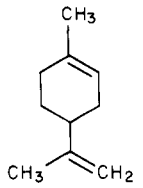
by added acid accords with this view. Nonconjugated isomers of α-terpinene were less readily rearranged to the structure 6 required for reaction with CH_3PCl_2 and were not useful in this process. Neither limonene (8) nor γ-



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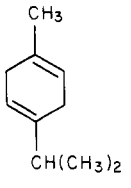

9

terpinene (9) gave detectable amounts of phospholene oxide 3 under conditions effective for the reaction with α-terpinene. With limonene, a complex black mixture resulted, while with γ-terpinene little reaction occurred.

Exploratory experiments under similar conditions showed that PCl_3 and $C_6H_5PCl_2$ reacted less readily than CH_3PCl_2 with α-terpinene. Some phosphorus incorporation in the product was detected, but the low yields and complexity of the product mixture discouraged detailed examination.

Experimental Section[12]

1,3,6-Trimethyl-2,3,4,5,6,7-hexahydrophosphindole 1-Oxide (3). To a Teflon bottle was added 16.7 g (0.12 mol) of freshly distilled α-terpinene (Aldrich), 0.1 g of copper stearate, and 13.1 g (0.11 mol) of methylphosphonous dichloride. The solution was sealed under nitrogen and heated at 82–86 °C for 3 weeks. A dense light-brown oil, constituting approximately one-half of the original total volume of the solution, was formed. ^{31}P NMR analaysis of the oil showed it to be a mixture of CH_3PCl_2 and adduct with minor impurities: ^{31}P NMR ($CDCl_3$) δ 101.4 (adduct 7, 66%), 190.0 (unreacted CH_3PCl_2, 21%), 87.7 and 88.1 (together 13%).

The thick oil was slowly hydrolyzed by addition to 200 g of ice in 200 mL of $CHCl_3$; care was taken to keep the temperature below 25 °C. The mixture was made pH 7 with solid $NaHCO_3$. The layers were separated, and the aqueous phase was extracted with six 40-mL portions of $CHCl_3$. The combined $CHCl_3$ layers were dried over Na_2SO_4 and $MgSO_4$. Concentration by rotoevaporation and high vacuum gave 7.9 g (36%) of a light-yellow oil which was distilled (125–127 °C (0.1 mm)) to yield a colorless oil: ^1H NMR ($CDCl_3$) δ 0.9–3.0 (complex, overlapping signals); ^{31}P NMR ($CDCl_3$) δ 64.0, 63.5, 62.6, 62.3; partial ^{13}C NMR, Figure 1. A persistent impurity (5%), preventing elemental analysis, had ^{31}P signals at δ 32.8 to 33.4.

1,3,6-Trimethyl-2,3,4,5,6,7-hexahydrophosphindole. To a solution of 1.0 g (5 mmol) of 3 in 40 mL of benzene was added dropwise under nitrogen a solution of 1.5 mL (15 mmol) of Cl_3SiH in 10 mL of benzene. A slight exotherm ensued; the mixture was refluxed for 1 h and then hydrolyzed with 80 mL of 30% NaOH in an ice–water bath. Extraction with two 20-mL portions of benzene was followed by drying over $MgSO_4$. Concentration under aspirator vacuum gave 0.9 g (98%) of 4 as a clear oil. Kugelrohr distillation gave 0.8 g (88%) of 4 (bp 30–50 °C 0.1 mm)); ^{31}P NMR ($CDCl_3$) δ −13.5, −14.9, −16.1; partial ^{13}C NMR ($CDCl_3$) CH_3 at δ 11.3 (21.5), 11.6 (20.0), 14.3 (23.1); C-2 at 30.7 (6.2), 33.2 (4.6), 34.1 (7.7); C-3a at 144–147 (coupling uncertain); C-7a at 133.5, 133.8 (apparent s).

The phosphine mixture was reacted with excess iodomethane in pentane. A white solid formed immediately, and the mixture was then allowed to stand at −18 °C. The solid was filtered and washed with pentane. Drying under high vacuum gave 1.1 g (77%), which was recrystallized from methanol–ethyl acetate to yield 3 as white flakes: mp 142–144 °C; ^{31}P NMR ($CDCl_3$) δ 46.7, 46.6. Anal. Calcd for $C_{12}H_{22}IP$: C, 44.46; H, 6.84; P, 9.55. Found: C, 44.30; H, 6.79; P, 9.59.

