icals derived from both compounds. In the presence of oxygen, formic acid and a rather important amount of acetone are formed. The hydroxy benzhydryl radicals are simultaneously reoxidized to benzophenone which therefore does not seem to be consumed.

Formation of benzene and acetone are likely to go unnoticed in practice due to the workup techniques generally employed. The other products, which are obtained in small quantities, may well remain undetected when photochemical reactions with higher quantum yields are in competition for photons. All of these products can pertub the photochemical processes in very unexpected ways. Therefore, the results of long-duration irradiations carried out in *tert*-butyl alcohol when using benzophenone as a sensitizer, with or without oxygen, have to be interpreted carefully.

Experimental Section

GC analyses were carried out on 10 ft × $^1/_8$ in. 5% Carbowax 20M on Chromosorb W columns at a flow rate of 30 mL/min. *tert*-Butyl alcohol was distilled before use; acetonitrile (Aldrich spectrophotometric grade) was used as supplied. Both solvents were checked spectrophotometrically for absence of traces of acetone and benzene before use. Irradiations were performed in a Pyrex glass vessel (capacity 150 mL, optical path length 0.5 cm) using a medium pressure mercury lamp (MEDA 400 W). The solution was flushed with a stream of dry oxygen or dry nitrogen. In all experiments, benzophenone (*c* 0.07 M) absorbed 99% of the incident light. The intensity of the lamp used was calculated by a Ph_2CO/Ph_2CHOH actinometry (c_0 0.1 M/0.05 M; $I = 4.5 \times 10^{-4}$ E/min). Thus, the quantum yield of the benzophenone cleavage was $\Phi = 5 \times 10^{-4}$.

Irradiation of the Ph_2CO/t-BuOH/O_2 System. A solution of benzophenone (2 g, 11 mmol) in *t*-BuOH (150 mL) was irradiated under a slow stream of oxygen for 168 h. The following compounds were detected or isolated from several similar experiments.

(a) Acetone and Benzene. GC Detection: Determination of concentrations was performed using a Perkin-Elmer F30 instrument and an electronic integrator (Perkin-Elmer M2). Concentrations were determined by comparison with standard *t*-BuOH/acetone and *t*-BuOH/benzene mixtures.

UV Detection: Determination of concentrations was performed on a CARY 15 instrument. Optical densities of benzene and acetone in *t*-BuOH solution were measured at the relevant λ_{max}. Both measures gave the same values: acetone 7.5 mmol and benzene 0.1 mmol (from 150 mL of *t*-BuOH).

(b) Formic Acid. Formic acid was isolated as *p*-bromophenacyl formate by action of *p*-bromophenacyl bromide on the reaction mixture. Weighing gave 0.15 mmol of formic acid.

(c) Phenol and Benzoic Acid.[9] After evaporation of solvent, the reaction mixture was dissolved in dichloromethane and washed with 10% aqueous sodium hydroxide, and the washings were neutralized with dilute hydrochloric acid. Benzoic acid and phenol were extracted with dichloromethane and the extracts were washed with sodium bicarbonate solution. The washings were acidified with dilute hydrochloric acid and extracted with dichloromethane. Evaporation gave benzoic acid (0.3 g, 2.5 mmol). Evaporation of the washed extract gave phenol (0.02 g, 0.2 mmol).

(d) 1,1-Diphenylethylene and Phenyl Benzoate. After evaporation of solvent, column chromatography on silica gel yielded 1,1-diphenylethylene (0.110 g, 0.6 mmol) and phenylbenzoate (0.05 g, 0.25 mmol) identified by IR, NMR, melting point, and comparison with authentic samples.

Irradiation of the $Ph_2CO/CH_3CN/O_2$ System. A solution of benzophenone (2 g) in acetonitrile (150 mL) was irradiated under a slow stream of dry oxygen for 170 h. UV detection of the reaction mixture gave 1 mmol of benzene/150 mL of CH_3CN. After evaporation of solvent, chromatography on silica gel gave benzoic acid (0.300 g, 2.5 mmol) and phenyl benzoate (0.04 g, 0.2 mmol). No formic acid, acetone, and 1,1-diphenylethylene could be detected by the appropriate methods.

