 6 CH_2 and OH), 1.16 (d, 6, J = 6.9 Hz, 2 CH_3), 2.26 (ddd, 1, J = 16.5, 6.9, and 2.3 Hz, a proton of CH_2), 2.40 (ddd, 1, J = 16.5, 4.6, and 2.3 Hz, a proton of CH_2), 2.45–2.64 (m, 1, CH), 3.57–3.75 (m, 1, CHO); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.2, 20.6, 22.8, 23.4 (2 C), 25.7, 27.8, 29.3, 29.6, 31.9, 36.3, 70.3, 75.3, 89.2; HRMS m/z calcd for $C_{14}H_{26}O$ (M^+) 210.1985, found 210.1984.

(*Z*)-10-Hexadecen-8-ol (22). 10-Hexadecyn-8-ol (**3f**, 8.8 mg, 3.69×10^{-5} mol) was placed in a 5-mL test tube and dissolved in ether (0.5 mL). Lindlar catalyst (2.0 mg) was added, and the mixture was stirred at 16 °C for 45 h under H_2 gas (1 atm). The catalyst was removed by filtration through a short Celite column and rinsed with ether. The filtrates were concentrated under reduced pressure, yielding colorless oily material (8.7 mg, 98%). This material was subjected to a capillary GLC analysis (see condition 1 described in general remarks), indicating the ratio of 30.2:1 for **22** and **23**. Retention times, t_R, of the products were: **3f**, 9.8 min; **22**, 7.7 min; **23**, 7.4 min. **22**: TLC R_f 0.48 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3600–3200 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.7–1.0 (m, 6, 2 CH_3), 1.1–1.7 (m, 19, 9 CH_2 and OH), 2.05 (dt, 2, J = 6.6 and 6.9 Hz, CH_2), 2.21 (dd, 2, J = 6.4 and 6.6 Hz, CH_2), 3.50–3.70 (m, 1, CHO), 5.41 (dt, 1, J = 10.7 and 6.4 Hz, vinyl), 5.58 (dt, 1, J = 10.7 and 6.6 Hz, vinyl); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.2 (2 C), 22.7, 22.8, 25.9, 27.5, 29.3, 29.4, 29.7, 31.6, 31.9, 35.4, 36.9, 71.6, 125.2, 133.7; HRMS m/z calcd for $C_{16}H_{32}O$ (M^+) 240.2454, found 240.2426.

(*E*)-10-Hexadecen-8-ol (23). Liquid ammonia (2 mL) was placed in a 10-mL Schlenk tube at −78 °C, and lithium wire (11.2 mg, 1.61×10^{-3} mol) was added. The mixture was gradually warmed up to 0 °C and cooled again to −78 °C. To this a solution of 10-hexadecyn-8-ol (**3f**, 127.6 mg, 5.35×10^{-4} mol) in ether (0.2 mL) and *t*-C_4H_9OH (0.101 mL, 1.07×10^{-3} mol) were added, and the mixture was rinsed with ether (0.8 mL). After being warmed up to 16 °C, the mixture was stirred for 28 h at this temperature, and then EtOH (0.3 mL) and a pH 7.4 phosphate buffer solution (3 mL) were added. The organic layer was separated, and the aqueous layer was extracted with ether (2 mL × 2). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure, yielding colorless oily material (128.0 mg, 99%). This material was subjected to a capillary GLC analysis (see condition 1 described in general remarks), indicating the ratio of 1:1.38:116 for **3f**, **22**, and **23**. **23**: TLC R_f 0.48 (5:1 hexane/ethyl acetate); IR ($CHCl_3$) 3650–3200 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.75–1.0 (m, 6, 2 CH_3), 1.1–1.6 (m, 19, 9 CH_2 and OH), 1.95–2.34 (m, 4, 2 CH_2), 3.5–3.7 (m, 1, CHO), 5.40 (dt, 1, J = 15.5 and 6.6 Hz, vinyl), 5.55 (dt, 1, J = 15.5 and 6.6 Hz, vinyl); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.1, 14.2, 22.6, 22.7, 25.8, 29.2, 29.4, 29.7, 31.5, 31.9, 32.7, 36.8, 40.8, 71.0, 125.9, 134.8; HRMS m/z calcd for $C_{16}H_{30}$ ($M^+ - H_2O$) 222.2349, found 222.2355.