Registry No. 1, 99-86-5; 3 (isomer I), 90432-46-5; 3 (isomer II), 90527-95-0; 3 (isomer III), 90527-96-1; 3 (isomer IV), 90527-97-2; 4 (isomer I), 90432-47-6; 4 (isomer II), 90527-98-3; 4 (isomer III), 90527-99-4; 4 (isomer IV), 90528-00-0; 5 (isomer I), 90432-48-7; 5 (isomer II), 90432-49-8; 8, 138-86-3; 9, 99-85-4; CH_3PCl_2, 676-83-5; Cl_3SiH, 10025-78-2.

(12) Melting points were taken on a Mel-Temp apparatus and are corrected. Carbon-13 FT NMR spectra (including the INEPT program) were taken on a JEOL FX-90Q spectrometer at 22.5 MHz, utilizing an internal deuterium lock with proton noise-decoupling. Chemical shifts are expressed in ppm downfield from tetramethylsilane. Phosphorus-31 FT NMR spectra were obtained with the JEOL FX-90Q at 36.2 MHz; chemical shifts are expressed in ppm relative to external 85% H_3PO_4 with positive shifts downfield. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

Method for the Preparation of Terminal and Internal Conjugated Diynes via Palladium-Catalyzed Cross-Coupling[1]

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The Pd- or Ni-catalyzed cross-coupling provides one of the most general methods for the formation of a carbon–carbon single bond between two unsaturated carbon groups, i.e., aryl, alkenyl, and alkynyl. In particular, the Pd-catalyzed cross-coupling has been successfully applied to various cases covering all possible categorical combinations except the alkynyl–alkynyl coupling.[3] In fact, all our attempts to cross-couple two alkynes via the Pd-catalyzed reaction of a haloalkyne with an alkynylmetal containing Li, Mg, Zn, Al, and Sn have led to the formation of nearly the 1:2:1 mixtures of homo- and cross-coupled products, even though the combined yields were generally ca. 100%.[4] Typically, the reaction of 1-heptynylzinc chloride with 1-iodo-1-hexyne in the presence of 5 mol % of either $Pd(PPh_3)_4$ or a Pd catalyst generated in situ by treating $Cl_2Pd(PPh_3)_2$ with 2 equiv of i-Bu_2AlH produced 5,7-tridecadiyne (ca. 50%), 5,7-dodecadiyne (ca. 25%), and 6,8-tetradecadiyne (ca. 25%).

In view of the above difficulty, coupled with the relative paucity of satisfactory methods for the synthesis of conjugated diynes,[5] we undertook to develop a general and

(1) Selective Carbon–Carbon Bond Formation via Transition-Metal Catalysis. 39. Part 38: Miller, J. A.; Negishi, E. *Isr. J. Chem.*, in press

(2) Present address: Department of Chemistry, Purdue University, West Lafayette, IN 47907.

(3) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340 and references therein.

(4) King, A. O. Ph.D. Dissertation, Syracuse University, 1979.

(5) (a) Probably the most widely used method for preparing internal conjugated diynes is the Cadiot–Chodkiewicz reaction [Cadiot, P.; Chodkiewicz, W. In "Chemistry of Acetylenes"; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; Chapter 9]. Although various types of bromoalkynes may be used, simple alkyl-substituted alkynes have seldom been used as reagents to be coupled with bromoalkynes. Other alkynes that may not be readily used include HC≡CR where R = Me_3Si, Ph_3Sn, Ph_2P, and CHO. (b) The stoichiometric reaction of alkynylcoppers with haloalkynes generally gives mixtures of three possible coupling products except in some special cases, such as the reaction of 1-bromo-2-(trimethylsilyl)ethyne with alkynylcoppers [Miller, J. A.; Zweifel, G, *Synthesis* **1983**, 128]. (c) Treatment of dialkynylborates with iodine provides an attractive alternative to the Cu-based methodologies [Pelter, A.; Hughes, R.; Smith, K.; Tabata, M. *Tetrahedron Lett.* **1976**, 4385. Sinclair, J. A.; Brown, H. C. *J. Org. Chem.* **1976**, *41*, 1078]. (d) Treatment of 1,4-dichloro-2-butyne with 3 equiv of $NaNH_2$ followed by the addition of an alkyl halide provides a convenient method for preparing alkyl-substituted terminal diynes [Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971]. The method cannot accommodate hindered alkyl and other types of carbon groups. (e) The Cadiot–Chodkiewicz reaction is applicable to the synthesis of terminal diynes by using 2-methyl-3-butyn-2-ol as an ethynyl synthon [Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971]. Deprotection of the ethynyl group, however, requires treatment of the cross-coupled diynes with powdered KOH at 150–200 °C.

