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Facile and Efficient Syntheses of (3*Z*,6*Z*,9*Z*)-3,6,9-Nonadecatriene and Homologues: Pheromone and Attractant Components of Lepidoptera

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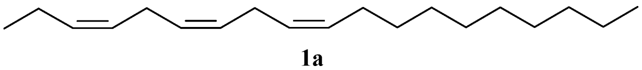
Facile and efficient chemical syntheses of (3*Z*,6*Z*,9*Z*)-3,6,9-nonadecatriene and homologues from commercially available α-linolenic acid [(9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienoic acid] are reported. These straight-chain homoconjugated trienes are common sex pheromone and attractant components for many lepidopterous insect pests. The metal-catalyzed cross-coupling reactions between (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienyl triflate and the appropriate Grignard reagents proceed very rapidly under notable mild conditions using Li_2CuCl_4 as catalyst in diethyl ether, and the resulting (3*Z*,6*Z*,9*Z*)-3,6,9-trienes with retention of geometrical configuration were in >92% isolated yield.

KEYWORDS: α-Linolenic acid; alkenyl triflate; Grignard reagents; cross-coupling reaction; homoconjugated triene; pheromone; sex attractant

INTRODUCTION

The straight-chain homoconjugated C_{17}–C_{25} (3*Z*,6*Z*,9*Z*)-3,6,9-trienes are the sex pheromone components of many worldwide distributed lepidopterous insect pests (*1*–*4*), and they are most likely biosynthesized from linolenic acid directly (*5*). Because these compounds are potent male attractants and can be used in integrated pest management to protect many important agricultural crops (*6*, *7*), a number of different synthetic methodologies have been developed (*8*–*12*). However, those methods require long reaction time, involve multiple steps, and give low yields, and some reactions result in low geometric purities. The metal-catalyzed cross-coupling reaction was reported as the most useful and reliable reaction for preparation of alkenes with retention of the configuration (*13*). In fact, preparation of straight-chain homoconjugated (3*Z*,6*Z*,9*Z*)-3,6,9-nonadecatriene **1a** and homologues by coupling reaction of the appropriate bromide (*14*) or tosylate (*15*, *16*) with appropriate Grignard reagents gave the desired (3*Z*,6*Z*,9*Z*)-3,6,9-trienes. Still, the low yield and long reaction time are the weakness. In this paper, we report metal-catalyzed cross-coupling reactions of (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienyl triflate **3** with the appropriate Grignard reagents using Li_2CuCl_4 as catalyst and diethyl ether as solvent. This pathway afforded (3*Z*,6*Z*,9*Z*)-3,6,9-nonadecatriene **1a** and homologues with retention of geometrical configuration in less than 1.5 h reaction time in >92% isolated yield from the (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrien-1-ol **2**, which was easily prepared from commercially available α-linolenic acid.



1a

MATERIALS AND METHODS

General. NMR spectra were recorded in $CDCl_3$ solution on a Bruker AV 400 spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C, respectively. The chemical shifts are expressed in ppm (δ scale) relative to the reference compound tetramethylsilane (TMS). Electron impact (EI) gas chromatography–mass spectrometry (GC–MS) was conducted on an Agilent 6890N GC coupled to an Agilent Technologies 5973 inert mass selective detector using a 30 m × 0.25 mm i.d., 0.25 μm film thickness HP-5MS capillary column (Agilent Technologies, Wilmington, DE) with helium as carrier gas (36 cm/s, 50 °C for 2 min, then programmed to 250 °C at 15 °C/min and held for 20 min). A 70 eV electron beam was employed for sample ionization. GC analyses were performed on an Agilent 6890 GC equipped with a flame ionization detector (FID) using a 30 m × 0.32 mm i.d., 0.25 μm film thickness HP-5 capillary column with hydrogen as carrier gas (38 cm/s, 50 °C for 2 min, then programmed to 250 °C at 10 °C/min and held for 20 min) in the splitless mode. Anhydrous diethyl ether was obtained by refluxing diethyl ether with sodium/benzophenone ketyl under nitrogen (*17*). All reactions were performed under a nitrogen atmosphere with magnetic stirring. The Grignard reagents and other chemicals were obtained from Aldrich Chemical Co. unless otherwise indicated, and solvents were obtained from EM Science. Flash column chromatography was carried out on silica gel 60 (EM Science, 230–400 mesh).