Irradiation of the $Ph_2CO/CH_3CN/N_2$ System. A solution of benzophenone (2 g) in acetonitrile (150 mL) was irradiated under nitrogen for 170 h. UV detection of the reaction mixture gave 1 mmol of benzene/150 mL of CH_3CN. After evaporation of solvent, chromatography on silica gel gave 0.1 g of benzopinacol (CH_2Cl_2/hexane (1:1)) and 0.05 g of benzoin (hexane/AcOEt (4:1)).

Baeyer–Villiger Type Reaction of Benzophenone. A solution of benzophenone (2 g) and *m*-chloroperbenzoic acid (0.1 g) in *t*-BuOH (70 mL) was stirred at 30 °C for 172 h. After evaporation of solvent, chromatography on silica gel gave 0.07 g (60%) of phenyl benzoate eluted with CH_2Cl_2/hexane (1:1).

Acknowledgment. We are grateful to Pr. J. Levisalles for helpful discussions and to Pr. J. Lemaire for his comments.

Registry No. Ph_2CO, 119-61-9; *t*-BuOH, 75-65-0; O_2, 7782-44-7; $Ph_2\dot{C}OH$, 4971-41-9; $\cdot CH_2C(OH)Me_2$, 5723-74-0; $Ph\dot{C}O$, 2652-65-5; $Ph\cdot$, 2396-01-2; phenyl benzoate, 93-99-2.

(9) Vogel, A. L. "Practical Organic Chemistry", 3rd ed.; Longman: 1956; p 362.
(10) Jeandrau, J. P.; Gramain, J. C.; Lemaire, J. *J. Chem. Res., Synop.* **1979**, 186; *J. Chem. Res., Miniprint* **1979**, 2240.
(11) Pitts, J. W.; Letsinger, R. L.; Taylor, R. P.; Patterson, J. M.; Recktenwald, G.; Martin, R. B. *J. Am. Chem. Soc.* **1959**, *81*, 1068.

Synthesis of Allenes by Nickel-Catalyzed Grignard Reactions with Silylpropargyl Alcohols

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In continuation of a study of nickel-catalyzed Grignard reactions with allyl alcohols and their derivatives[1] it became of interest to investigate the behavior of propargyl alcohols in such reactions.[2] In the absence of any possibility for the formation of (π-allyl)nickel intermediates and in view of the known tendency for acetylenes to undergo nickel-catalyzed Grignard addition reactions,[3] three

(1) (a) Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735. (b) Buckwalter, B. L.; Burfitt, I. R.; Felkin, H.; Joly-Goudket, M.; Naemura, K.; Salomon, M. F.; Wenkert, E.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 6445. (c) Swindell, C. S., Ph. D. Dissertation 1979, Rice University, Houston, TX 77001. (d) Wenkert, E. *Chimia* **1981**, *35*, 257. (e) Wenkert, E.; Ferreira, T. W. *Organometallics* **1982**, *1*, 1670. (f) Wenkert, E.; Fernandes, J. B.; Michelotti, E. L.; Swindell, C. S. *Synthesis* **1983**, 701.

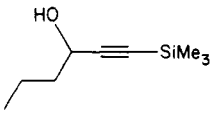
(2) For reactions of propargyl alcohols and their derivatives with organometallic reagents in the presence of other transition-metal species, see the following examples. (a) Pasternak, Y.; Delepine, M. *C. R. Acad. Sci. Fr.* **1962**, 3429. (b) Serratosa, F. *Tetrahedron Lett.* **1964**, 895. (c) Rona, P.; Crabbé, P. *J. Am. Chem. Soc.* **1968**, *90*, 4733. (d) Luche, J. L.; Barreiro, E.; Dollat, J. M.; Crabbé, P. *Tetrahedron Lett.* **1975**, 4615. (e) Moreau, J. L.; Gaudemar, M. *J. Organomet. Chem.* **1976**, *108*, 159. (f) Pasto, D.; Shultz, R.; McGrath, J.; Waterhouse, A. *J. Org. Chem.* **1978**, *43*, 1382. (g) Pasto, D.; Chou, S.; Waterhouse, A.; Shultz, R.; Hennion, G. *J. Org. Chem.* **1978**, *43*, 1385. (h) Pasto, D.; Chou, S.; Fritzen, E.; Shultz, R.; Waterhouse, A.; Hennion, G. *J. Org. Chem.* **1978**, *43*, 1389. (i) Vermeer, P., Westmijze, H.; Kleijn, H.; van Dijeck, L. A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 56. (j) Jeffery-Luong, T.; Linstrumelle, G. *Tetrahedron Lett.* **1980**, *21*, 5019. (k) Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1981**, *22*, 1451. (l) Kleijn, H.; Meijer, J.; Overbeek, G. C.; Vermeer, P. *Recl. Trav. Chem. Pays-Bas* **1982**, *101*, 97. (m) Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103. (n) Ruitenberg, K.; Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 405. (o) Elsevier, C. J.; Kleijn, H.; Ruitenberg, K.; Vermeer, P. *J. Chem Soc., Chem. Commun.* **1983**, 1529. (p) Colas, Y.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 845.