0022-3263/84/1949-2629$01.50/0

Scheme I

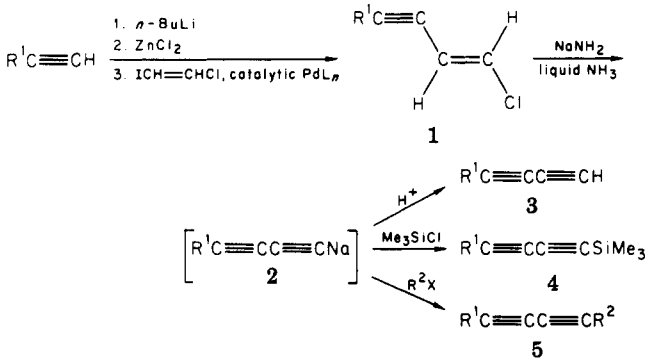


Table I. Conversion of Terminal Alkynes into 1-Chloro-1-buten-3-yne Derivatives and Conjugated Diynes

$R^1C{\equiv}CH$	yield[a] $R^1C{\equiv}CCH{=}CHCl$, %	R^2 of $R^1C{\equiv}CC{\equiv}CR^2$	yield, %
1-octyne	73	H	68
		Me	67 (86)
		$SiMe_3$	70 (75)
1-heptyne	68 (83)		
2-methyl-1-buten-3-yne	75 (86)		
phenylethyne	91 (95)	Me	89
		$SiMe_3$	71
1,3-decadiyne	78 (94)		

[a] Isolated yield. The number in parentheses is the GLC yield.

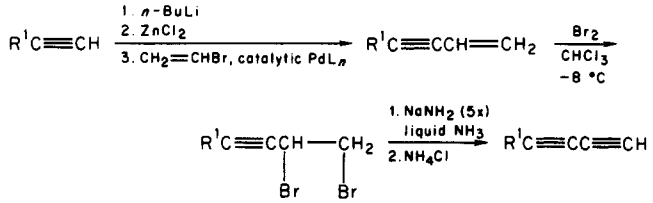
convenient route to conjugated diynes, especially terminal diynes.

We have found that (*E*)-1-iodo-2-chloroethylene,[6] readily obtainable in 80–85% yield by treating acetylene with ICl and 6 N HCl, reacts cleanly with alkynylzinc derivatives in the presence of a catalytic amount (1–5 mol %) of a Pd–phosphine complex, e.g., $Pd(PPh_3)_4$, to produce (*E*)-1-chloro-1-buten-3-yne derivatives **1** in high yields. The chloro enynes **1** can be readily converted into the corresponding 1-sodio 1,3-diynes **2**, which, in turn, can be converted into the corresponding terminal diynes **3**, silylated 1,3-diynes **4**, and internal diynes **5** by known procedures (Scheme I).

Although the conversion of terminal alkynes into conjugated diynes by this method requires two steps, in addition to the preparation of (*E*)-1-iodo-2-chloroethylene, it avoids the preparation of 1-bromoalkynes required in the Cu-promoted methods.[5a,b,e] Since both the conversion of **1** into **2** and the formation of the bond between the R^2 and the diyne unit may generally be carried out in one pot, the overall process can be not only general but quite efficient, even when compared with the convergent Cadiot–Chodkiewicz method requiring the prior syntheses of two alkynes and the formation of the alkynyl–Br bond.