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(9*Z*,12*Z*,15*Z*)-9,12,15-Octadecatrien-1-ol (2). A 250 mL dried flask was charged with fresh-prepared anhydrous diethyl ether (60 mL) under a nitrogen atmosphere and cooled with an ice−salt bath to 0 °C, while lithium aluminum hydride (681.2 mg, 17.96 mmol, 2.0 equiv) was added in portions. A solution of 2.50 g (8.98 mmol) of α-linolenic acid [(9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienoic acid ethanol solution, Cayman Chemical Company, Ann Arbor, MI, ethanol was removed by vacuum at 40 °C in a water bath] in 10 mL of anhydrous diethyl ether was added in to the flask using a syringe, and the syringe was washed several times with ∼7 mL of ether. The resulting mixture was stirred for 30 min at 0 °C and then warmed to room temperature. The reaction was monitored by GC until the peak of α-linolenic acid disappeared (∼4 h). The reduction mixture was cooled with ice bath, and treated by successive dropwise addition of 0.68 mL of water and stirred for 15 min; 0.68 mL of 15% sodium hydroxide solution and stirred for 15 min; and then 2.04 mL of water and stirred for 30 min at room temperature. The dry granular precipitate was removed by filtration, the filtrate was dried over Na$_2$SO$_4$ or MgSO$_4$, and the solvent was evaporated to dryness. The crude material was purified by flash chromatography on silica gel (60 g) using hexane−ethyl acetate (100:8 v/v) as eluent to provide 2.31 g (8.73 mmol, 97% yield) of (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrien-1-ol **2** as a colorless liquid. ^{1}H NMR: δ 0.99 (3H, t, *J* = 7.6 Hz, CH$_3$, C$_{18}$), 1.26−1.38 (10H, m, CH$_2$, C$_{3-7}$), 1.56 (2H, quintet, *J* = 7.2 Hz, CH$_2$, C$_2$), 1.67 (1H, br, OH), 2.03−2.12 (4H, m, CH$_2$−C=, C$_{8,17}$), 2.80 (4H, t, *J* = 6.0 Hz, =C−CH$_2$−C=, C$_{11,14}$), 3.62 (2H, t, *J* = 6.8 Hz, CH$_2$−O, C$_1$), 5.30−5.41 (6H, m, CH=). ^{13}C NMR: δ 14.21, 20.49, 25.47, 25.56, 25.69, 27.17, 29.18, 29.35, 29.44, 29.58, 32.71, 62.92, 127.06, 127.62, 128.20, 130.26, 131.88. EI-MS *m*/*z* (%): 264 [M]$^+$ (7), 235 (4), 208 (11), 149 (7), 135 (15), 121 (20), 108 (49), 95 (52), 93 (50), 79 (100), 67 (60), 55 (37).

(9*Z*,12*Z*,15*Z*)-9,12,15-Octadecatrienyl Triflate (3). To a solution of 103.2 mg (0.39 mmol) of (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrien-1-ol **2** in 5 mL of CH$_2$Cl$_2$ was added 32 μL (0.39 mmol, 1.0 equiv) of pyridine at dry ice/acetone cooling (−30 °C) followed by 79 μL (0.47 mmol, 1.2 equiv) of triflic anhydride. After 30 min the reaction was warmed to about −7 °C in an ice−salt bath and stirred for another 2.5 h, diluted with 10 mL of hexane, and filtered through a Celite pad. The filtrate was then concentrated by a rotor evaporator to remove the most of solvent, and the afforded crude triflate was directly used for coupling reaction without further purification.