Typical Procedure for NMR Study. Samples for NMR study were prepared as follows: Methyllithium (1.27 M ether solution, 0.323 mL, 0.41 mmol) was placed in a dry 5-mm NMR tube, and the solvent was removed under vacuum. The powdered methyllithium was cooled to −95 °C and dissolved in THF-d_8 (0.2 mL). To this a THF-d_8 (0.3 mL) solution of allenylstannane **13** (100 mg, 0.41 mmol) was added at −95 °C. The NMR tube was sealed under vacuum.

Competition Reaction of Allenylstannanes, 11, 12b, and 14/*n*-Butyllithium Mixed Reagents with Octanal. Allenylstannane **11** (182.4 mg, 0.554 mmol), **12b** (151.3 mg, 0.554 mmol), and **14** (143.5 mg, 0.554 mmol) were placed in a 20-mL test tube and dissolved in THF (7 mL). This mixture was cooled to −95 °C, and *n*-butyllithium (1.48 M hexane solution, 1.12 mL, 1.66 mmol) was added. After the mixture was stirred at −95 °C for 10 min, octanal (8.65 μL, 0.0554 mmol) was added. The mixture was stirred at −95 °C for 5 min and poured into a pH 7.4 phosphate buffer solution (6 mL). Ether (5 mL) was added, the mixture was vigorously shaken, and then the organic layer was subjected to a capillary GLC analysis (see condition 2 described in general remarks). Retention times, t_R, of products were: **3a**, 12.4 min; **4a**, 12.9 min; **3f**, 27.1 min; **4f**, 24.0 min; **3s**, 16.7 min; **4s**, 17.2 min. The ratio of **3a**, **4a**, **3f**, **4f**, **3s**, and **4s** was 5.2:1.1:8.6:3.0:11.3:1.0.

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Registry No. **3a**, 22127-86-2; **3b**, 53723-35-6; **3c**, 19135-04-7; **3d**, 19135-08-1; **3e**, 124155-82-4; **3f**, 69754-60-5; **3g**, 124155-83-5; **3h**, 35281-68-6; **3i**, 124155-84-6; **3j**, 124155-85-7; **3k**, 59148-52-6; **3l**, 124155-86-8; **3m**, 124155-89-1; **3n**, 124155-90-4; **3o**, 69754-61-6; **3p**, 124155-94-8; **3q**, 124155-97-1; **3r**, 124155-98-2; **3s**, 124156-17-8; **3t**, 98405-10-8; **3u**, 124156-18-9; **3v**, 124156-11-2; **3w**, 124156-12-3; **3x**, 124156-14-5; **3y**, 124156-15-6; **3z**, 124156-16-7; **4a**, 79090-73-6;

4b, 52547-77-0; **4c**, 124155-99-3; **4d**, 34761-56-3; **4e**, 124175-14-0; **4f**, 69754-59-2; **4g**, 124156-00-9; **4h**, 35281-64-2; **4i**, 124156-01-0; **4j**, 124156-02-1; **4k**, 59148-51-5; **4l**, 124156-03-2; **4m**, 124156-04-3; **4n**, 124156-05-4; **4o**, 69754-58-1; **4p**, 79090-78-1; **4q**, 124156-06-5; **4r**, 124156-07-6; **4s**, 124156-08-7; **4t**, 124156-09-8; **4u**, 124156-10-1; **4w**, 124156-13-4; **11**, 53915-69-8; **12b**, 111847-83-7; **13**, 124155-87-9; **14**, 124155-88-0; **15b**, 69165-98-6; **16**, 61157-32-2; **17**, 124155-91-5; **18**, 124155-92-6; **19**, 124155-93-7; **21**, 124156-19-0; **22**, 124155-95-9; **23**, 124155-96-0; i-PrMgCl, 1068-55-9; t-BuMgCl, 677-22-5; $H_3C(CH_2)_6CHO$, 124-13-0; $(CH_3)_3CCHO$, 630-19-3; PhCHO, 100-52-7; PhCH=CHCHO, 14371-10-9; $(Et)_2CO$, 96-22-0; $(i\text{-}Pr)_2CO$, 565-80-0; $H_3CCOC(CH_3)_3$, 75-97-8; t-$BuCO(CH_2)_6CH_3$, 61759-36-2; i-PrCOPh, 611-70-1; $H_3CC{\equiv}C(CH_2)_4CH_3$, 2809-67-8; $BrCH_2C{\equiv}CC(CH_3)_3$, 52323-99-6; cyclohexanone, 108-94-1; 2-cyclohexenone, 930-68-7; (1*R*)-(+)-camphor, 464-49-3; 2-adamantanone, 700-58-3; estrone 3-*O*-*tert*-butyldimethylsilyl ether, 57711-40-7.