The experimental results are summarized in Table I. Various types of carbon groups, such as alkyl, alkenyl, aryl, and alkynyl groups, may be accommodated as the R^1 group. Since this study emphasizes the synthesis of terminal diynes **3** and **4**, only the Me group was used as the R^2 group. It may be pointed out, however, that various types of carbon groups, such as alkyl,[5d] alkenyl,[7] and aryl[8]

Scheme II



groups, should readily be incorporated as the R^2 group by known methods.

The use of other ethyne synthons more readily available than (*E*)-1-iodo-2-chloroethyne was considered to further simplify the method shown in Scheme I. The Pd-catalyzed reaction of alkynylzinc derivatives with 1,1- or 1,2-dibromoethylene produced mixtures of cross-coupled products. Since the ethenyl group was known to be brominated in preference to the ethynyl group,[9] we considered the use of vinyl bromide for the synthesis of conjugated diynes. Indeed, the reaction of 1-octynylzinc chloride with vinyl bromide in the presence of 5 mol % of $Pd(PPh_3)_4$ cleanly provided 1-decen-3-yne in 78% yield (94% by GLC). Treatment of 1-decen-3-yne with 1 equiv of bromine in $CHCl_3$ at −8 °C produced 1,2-dibromo-3-decyne in 76% yield (85% by GLC) along with 5–10% of 1,4-dibromo-2,3-decadiene. Finally, the reaction of the crude product obtained above with 5 equiv of $NaNH_2$ in liquid NH_3,[10] followed by neutralization with aqueous NH_4Cl provided 1,3-decadiyne in 82% yield, which was contaminated with a minor amount (~5%) of an unidentified byproduct with a shorter GLC (SE-30) retention time (Scheme II). Although the requirement for brominating the enyne intermediates limits the scope of this method, it provides a convenient alternative to the procedure involving the use of (*E*)-1-iodo-2-chloroethylene in cases where the bromination step is not further complicated by other side reactions.

Experimental Section

All organometallic reactions were carried out under an atmosphere of nitrogen. Unless otherwise mentioned, the chemicals were used as received from commercial sources. Zinc chloride was dried before use at ≥50 °C and at ≤1 mm for several hours. Tetrahydrofuran (THF) was purified by distillation over Na and benzophenone. The preparation of $Pd(PPh_3)_4$ was carried out according to the literature method.[11] Acetylene from a cylinder was purified by passing it through water, H_2SO_4, KOH pellets, and a trap kept at −78 °C. Iodine monochloride was purified by distillation at 1 atm.

(*E*)-1-Chloro-2-iodoethylene.[6] Acetylene was absorbed slowly at 0 °C over 3 h in a dark solution of ICl (8.11 g, 50 mmol) in 60 mL of 6 N HCl. The reaction mixture was extracted 3 times with pentane. The extract was washed with saturated NaCl, dried over $MgSO_4$, concentrated, and distilled to give 7.8 g (83%) of the title compound: bp 110–113 °C; n_D^{24} 1.5822; IR (neat) 3080 (s), 1710 (w), 1630 (m), 1600 (m), 1545 (m), 1260 (w), 1150 (s), 1125 (s), 890 (s), 790 (s), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 6.48 (d, J = 14 Hz, 1 H), 6.72 (d, J = 14 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 76.86, 124.75.

Preparation of (*E*)-1-Chloro-1-buten-3-yne Derivatives by the Palladium-Catalyzed Reaction of Alkynylzinc Chlorides with (*E*)-1-Chloro-2-iodoethylene. The following procedure for the preparation of (*E*)-1-chloro-1-decen-3-yne from 1-octyne is representative. To 1-octyne (2.76 g, 25 mmol) in 40 mL of THF was added at 0 °C 12 mL (26 mmol) of 2.2 M *n*-BuLi in hexane. After the mixture was stirred for 30 min, $ZnCl_2$ (3.40 g, 25 mmol)