(3*Z*,6*Z*,9*Z*)-3,6,9-Nonadecatriene (1a). The freshly prepared crude triflate **3** (0.39 mmol) from above reaction was dissolved in 9 mL of dry diethyl ether and cooled with a dry ice/acetone bath at −50 °C. Copper catalyst, Li$_2$CuCl$_4$ (59 μL 0.1 M THF solution, 0.015 equiv), was added using a syringe, and the solution was stirred for 20 min. The solution then was cooled to −78 °C, while 520 μL of methyl magnesium bromide (3 M ether solution, 1.56 mmol, 4 equiv) was added slowly. The reaction mixture was stirred at −78 °C for 20 min and at −10 °C for 1 h and then treated with 1 mL of water. After the cooling bath was removed, the mixture was diluted with 5 mL of hexane, followed by the addition of 2 mL of 0.5 N HCl, and stirred for another 30 min at room temperature, and then the mixture was extracted with hexane (2 × 5 mL). The combined organic layers were washed with water and saturated brine, dried over anhydrous Na$_2$SO$_4$, and concentrated to afford 120 mg of crude product, which was purified by flash chromatography on silica gel (10 g) using hexanes as an eluent to provide 96.60 mg (0.37 mmol, 94% isolated yield) of **1a** as a colorless liquid. ^{1}H NMR: δ 0.86 (3H, t, *J* = 7.2 Hz, CH$_3$, C$_{19}$), 0.96 (3H, t, *J* = 7.6 Hz, CH$_3$, C$_1$), 1.25−1.33 (14H, m, CH$_2$, C$_{12-18}$), 2.01−2.10 (4H, m, CH$_2$−C=, C$_{2,11}$), 2.79 (4H, t, *J* = 5.9 Hz, =C−CH$_2$−C=, C$_{5,8}$), 5.27−5.37 (6H, m, CH=). ^{13}C NMR: δ 14.10, 14.26, 20.54, 22.68, 25.52, 25.61, 27.25, 29.32, 29.34, 29.56, 29.61, 29.66, 31.91, 127.12, 127.61, 128.23, 128.29, 130.40, 131.93. EI-MS *m*/*z* (%): 262 [M]$^+$ (9), 233 (4), 219 (2), 206 (47), 180 (2), 163 (3), 149 (6), 135 (13), 121 (16), 108 (72), 95 (41), 93 (43), 79 (100), 67 (45), 55 (21).

(3*Z*,6*Z*,9*Z*)-3,6,9-Eicosatriene (1b). The compound **1b** (99.01 mg, 0.36 mmol) was prepared in 92% isolated yield by coupling reaction of the triflate **3** with 2.0 equiv of ethyl magnesium bromide (3.0 M ether solution) in the same manner as **1a**. ^{1}H NMR: δ 0.86 (3H, t, *J* = 6.8 Hz, CH$_3$, C$_{20}$), 0.96 (3H, t, *J* = 7.4 Hz, CH$_3$, C$_1$), 1.25−1.35 (16H, m, CH$_2$, C$_{12-19}$), 2.01−2.10 (4H, m, CH$_2$−C=, C$_{2,11}$), 2.79 (4H, t, *J* = 5.8 Hz, =C−CH$_2$−C=, C$_{5,8}$), 5.29−5.41 (6H, m, CH=). ^{13}C NMR: δ 14.11, 14.26, 20.54, 22.69, 25.52, 25.61, 27.25, 29.33, 29.35, 29.56, 29.64, 29.65, 29.66, 31.92, 127.12, 127.61, 128.23, 128.29, 130.40, 131.93. EI-MS *m*/*z* (%): 276 [M]$^+$ (3), 247 (1), 233 (1), 220 (19), 194 (1), 177 (1), 163 (2), 149 (5), 135 (12), 121 (16), 108 (81), 95 (46), 93 (49), 79 (100), 67 (63), 55 (32).

(3*Z*,6*Z*,9*Z*)-3,6,9-Heneicosatriene (1c). The compound **1c** (105.14 mg, 0.37 mmol) was prepared in 93% isolated yield by coupling reaction of the triflate **3** with 2.0 equiv of propyl magnesium chloride (2.0 M ether solution) in the same manner as **1a**. ^{1}H NMR: δ 0.88 (3H, t, *J* = 6.8 Hz, CH$_3$, C$_{21}$), 0.98 (3H, t, *J* = 7.4 Hz, CH$_3$, C$_1$), 1.261−1.367 (18H, m, CH$_2$, C$_{12-20}$), 2.03−2.10 (4H, m, CH$_2$−C=C, C$_{2,11}$), 2.81 (4H, t, *J* = 6.0 Hz, =C−CH$_2$−C=, C$_{5,8}$), 5.32−5.41 (6H, m, CH=). ^{13}C NMR: δ 14.11, 14.27, 20.55, 22.69, 25.53, 25.62, 27.26, 29.33, 29.36, 29.57, 29.64, 29.65, 29.66, 29.68, 31.93, 127.13, 127.62, 128.24, 128.30, 130.42, 131.94. EI-MS *m*/*z* (%): 290 [M]$^+$ (2), 261 (1), 234 (11), 180 (1), 163 (2), 149 (4), 135 (10), 121 (13), 108 (68), 95 (38), 93 (38), 79 (100), 67 (51), 55 (28).