Supplementary Material Available: Spectral data (IR, ^1H and ^{13}C NMR) of **3p**, **3q**, **4q**, **3r**, **4r**, **3s**, **4s**, **3u**, **4u**, **3v**, **3w**, **3x**, and **3y** and copies of actual ^1H and ^{13}C NMR spectra of **3i**, **4i**, **3l**, **3m**, **3n**, **4n**, **3p**, **3w**, **3y**, **17**, **19**, **21**, **22**, and **23** (32 pages). Ordering information is given on any current masthead page.

Cobalt Carbonyl Catalyzed Hydrosilylation of Nitriles: A New Preparation of *N,N*-Disilylamines

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Cobalt carbonyl catalyzed hydrosilylation of a wide variety of nitriles with $HSiMe_3$ has been examined. The reaction generally proceeded at 60 °C to give *N,N*-disilylamines in good yields. Electron-donating groups on aromatic nitriles facilitated the reaction, and electron-withdrawing groups decreased the rate. The reaction of aliphatic nitriles at 60 °C was sluggish except for cyclopropanenitriles, whereas raising the temperature to 100 °C greatly enhanced the reaction rate. In the case of acrylonitrile, four types of products were obtained. For monosubstituted acrylonitriles, consecutive 1,2- and 1,4-addition of $HSiMe_3$ were observed as a major route to give (*Z*)-*N,N*-disilylenamines exclusively. The introduction of two kinds of alkyl substituents to acrylonitrile lowered the reactivity and reversed the selectivity to give (*E*)-*N,N*-disilylenamines in ca. 20% yield. A plausible reaction pathway discussed.

Transition-metal-catalyzed hydrosilylation of carbonyl compounds, imines, oximes, acetylenes, and olefins has been developed for the last 30 years because of its importance as a method not only for reduction but also for introducing silyl groups into organic molecules.[1] The recent development of asymmetric hydrosilylation has further illustrated the applicability of this process.[2] In contrast to these well-established and useful reactions, little[3] is known about hydrosilylation of the C–N triple bond, since the cyano group has been believed to be inert under the usual hydrosilylation conditions. For example, rhodium(III)-catalyzed hydrosilylation of α,β-unsaturated nitriles has been developed as a method for the preparation of α-silyl nitriles,[4] and molybdenum-catalyzed reduction of α,β-unsaturated nitriles with H_3SiPh gave only alkyl nitriles in good yields.[5] As exceptional cases, Corriu et al. have reported that 1,2-bis(dimethylsilyl)benzene added to aklyl nitriles in the presence of an Rh catalyst to give a mixture of *N,N*-disilylenamines and amines,[6a] and Chalk has found that cobalt carbonyl catalyzed addition of $HSiMe_2Cl$ to $CH_2{=}CH(CH_3)CN$ gave $(CH_3)_2C{=}CHN(SiMe_2Cl)_2$, but in only 20% yield after 6 days.[6b] Recently, we have found that $HSiMe_3$ cleanly added to the C–N triple bond in aromatic nitriles in the presence of a catalytic amount of $Co_2(CO)_8$.[7] This process provides a new

Table I. Cobalt Carbonyl Catalyzed Addition of Trimethylsilane to Aromatic Nitriles[a]

$$ArCN + HSiMe_3 \xrightarrow[CO\ atm.]{cat.\ Co_2(CO)_8} ArCH_2N(SiMe_3)_2$$

entry	ArCN	yields of product, %[b]
1	C_6H_5CN	61
2	$2\text{-}CH_3C_6H_4CN$	11 (22)
3	$3\text{-}CH_3C_6H_4CN$	57 (68)
4	$4\text{-}CH_3C_6H_4CN$	91
5	$4\text{-}NCCH_2C_6H_4CN$	(36)[c]
6	$4\text{-}CH_3OC_6H_4CN$	67 (88)
7	$4\text{-}(CH_3)_2NC_6H_4CN$	51 (73)
8	$3\text{-}ClC_6H_4CN$	(50)[d]
9	$4\text{-}ClC_6H_4CN$	(53)[e]
10	$4\text{-}CH_3CO_2C_6H_4CN$	(46)[e]
11	1-naphtyl nitrile	0
12	2-naphtyl nitrile	68

[a] Reaction conditions: nitrile (2.5 mmol), $HSiMe_3$ (25 mmol), $Co_2(CO)_8$ (0.2 mmol), $CH_3C_6H_5$ (10 mL), CO atmosphere, 60 °C, 20 h. [b] GLC yields in parentheses. [c] $Co_2(CO)_8$ (0.625 mmol) was used. [d] 48 h. [e] 40 h.

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