0022-3263/85/1950-1122$01.50/0

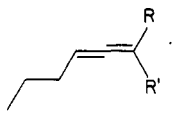
types of primary products could be anticipated (Scheme I).

Since early experiments on fully substituted propargyl alcohols with alkylmagnesium and arylmagnesium halides led to mixtures of many products and thus served no purpose for organic synthesis, the study was limited to ethynylcarbinols, whose terminal acetylenic carbon was protected by a trimethylsilyl group. On the basis of previous experience,[4] the catalyst of choice was [1,3-bis(diphenylphosphino)propane]nickel dichloride (dpppNiCl$_2$). Whereas, as the following discussion indicates, all propargyl systems underwent the desired reaction exceedingly well, the simplest member of the series, i.e., the primary alcohol 3-(trimethylsilyl)-2-propynol, unfortunately also yielded many products.

Nickel-catalyzed reactions of the secondary alcohol **1** with methylmagnesium and (*p*-methoxyphenyl)magnesium bromides produced allenes **2a** and **2b**, respectively, in 97% yield each. In accord with previous experience,[5] the reaction with the aromatic Grignard reagent was much faster than that with the aliphatic one.

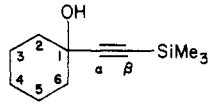


1

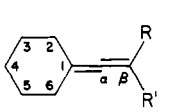


2a, R=Me; R'=SiMe$_3$
b, R=C$_6$H$_4$OMe-*p*; R'=SiMe$_3$
c, R=C$_6$H$_4$OMe-*p*; R'=H

Nickel-assisted reactions of the tertiary alcohol **3** with methylmagnesium, phenylmagnesium, and (*p*-methoxyphenyl)magnesium bromides led in over 95% yield to allenes **4a**, **4b**, and **4c**, respectively. Once again the aromatic organomagnesium compounds were more reactive than the aliphatic counterpart.

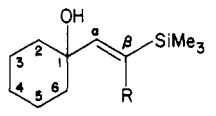


3

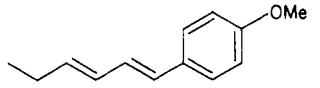


4a, R=Me; R'=SiMe$_3$
b, R=C$_6$H$_5$; R'=SiMe$_3$
c, R=C$_6$H$_4$OMe-*p*; R'=SiMe$_3$
d, R=C$_6$H$_4$OMe-*p*; R'=H
e, R=H; R'=SiMe$_3$

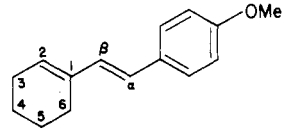
Whereas all above reactions had yielded compounds of structure type C (Scheme I), the reduction[3e] of alcohol **3** followed a pathway to a product of structure type A.[6] Thus a reaction of carbinol **3** with isopropylmagnesium bromide in the presence of bis(triphenylphosphino)nickel dichloride, [(C$_6$H$_5$)$_3$P]$_2$NiCl$_2$,[7] gave the allyl alcohol **5a** in 92% yield. The reaction was exceedingly slow, causing isomerization of the double bond.[3e] Workup of the reaction



5a, R=H
b, R=D



6



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with deuterium oxide yielded alcohol **5b**, indicative of the intermediacy of a compound of structure type A (Scheme I).[8]

Desilylation of allenes **2b** and **4c** with cesium fluoride in acetonitrile[9] produced allenes **2c** and **4d**, respectively; whose acid-catalyzed isomerization led to conjugated dienes **6** and **7**, respectively. Thus the new organometallic reaction with propargyl alcohols has given access in high yield not only to allenes and conjugated dienes but also to silicon compounds whose rich chemistry[10] permits their use for the preparation of variously functionalized compounds.