(3*Z*,6*Z*,9*Z*)-3,6,9-Docosatriene (1d). The compound **1d** (110.21 mg, 0.36 mmol) was prepared in 93% isolated yield by coupling reaction of the triflate **3** with 2.0 equiv of butyl magnesium chloride (2 M THF solution) in the same manner as **1a**. ^{1}H NMR: δ 0.87 (3H, t, *J* = 6.8 Hz, CH$_3$, C$_{22}$), 0.96 (3H, t, *J* = 7.4 Hz, CH$_3$, C$_1$), 1.25−1.34 (20 H, m, CH$_2$, C$_{12-21}$), 2.02−2.10 (4H, m, CH$_2$−C=, C$_{2,11}$), 2.80 (4H, t, *J* = 6.0 Hz, =C−CH$_2$−C=, C$_{5,8}$), 5.27−5.41 (6H, m, CH=). ^{13}C NMR: δ 14.11, 14.26, 20.55, 22.70, 25.52, 25.61, 27.25, 29.33, 29.37, 29.57, 29.65, 29.66, 29.67, 29.68, 29.70, 31.93, 127.12, 127.61, 128.23, 128.29, 130.40, 131.93. EI-MS *m*/*z* (%): 304 [M]$^+$ (4), 275 (2), 248 (15), 194 (1), 163 (2), 149 (6), 135 (12), 121 (16), 108 (82), 95 (42), 93, (39), 79 (100), 67 (50), 55 (27).

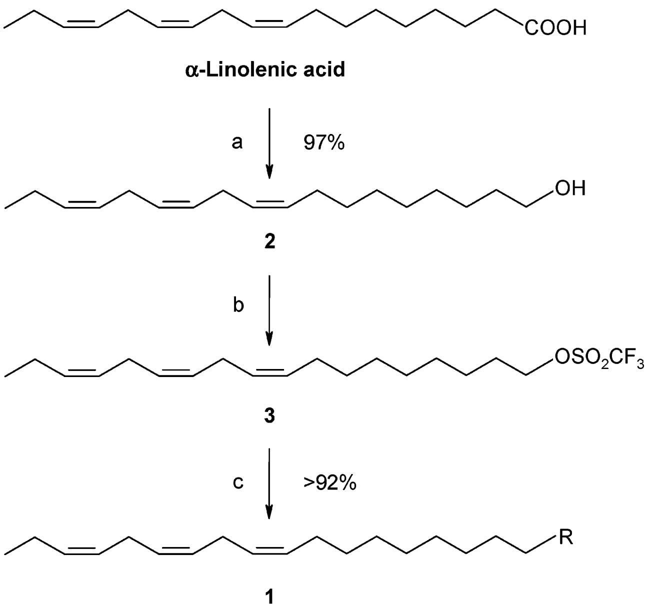
(3*Z*,6*Z*,9*Z*)-3,6,9-tricosatriene (1e). The compound **1e** (117.10 mg, 0.37 mmol) was prepared in 94% isolated yield by coupling reaction of the triflate **3** with 2.0 equiv of pentyl magnesium bromide (2 M, ether solution) in the same manner as **1a**. ^{1}H NMR: δ 0.86 (3H, t, *J* = 6.8 Hz, CH$_3$, C$_{23}$), 0.96 (3H, t, *J* = 7.4 Hz, CH$_3$, C$_1$), 1.24−1.35 (22 H, m, CH$_2$, C$_{12-22}$), 2.01−2.10 (4H, m, CH$_2$=C, C$_{2,11}$), 2.80 (4H, t, *J* = 7.0 Hz, =C−CH$_2$−C=, C$_{5,8}$), 5.26−5.41 (6H, m, CH=). ^{13}C NMR: δ 14.11, 14.26, 20.55, 22.70, 25.53, 25.62, 27.26, 29.34, 29.38, 29.57, 29.65, 29.66, 29.67, 29.68, 29.69, 29.70, 31.94, 127.13, 127.61, 128.24, 128.29, 130.41, 131.93. EI-MS *m*/*z* (%): 318 [M]$^+$ (7), 289 (3), 262 (20), 163 (3), 149 (7), 135 (17), 121 (20), 108 (91), 95 (54), 93 (42), 79 (100), 67 (53), 55 (29).