(6) Van de Walle, H.; Henne, A. *Bull. Cl. Sci., Acad. R. Belg.* **1925**, *11*, 360 [*Chem. Abstr.* **1926**, *20*, 1050].
(7) King, A. O.; Okukado, N.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1977**, 638.
(8) King, A. O.; Negishi, E.; Villani, F. J., Jr.; Silveira, A., Jr. *J. Org. Chem.* **1978**, *43*, 358.
(9) For a review, see: Melloni, G.; Modena, G.; Tonellato, U. *Acc. Chem. Res.* **1981**, *14*, 227.
(10) Reference 5d, p 103.
(11) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

dissolved in 20 mL of THF was added dropwise at 0 °C. The resultant mixture was added to a mixture of (*E*)-1-chloro-2-iodoethylene (4.70 g, 25 mmol), $Pd(PPh_3)_4$ (1.15 g, 1 mmol), and 20 mL of THF. The reaction mixture was stirred for 3 h at room temperature, treated with 3 N HCl, and extracted with pentane. The organic layer was washed with saturated NaCl, dried over $MgSO_4$, and distilled to give 3.09 g (73%) of (*E*)-1-chloro-1-decen-3-yne: bp 34–35 °C (0.1 mm); $n_D^{22.5}$ 1.4814; IR (neat) 2120 (m), 1700 (w), 910 (s), 840 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, *J* = 7 Hz, 3 H), 1.1–1.8 (m, 8 H), 2.1–2.5 (m, 2 H), 5.91 (td, *J* = 2 and 14 Hz, 1 H), 6.66 (d, *J* = 14 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.16, 19.67, 22.94, 29.00, 31.80, 76.07, 93.11, 114.74, 128.62. Anal. Calcd for $C_{10}H_{15}Cl$: C, 70.37; H, 8.86. Found: C, 70.31; H, 8.63.

The yields and the spectral data of the other (*E*)-1-chloro-1-buten-3-yne derivatives are as follows.

(*E*)-1-Chloro-1-nonen-3-yne. The yield of this compound isolated by distillation was 68% (83% by GLC): bp 60–63 °C (4 mm); IR (neat) 2200 (w), 1700 (w), 915 (s), 850 (s) cm^{-1}; ^1H NMR (CCl_4, Me_4Si) δ 0.83 (t, *J* = 7 Hz, 3 H), 1.0–1.8 (m, 6 H), 2.0–2.4 (m, 2 H), 5.80 (td, *J* = 2 and 14 Hz, 1 H), 6.35 (d, *J* = 14 Hz, 1 H). Anal. Calcd for $C_9H_{13}Cl$: C, 69.00; H, 8.36. Found: C, 69.21; H, 8.53.

(*E*)-1-Chloro-5-methyl-1,5-hexadien-3-yne. The yield of this compound isolated by distillation was 75% (86% by GLC): bp 55–60 °C (15 mm); IR (neat) 3050 (w), 1800 (w), 1700 (w), 1620 (m), 1580 (m), 1290 (s), 915 (s), 895 (s), 845 (s) cm^{-1}; ^1H NMR (CCl_4, Me_4Si) δ 1.91 (d, *J* = 1.5 Hz, 3 H), 5.1–5.4 (m, 2 H), 6.00 (d, *J* = 14 Hz, 1 H), 6.53 (d, *J* = 14 Hz, 1 H). Anal. Calcd for C_7H_7Cl: C, 66.42; H, 5.57. Found: C, 66.27; H, 5.49.

(*E*)-1-Chloro-4-phenyl-1-buten-3-yne.[12] The yield of this compound isolated by distillation was 91% (95% by GLC): bp 52–54 °C (0.2 mm); n^{22}_D 1.6221; IR (neat) 3080 (m), 3030 (w), 2110 (w), 1700 (w), 1580 (m), 1485 (m), 1440 (m), 1270 (m), 1225 (m), 905 (s), 840 (s), 750 (s), 685 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 6.03 (d, *J* = 14 Hz, 1 H), 6.45 (d, *J* = 14 Hz, 1 H), 7.1–7.6 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 84.42, 92.09, 113.66, 122.51, 128.03, 128.21, 129.78, 131.31 ppm.

(*E*)-1-Chloro-1-dodecene-3,5-diyne. The yield of this compound isolated by distillation was 78% (94% by GLC): bp 65–68 °C (0.1 mm); IR (neat) 3080 (m), 2230 (s), 1700 (w), 1580 (s) 1460 (s), 1260 (s), 1220 (m), 905 (s), 835 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88 (t, *J* = 7 Hz, 3 H), 1.1–1.8 (m, 8 H), 2.30 (t, *J* = 7 Hz, 2 H), 5.90 (d, *J* = 14 Hz, 1 H), 6.60 (d, *J* = 14 Hz, 1 H); high-resolution MS calcd for $C_{12}H_{15}Cl$ 194.0862, found 194.086.