Experimental Section

Ultraviolet spectra of methanol solutions and infrared spectra of liquid films were recorded on Perkin-Elmer Model 550 and 1330 spectrophotometers, respectively. ^{1}H NMR spectra of CCl_4 solutions were obtained on a Varian Model EM-390 spectrometer and a 360-MHz instrument with a highly modified Varian Model HR-220 console, an Oxford magnet, and a Nicolet Model 1180-E computer system. ^{13}C NMR spectra of $CDCl_3$ solutions were taken on a Nicolet Model NT-200 (wide-bore, broad-band, with Oxford magnet) spectrometer, operating at 50.31 MHz in the Fourier transform mode. The carbon shifts are in parts per million downfield from Me$_4$Si; δ(Me$_4$Si) = δ(CDCl$_3$) + 76.9 ppm.

Alcohols 1 and 3. A 1.80 M ethereal solution of methyllithium, 6.7 mL (12 mmol), was added slowly at 0 °C to a solution of 1.08 g (11 mmol) of (trimethylsilyl)acetylene in 50 mL of dry ether under nitrogen, and the mixture was stirred at 0 °C for 1 h. *n*-Butyraldehyde, 720 mg (10 mmol), or 982 mg (10 mmol) of cyclohexanone was added and the solution permitted to warm to room temperature. After 1 h it was poured into a saturated ammonium chloride solution and extracted with ether. The extract was dried (Na$_2$SO$_4$) and evaporated. Distillation of the residue gave 1.35 g (79%) of liquid 1-(trimethylsilyl)-1-hexyn-3-ol (**1**): IR ($CHCl_3$) 3370 (m, OH), 2170 (m, C≡C) cm^{-1}. Sublimation of the other residue gave 1.65 g (84%) of solid 1-[(trimethylsilyl)ethynyl]cyclohexanol (**3**): IR 3580 (w, OH), 3410 (m), 2160 (m, C≡C) cm^{-1}; ^{13}C NMR δ −0.10 (Me$_3$), 23.2 (C-3, C-5), 25.1 (C-4), 39.8 (C-2, C-6), 68.7 (C-1), 82.2 (α-C), 109.6 (β-C).

General Procedure for the Reactions of Alcohols 1 and 3 with Grignard Reagents. A 2.85 M ethereal solution of methylmagnesium bromide, 0.85 mL (2.4 mmol), was added

(3) (a) Duboudin, J.; Jousseaume, B. *J. Organomet. Chem.* **1972**, *44*, C1; (b) **1975**, *96*, C47. (c) Radchenko, S.; Cherkasov, L.; Petrov, A. *J. Org. Chem. USSR* **1976**, *12*, 911. (d) Duboudin, J.; Jousseaume, B. *J. Organomet. Chem.* **1978**, *162*, 209. (e) Snider, B.; Karras, M.; Conn, R. *J. Am. Chem. Soc.* **1978**, *100*, 4624. (f) Snider, B.; Conn, R.; Karras, M. *Tetrahedron Lett.* **1979**, 1679. (g) Ten Hoedt, R.; van Koten, G.; Noltes, J. *J. Organomet. Chem.* **1979**, *170*, 131.

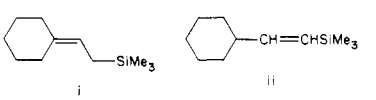
(4) Wenkert, E.; Leftin, M. H.; Michelotti, E. L. *J. Chem. Soc., Chem. Commun.* **1984**, 617.

(5) E.g.: (a) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246. (b) Reference 4.

(6) Products of structure type B are unlikely to form in view of the expected rapid elimination of magnesium halide and oxide from its precursor, thus producing allenes.

(7) (a) Trost, B. M.; Ornstein, P. L. *Tetrahedron Lett.* **1981**, *22*, 3463. (b) Wenkert, E.; Ferreira, T. W. *J. Chem. Soc., Chem. Commun.* **1982**, 840.

(8) At the end of a 72-h reaction the allyl alcohol **5a** was accompanied by a mixture of allene **4e** and olefins i and ii, products observed in less than 3% overall yield. The olefin content increased at the expense of alcohol **5a** on addition of more catalyst and extension of the reaction time. The slow formation of the olefins constitutes a fascinating example of a Felkin reaction[1a] of a C-magnesio derivative of an allyl alcohol (the product A precursor of Scheme I).