RESULTS AND DISCUSSION

α-Linolenic acid [(9*Z*,*12Z*,*15Z*)-9,12,15-octadecatrienoic acid] was selected as starting material because it was commercially available and contained the required unsaturation and geometric configurations. The α-linolenic acid was cleanly converted into the corresponding alcohol, (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrien-1-ol **2**, in 97% isolated yield by reduction with lithium aluminum hydride (LAH) in ether under inert atmosphere (*18*). An improvement that could be made is to convert the α-linolenic acid to the methyl ester first and then reduce it with LAH to the alcohol. Although there is one more step reaction, the reduction time of methyl ester to the alcohol was usually much shorter than that of the free acid (*19*).

It has been noticed that cross-coupling reaction of alkyl tosylate with Grignard reagents proceeds well (*20*) in THF in the presence of a catalytic amount of copper catalyst, Li$_2$CuCl$_4$, and a primary triflate showed higher activity than that of a primary tosylate in the alkylation of triflates with alkynyllithium reagents (*21*). It seemed that the (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienyl triflate might be a good candidate for sequential coupling reaction with Grignard reagents. Treatment of the (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienyl triflate **3**, which was easily prepared from (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrien-1-ol **2**, trifluromethanesulfonic anhydride, and pyridine in dichloromethane (*22*, *23*), with methyl magnesium bromide in the

Scheme 1 [a]



1a	$R=CH_3$	**1b**	$R=C_2H_5$
1c	$R=C_3H_7$	**1d**	$R=C_4H_9$
1e	$R=C_5H_{11}$		

[a] (a) $LiAlH_4$/ether, 2.0 equiv, 0 °C, 30 min, room temperature, 4 h; (b) $(CF_3SO_2)O$, 1.2 equiv, pyridine, 1.0 equiv, –25 °C, CH_2Cl_2, 30 min, –7 °C, 1.5 h; (c) RMgX/ether, 2–4 equiv, Li_2CuCl_4, 0.015 equiv, –78 °C, ether, 20 min, –10 °C, 1 h.

presence of a catalytic amount of Li_2CuCl_4 at −78 °C for 20 min, and then at −10 °C for 1 h in diethyl ether led to the clean formation of the expected (3*Z*,6*Z*,9*Z*)-3,6,9-nonadecatriene **1a** in 94% isolated yield from alcohol **2** (**Scheme 1**). The homologues (3*Z*,6*Z*,9*Z*)-3,6,9-eicosatriene **1b**, (3*Z*,6*Z*,9*Z*)-3,6,9-heneicosatriene **1c**, (3*Z*,6*Z*,9*Z*)-3,6,9-docosatriene **1d**, and (3*Z*,6*Z*,9*Z*)-3,6,9-tricosatriene **1e** were also obtained from the (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrien-1-ol **2** in the same manner with the appropriate alkyl Grignard reagents in 92, 93, 93, and 94% isolated yields, respectively.

A number of different synthetic methodologies have been developed for the syntheses of (3*Z*,6*Z*,9*Z*)-3,6,9-nonadecatriene and the homologues. For example, the routes via Wittig-type olefination reported by Bestmann et al. (*8*), semihydrogenation/Wittig reaction reported by Becker et al. (*9*), desilylation/Wittig reaction reported by Bestmann et al. (*12*), and sila-Cope elimination reported by Langlois et al. (*24*) involve multiple steps, produce low yields, and result in low geometric purities. In addition, the route via nucleophilic addition/reduction reported by Cabrera et al. (*10*) and Badioli et al. (*11*) also involves multiple steps and produces low yields although the geometric configuration was retained. Furthermore, the routes via coupling reaction of (2*Z*,5*Z*,8*Z*)-2,5,8-undecatrienyl bromide (*14*) or of (9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienyl tosylate (*25*) with appropriate Grignard reagents only give 35% and 48% yields of target compounds, respectively, which were hardly satisfactory.

In conclusion, the results presented in this paper clearly illustrated the usefulness and advantage of metal-catalyzed cross-coupling methodology during the syntheses of straight-chain homoconjugated trienes. It afforded desired trienes in fewer reaction steps, shorter reaction time, and higher isolated yields with retention of configuration, and the resulting (3*Z*,6*Z*,9*Z*)-3,6,9-nonadecatriene **1a** and homologues were obtained in geometrically pure form. In addition, the facile and efficient syntheses of (3*Z*,6*Z*,9*Z*)-3,6,9-nonadecatriene **1a** and the homologues should make these compounds easily accessible to the farmers and scientists and facilitate the management program to protect agricultural important crops from lepidopterous insect pests.

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