Preparation of Terminal 1,3-Diynes via (*E*)-1-Chloro-1-buten-3-yne Derivatives. The following procedure for the preparation of 1,3-decadiyne is representative.

(*E*)-1-Chloro-1-decen-3-yne (1.71 g, 10 mmol) in 20 mL of ethyl ether was added dropwise, under nitrogen, to a suspension of $NaNH_2$ (0.86 g, 22 mmol) in 60 mL of anhydrous liquid ammonia (dried by passing through KOH pellets). The reaction mixture was stirred for 1 h and warmed to room temperature. The resulting solution was treated with aqueous NH_4Cl and extracted with pentane. The organic layer was washed with saturated NaCl and dried over $MgSO_4$. The crude product was purified by flash chromatography (silica gel, hexane). Concentration of the elute gave 0.91 g (68%) of 1,3-decadiyne:[5b] IR (neat) 3325 (s), 2300 (m), 2230 (s), 1935 (w) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, *J* = 7 Hz, 3 H), 1.1–1.8 (m, 8 H), 1.93 (s, 1 H), 2.24 (t, *J* = 7 Hz, 2 H).

4-Phenyl-1,3-butadiyne. The sodio derivative of this compound may be generated as described above and used for further transformation. 4-Phenyl-1,3-butadiyne itself is known to be highly unstable to polymerization.[13] Therefore, no attempts were made to isolate the compound.

1-Decen-3-yne.[14] To 1-octyne (5.51 g, 50 mmol) in 50 mL of THF was added at 0 °C 2.2 M *n*-BuLi in hexane (23 mL, 50 mmol). After stirring for 30 min, $ZnCl_2$ (6.81 g, 50 mmol) dissolved in THF (30 mL) was added dropwise at 0 °C. The resulting mixture was warmed to room temperature and added to a mixture of vinyl bromide (10.69 g, 100 mmol) and $Pd(PPh_3)_4$ (2.31 g, 2 mmol) in dry THF (20 mL). After being stirred for 2 h at room temperature, the reaction mixture was quenched with 3 N HCl and extracted with pentane. The organic layer was washed with aqueous $NaHCO_3$ and NaCl and then dried over $MgSO_4$. Distillation provided 5.30 g (78%) of the title compound: bp 66–68 °C (15 mm); n_D^{22} 1.4568; IR (neat) 3110 (w), 3020 (w), 2225 (m), 1610 (s), 1465 (s), 1160 (w), 970 (s), 910 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, *J* = 7 Hz, 3 H), 1.1–1.8 (m, 8 H), 2.30 (t, *J* = 7 Hz, 2 H), 5.34 (dd, *J* = 4 and 10 Hz, 1 H), 5.5–6.0 (m, 2 H).

1,2-Dibromo-3-decyne. To 1.36 g (10 mmol) of 1-decen-3-yne in 20 mL of chloroform was added at −10 °C bromine (1.59 g, 10 mmol) in 10 mL of chloroform. The reaction mixture was quenched with aqueous Na_2CO_3 and extracted with pentane. The organic layer was dried over $MgSO_4$ and distilled to give 2.22 g (76%) of the title compound: bp 73–75 °C (0.3 mm): IR (neat) 2240 (s), 1335 (s), 1230 (m), 1205 (m), 1155 (s), 1120 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88 (t, *J* = 7 Hz, 3 H), 1.0–1.7 (m, 8 H), 2.1–2.4 (m, 2 H), 3.6–3.8 (m, 2 H), 4.5–4.8 (m, 1 H). In addition to the above signals, the following signals for 1,4-dibromo-2,3-decadiene were also present: δ 2.6–2.85 (m, 2 H), 5.5–5.7 (m, 1 H). The ratio of the 1,2-adduct to the 1,4-adduct was ca. 95:5.