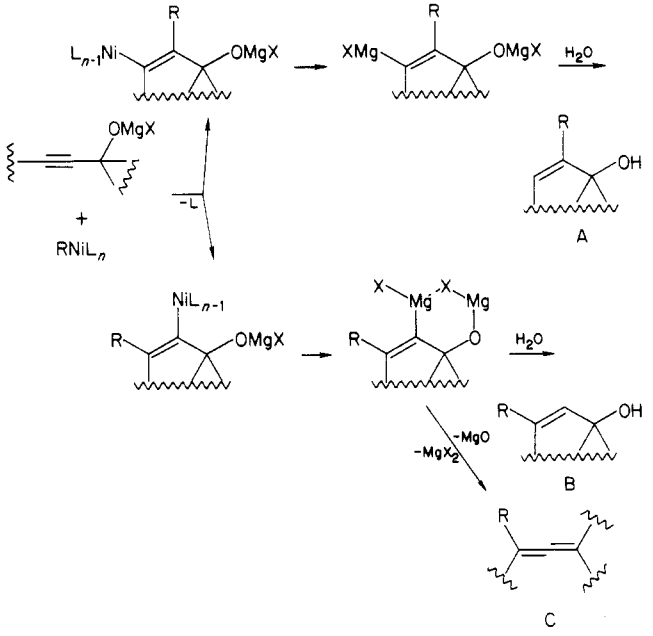


i ii

(9) Corey, E. J.; Katzenellenbogen, J. A.; Gilman, N. W.; Roman, S. A.; Erickson, B. W. *J. Am. Chem. Soc.* **1968**, *90*, 5618.

(10) Cf. Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981.

Scheme I



dropwise to a stirring suspension of 108 mg (0.20 mmol) of dpppNiCl$_2$ in 15 mL of dry benzene under argon, and the mixture was refluxed for 15 min. After this catalyst reduction, there were added sequentially a solution of 2.00 mmol of alcohol **1** or **3** in 10 mL of dry benzene and 2.20 mmol of the required Grignard reagent, and the mixture was heated at 80 °C for the length of time cited below. It then was cooled, poured into 50 mL of saturated ammonium chloride solution, and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed on medium-pressure silica gel columns (elution with hexane).

2-(Trimethylsilyl)-2,3-heptadiene (2a), prepared from a 2.85 M ethereal solution of methylmagnesium bromide and **1** (for 48 h): liquid; IR 1950 (m, C=C=C) cm^{-1}; ^{1}H NMR δ 0.20 (s, 9, $SiMe_3$), 1.02 (t, 3, J = 7 Hz, Me), 1.3–1.7 (m, 2, CH_2), 1.73 (d, 3, J = 3 Hz, olefinic Me), 1.9–2.2 (m, 2, allyl Hs), 4.7–5.0 (m, 1, olefinic H); MS, m/e (relative intensity) 168 (M^+, 2), 73 (base).

1-(*p*-Methoxyphenyl)-1-(trimethylsilyl)-1,2-hexadiene (2b), prepared from a 2.40 M ethereal solution of (*p*-methoxylphenyl)magnesium bromide and **1** (for 3 h): liquid; UV λ_{max} 249 nm (log ϵ 4.00); IR 1940 (m, C=C=C), 1600 (m, C=C) cm^{-1}; ^{1}H NMR δ 0.20 (s, 9, $SiMe_3$), 0.95 (t, 3, J = 7 Hz, Me), 1.2–1.5 (m, 2, CH_2), 1.8–2.1 (m, 2, allyl Hs), 3.75 (s, 3, OMe), 5.05 (t, 1, J = 6 Hz, olefinic H), 6.80, 7.10 (d, 2 each, J = 10 Hz, aromatic Hs); exact mass m/e 260.1595 (calcd for $C_{16}H_{24}OSi$, m/e 260.1596).

1,1-Pentamethylene-3-(trimethylsilyl)-1,2-butadiene (4a), prepared from a 2.85 M ethereal solution of methylmagnesium bromide and **3** (for 48 h): liquid (95% yield);[11] IR 1965 (m, C=C=C) cm^{-1}; ^{1}H NMR δ 0.20 (s, 9, $SiMe_3$), 1.1–1.5 (m, 6, methylenes), 1.60 (s, 3, Me), 1.7–2.0 (m, 4, allyl Hs).

1,1-Pentamethylene-3-phenyl-3-(trimethylsilyl)-1,2-propadiene (4b), prepared from a 3.00 M ethereal solution of phenylmagnesium bromide and **3** (for 3 h): liquid (96% yield);[11] IR 1930 (m, C=C=C), 1598 (m, C=C) cm^{-1}; ^{1}H NMR δ 0.20 (s, 9, $SiMe_3$), 1.5–1.8 (m, 6, methylenes), 2.2–2.4 (m, 4, allyl Hs), 7.19 (br s, 5, aromatic Hs); ^{13}C NMR δ −0.10 (Me_3), 26.2 (C-4), 27.5 (C-3, C-5), 30.8 (C-2, C-6), 65.7 (β-C), 98.3 (C-1), 125.5 (*p*-C), 127.5 (*m*-C), 128.1 (*o*-C), 138.9 (ipso-C), 204.2 (α-C).

1,1-Pentamethylene-3-(*p*-methoxyphenyl)-3-(trimethylsilyl)-1,2-propadiene (4c), prepared from a 2.40 M ethereal solution of (*p*-methoxylphenyl)magnesium bromide and **3** (for 3 h): liquid (96% yield); UV λ_{max} 249 nm (log ϵ 4.10); IR 1930 (m, C=C=C), 1600 (m, C=C) cm^{-1}; ^{1}H NMR δ 0.20 (s, 9, $SiMe_3$), 1.5–1.7 (m, 6, methylenes), 2.0–2.2 (m, 4, allyl Hs), 3.60 (s, 3, OMe), 6.70, 7.08 (d, 2 each, J = 10 Hz, aromatic Hs); exact mass, m/e 286.1754 (calcd for $C_{18}H_{26}OSi$, m/e 287.1753).

(*E*)-1-[β-(Trimethylsilyl)vinyl]cyclohexanol (5a), prepared from a 1.40 M ethereal solution of isopropylmagnesium bromide, **3** (for 72 h), and 131 mg (0.20 mmol) of $[(C_6H_5)_3P]_2NiCl_2$ (in place of dpppNiCl$_2$) and worked up by chromatography on silica gel impregnated with silver nitrate (15%) and elution with hexane up to 20:1 hexane–ethyl acetate mixtures: crystalline solid (60% yield and recovery of 35% of starting material); mp 38–40 °C; IR ($CHCl_3$) 3420 (m, OH), 1630 (w, C=C) cm^{-1}; ^{1}H NMR δ 0.20 (s, 9, 3 Me), 1.3–1.8 (m, 10, methylenes), 5.70 (d, 1, J = 18 Hz, olefinic β-H), 6.07 (d, 1, J = 18 Hz, olefinic α-H); ^{13}C NMR δ 0.00 (Me_3), 26.2 (C-4), 27.5 (C-3, C-5), 30.8 (C-2, C-6), 55.1 (C-1), 113.7 (β-C), 128.4 (α-C); exact mass, m/e 198.1441 (calcd for $C_{11}H_{22}OSi$, m/e 198.1440).

Workup with deuterium oxide gave **5b**: ^{1}H NMR δ 5.70 signal missing, 6.17 (t, 1, J = 3 Hz, olefinic α-H).

1-(*p*-Methoxyphenyl)-1,2-hexadiene (2c). Cesium fluoride, 84 mg (0.55 mmol), was added to a solution of 130 mg (0.50 mmol) of allene **2b** in 20 mL of freshly distilled acetonitrile (purified by sequential distillations over phosphorus pentoxide and calcium hydride), and the mixture was stirred under argon at room temperature for 8 h. The solution was poured into water and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. Rapid chromatography of the residue on basic alumina and elution with hexane afforded 90 mg (98%) of liquid allene **2c**: UV λ_{max} 248 nm (log ϵ 4.00); IR 1945 (m, C=C=C), 1600 (m, C=C) cm^{-1}; ^{1}H NMR δ 0.98 (t, 3, J = 7 Hz, Me), 1.4–1.5 (m, 2, CH_2), 2.0–2.2 (m, 2, allyl Hs), 3.74 (s, 3, OMe), 5.45 (q, 1, J = 7 Hz, H-3), 5.98 (dt, 1, J = 7, 3 Hz, H-1), 6.70, 7.10 (d, 2 each, J = 9 Hz, aromatic Hs); exact mass, m/e 188.1203 (calcd for $C_{13}H_{16}O$, m/e 188.1201).