Preparation of 1,3-Decadiyne via 1,2-Dibromo-3-decyne. 1,2-Dibromo-3-decyne (0.59 g, 2 mmol) in 4 mL of ethyl ether was added dropwise to a suspension of $NaNH_2$ (0.39 g, 10 mmol) in 20 mL of anhydrous liquid ammonia. After being stirred for 1 h, the reaction mixture was warmed to room temperature, hydrolyzed with aqueous NH_4Cl, and extracted with pentane. The organic layer was washed with aqueous NaCl and dried over $MgSO_4$. Examination by GLC using nonane as an internal standard indicated the presence of 1,3-decadiyne (82%) along with an unidentified product of a slightly shorter retention time (ca. 5% of 1,3-decadiyne in peak size).

1-Phenyl-1,3-pentadiyne.[15] The following preparation of 1-phenyl-1,3-pentadiyne is representative of the conversion of 1-buten-3-yne derivatives into methylated diynes. 1-Sodio-4-phenyl-1,3-butadiyne was prepared on a 10-mmol scale according to the general procedure described above. To this was added at −78 °C sequentially THF (20 mL), HMPA (10 mL), and MeI (1.70 g, 12 mmol). After being stirred for 1 h at −78 °C, the reaction mixture was warmed to room temperature and treated with 3 N HCl. The organic layer was extracted with ether, washed with saturated $NaHCO_3$ and NaCl, and then dried over $MgSO_4$. Distillation provided 1.25 g (89%) of the title compound: bp 54–56 °C (0.2 mm) [lit.[16] bp 127–131 °C (16 mm)]; IR (neat) 3070 (w), 2250 (w), 1595 (w), 1490 (m), 1440 (m), 1375 (w), 750 (s), 685 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.81 (s, 3 H), 7.1–7.5 (m, 5 H).

2,4-Undecadiyne. This compound was obtained in 67% yield (86% by GLC) from (*E*)-1-chloro-1-decen-3-yne in a manner similar to that described above for the preparation of 1-phenyl-1,3-pentadiyne: bp 41–43 °C (0.1 mm); IR (neat) 2210 (w), 1460 (m), 1425 (m), 1375 (w), 1325 (w), 720 (w) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88 (t, *J* = 7 Hz, 3 H), 1.1–1.7 (m, 8 H), 1.88 (s, 3 H), 2.22 (t, *J* = 7 Hz, 2 H); high-resolution MS calcd for $C_{11}H_{16}$ 148.1252, found 148.124.

1-(Trimethylsilyl)-1,3-decadiyne.[5b] This compound was prepared in 70% yield (75% by GLC) from (*E*)-1-chloro-1-decen-3-yne in a manner similar to that for the preparation of 2,4-undecadiyne by using 2 equiv of Me_3SiCl instead of MeI: bp 55–57 °C (0.1 mm); IR (neat) 2220 (s), 2105 (s), 1245 (s), 1180 (s), 835 (s), 755 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 0.89 (t, *J* = 7 Hz, 3 H), 1.1–1.8 (m, 8 H), 2.25 (t, *J* = 7 Hz, 2 H).

1-(Trimethylsilyl)-4-phenyl-1,3-butadiyne.[16] The conversion of (*E*)-1-chloro-4-phenyl-1-buten-3-yne into the title compound may be performed as above. The use of 2.5 equiv of PhLi in place of $NaNH_2$ in liquid NH_3 was also satisfactory. The title compound was obtained in 71% yield by using PhLi: bp 90–92 °C (0.2 mm) [lit.[16] bp 120 °C (0.5 mm)]; IR (neat) 3060 (w), 2210 (m), 2100 (m), 1490 (w), 1440 (w), 1245 (s), 830 (s), 745 (s), 720 (s), 680 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.18 (s, 9 H), 7.1–7.5 (m, 5 H).

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Registry No. $Ph(PPh_3)_4$, 14221-01-3; (*E*)-1-chloro-2-iodoethylene, 28540-81-0; (*E*)-1-chloro-1-decen-3-yne, 90320-86-8; (*E*)-1-chloro-1-nonen-3-yne, 77973-37-6; (*e*)-1-chloro-5-methyl-1,5-hexadien-3-yne, 90320-87-9; (*E*)-1-chloro-4-phenyl-1-buten-3-yne, 18685-03-5; (*E*)-1-chloro-1-dodecene-3,5-diyne, 90320-88-0; 1,3-decadiyne, 55682-66-1; 4-phenyl-1,3-butadiyne, 5701-81-5; 1-decen-3-yne, 33622-26-3; 1,2-dibromo-3-decyne, 90320-89-1; 1-phenyl-1,3-pentadiyne, 4009-22-7; 2,4-undecadiyne, 90320-90-4; 1-(trimethylsilyl)-1,3-decadiyne, 84751-17-7; 1-(trimethylsilyl)-4-phenyl-1,3-butadiyne, 38177-56-9; acetylene, 74-86-2; 1-octyne, 629-05-0; 1-heptyne, 628-71-7; 2-methyl-1-buten-3-yne, 78-80-8; phenylethyne, 536-74-3; 1-sodio-4-phenyl-1,3-butadiyne, 90320-91-5; vinyl bromide, 593-60-2.