1,1-Pentamethylene-3-(*p*-methoxyphenyl)-1,2-propadiene (4d). The same reaction and workup were executed on 143 mg (0.50 mmol) of allene **4c**, leading to 106 mg (99%) of liquid **4d**: UV λ_{max} 250 nm (log ϵ 4.14); IR 1945 (m, C=C=C), 1604 (m, C=C) cm^{-1}; ^{1}H NMR δ 1.5–1.9 (m, 6, methylenes), 2.1–2.4 (m, 4, allyl Hs), 3.75 (s, 3, OMe), 5.8–5.9 (m, 1, β-H), 6.75, 7.10 (d, 2 each, J = 9 Hz, aromatic Hs); ^{13}C NMR δ 26.0 (C-4), 27.6 (C-3, C-5), 31.4 (C-2, C-6), 55.1 (Me), 91.6 (β-C), 106.2 (C-1), 113.8 (*m*-C), 127.3 (*o*-C), 128.3 (ipso-C), 158.1 (*p*-C), 198.7 (α-C); exact mass, m/e 214.1350 (calcd for $C_{15}H_{18}O$, m/e 214.1360).

1-(*p*-Methoxyphenyl)-1,3-hexadiene (6). A solution of 94 mg (0.50 mmol) of allene **2c** and 1.0 mL of 12 N hydrochloric acid in 30 mL of methanol was heated at 50 °C for 24 h and then cooled and neutralized by being poured into sodium bicarbonate solution. The mixture was extracted with hexane and the extract dried (Na_2SO_4) and evaporated. Rapid chromatography of the residue on basic alumina and elution with hexane produced 81 mg (86%) of liquid diene **6**: UV λ_{max} 282 nm (log ϵ 4.29); IR 1610 (m, C=C) cm^{-1}; ^{1}H NMR δ 1.05 (t, 3, J = 7 Hz, Me), 2.1–2.2 (m, 2, CH_2), 3.75 (s, 3, OMe), 5.75 (dt, 1, J = 15, 7 Hz, H-4), 6.12 (dd, 1, J = 15, 10 Hz, H-3), 6.33 (d, 1, J = 15 Hz, H-1), 6.55 (dd, 1, J = 15, 10 Hz, H-2), 6.78, 7.25 (d, 2 each, J = 9 Hz, aromatic Hs); exact mass, m/e 188.1204 (calcd for $C_{13}H_{16}O$, m/e 188.1201).

(*E*)-1β-(*p*-Methoxystyryl)-1-cyclohexene (7). The same reaction (for 6 h) and workup on 107 mg (0.50 mmol) of allene **4d** led to 103 mg (96%) of crystalline diene **7**: mp 44–45 °C; UV λ_{max} 279 nm (log ϵ 4.15); IR 1595 (m, C=C) cm^{-1}; ^{1}H NMR δ 1.4–1.8 (m, 4, methylenes), 2.0–2.3 (m, 4, allyl Hs), 3.75 (s, 3, OMe), 5.6–5.8 (m, 1, H-2), 6.20 (d, 1, J = 15 Hz, α-H), 6.50 (d, 1, J = 15 Hz, β-H), 6.68, 7.20 (d, 2 each, J = 9 Hz, aromatic Hs); exact mass, m/e 214.1350 (calcd for $C_{15}H_{18}O$, m/e 214.1360).

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Registry No. **1**, 17889-42-8; **2a**, 25909-10-8; **2b**, 95046-14-3; **2c**, 95046-15-4; **3**, 17962-22-0; **4a**, 71321-11-4; **4b**, 71321-12-5; **4c**, 95046-16-5; **4d**, 90598-36-0; **4e**, 86936-06-3; **5a**, 87428-68-0; **5b**, 95069-32-2; **6**, 95046-17-6; **7**, 95046-18-7; i, 63922-76-9; ii, 95046-19-8; dpppNiCl$_2$, 15629-92-2; $[(C_6H_5)_3P]_2NiCl_2$, 14264-16-5; (*p*-methoxyphenyl)bromide, 104-92-7; (trimethylsilyl)acetylene, 1066-54-2; butyraldehyde, 123-72-8; cyclohexanone, 108-94-1; methyl bromide, 74-83-9; phenyl bromide, 108-86-1; isopropyl bromide, 75-26-3.

(11) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390.