Synthesis of β,γ-Unsaturated Amino Acids by the Strecker Reaction

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In recent years, numerous studies of β,γ-unsaturated amino acids have been reported. These are of interest not only for their antibiotic[1] and enzyme inhibitory properties[2] but also as synthetic intermediates.[3] Synthetic routes to a number of such amino acids have been reported.[4] Conceptually, many β,γ-unsaturated amino acids could be prepared readily from α,β-unsaturated aldehydes by use of a Stecker condensation. The low yields of vinylglycine and β-methylenenorvaline obtained by using this approach (<1%)[5] have perhaps discouraged its use. We now report a versatile route to β,γ-unsaturated amino acids which utilizes a Strecker reaction.

Treatment of α,β-unsaturated aldehydes with primary amines in the presence of molecular sieves (Scheme I) afforded the corresponding imines **2**.[6] These, without isolation, were subjected to the action of trimethylsilyl cyanide,[7] which, by 1,2-addition, produced β,γ-unsaturated aminonitriles **3**. These could be isolated and purified, but due to their instability on silica gel, they were usually treated directly with aqueous HCl (6 N), providing, after ion-exchange chromatography, the β,γ-unsaturated amino acids **4**.

In initial attempts to prepare N-unsubstituted β,γ-unsaturated amino acids, ammonium acetate was used as the amine component. Thus treatment of (*E*)-2-methyl-3-butenal with NH_4OAc and KCN in ethanol for 4–5 h afforded an aminonitrile, which, when subjected to acidic hydrolysis and then ion-exchange chromatography, afforded pure amino acid **4e**. However, the presence of impurities in the aminonitrile **3** (R = H) (several spots by

Scheme I

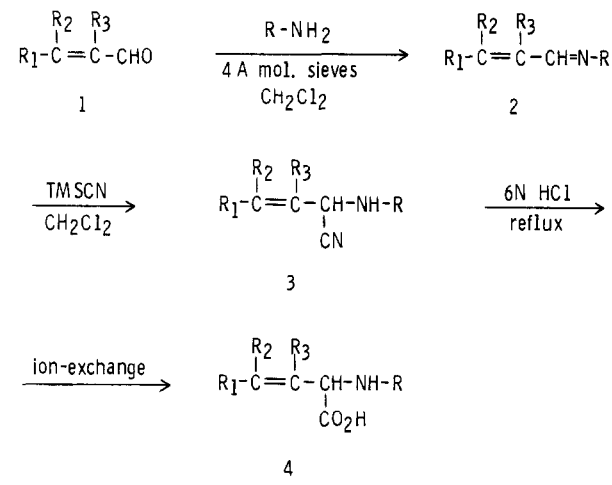
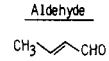
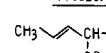
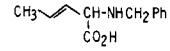
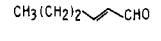
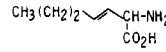
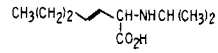
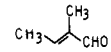
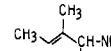
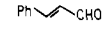
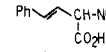
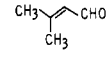
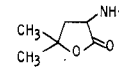
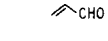
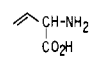


Table I. Preparation of β,γ-Unsaturated Amino Acids

Aldehyde	Amine	Product	Yield (%)
	5	 4a	48
	$PhCH_2NH_2$	 4b	43
	5	 4c	45
	$(CH_3)_2CH-NH_2$	 4d	68
	5 NH_4OAc	 4e	44 27
	5	 4f	15
	$PhCH_2NH_2$	 6	68
	5	 4g	7

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