Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A Short and Efficient Synthesis of (3E,5Z)-1,3,5-Undecatriene from (1E)-1-Chloro-1,3-butadiene

Chanh Huynh [a], Mou[acaron]d Alami [a] & Gérard Linstrumelle [a]

[a] Laboratoire de Chimie, Ecole Normale Supérieure, 24, Rue Lhomond 75231, Paris, Cedex, 05, France

To cite this article: Chanh Huynh, Mou[acaron]d Alami & Gérard Linstrumelle (1994) A Short and Efficient Synthesis of (3E,5Z)-1,3,5-Undecatriene from (1E)-1-Chloro-1,3-butadiene, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 24:16, 2273-2280, DOI: 10.1080/00397919408019052

To link to this article: http://dx.doi.org/10.1080/00397919408019052

SYNTHETIC COMMUNICATIONS, 24(16), 2273-2280 (1994)

A SHORT AND EFFICIENT SYNTHESIS OF (3E,5Z)-1,3,5-UNDECATRIENE FROM (1E)-1-CHLORO-1,3-BUTADIENE

Chanh Huynh, Mouâd Alami and Gérard Linstrumelle

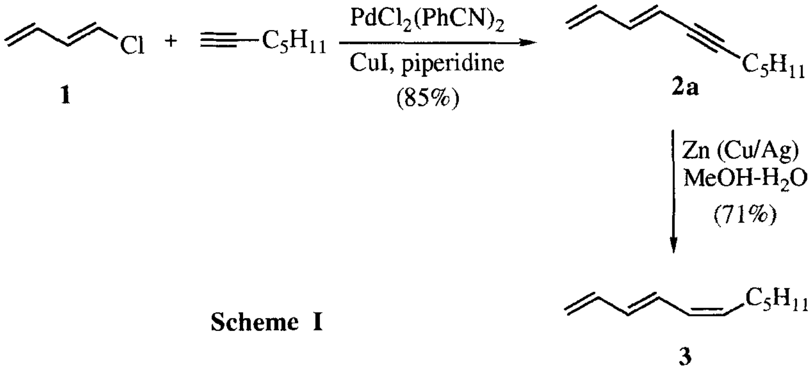
Laboratoire de Chimie, Ecole Normale Supérieure
24, Rue Lhomond 75231 Paris Cedex 05, France

Abstract: A short synthesis of (3E,5Z)-1,3,5-undecatriene (cis-galbanolene) is described. The key step is the Pd/Cu-catalyzed coupling reaction of (E)-1-chloro-1,3-butadiene with 1-alkynes followed by stereoselective zinc reduction of the triple bond.

As part of our continuing studies in stereoselective polyene synthesis via palladium catalysis,[1] we recently showed that vinyl chlorides react efficiently and rapidly with terminal alkynes in the presence of a catalytic amount of bis(benzonitrile)palladium chloride in piperidine.[2] We now wish to report a short synthesis of cis-galbanolene **3** by using this coupling reaction which is experimentally simple and takes place under mild conditions (room temperature).

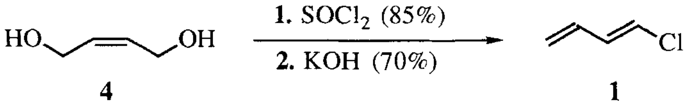
(3E,5Z)-1,3,5-Undecatriene **3** (cis-galbanolene), isolated from essential oils of galbanum[3] and seaweed[4,5] is known to act as the sexual pheromone on male gametes of the Australian brown alga *Cystophora siliquosa.*[5] It is also known to display interesting olfactive properties[3,6] and is therefore used in the perfume industry.

Several syntheses of this compound have been described.[7] However, few of them are short and high yielding at the same time. In our approach (scheme I), based on the coupling of (1E)-1-chloro-1,3-butadiene **1** with 1-heptyne followed by stereoselective zinc reduction, cis-galbanolene **3** was obtained (90% isomeric purity) in 60% overall yield (2 steps).

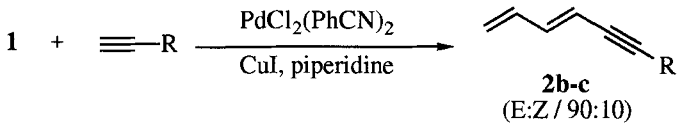


Scheme I

Chlorodiene **1** was easily prepared from (2Z)-butene-1,4-diol **4** according to the literature procedure[8] in a 90% E purity.



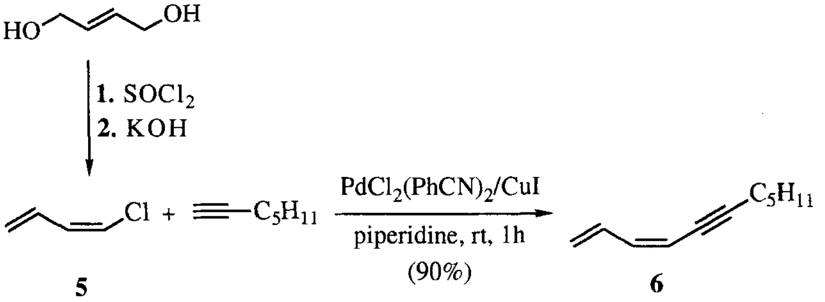
The cross-coupling of 1-heptyne and chlorodiene **1** in the presence of bis(benzonitrile)palladium chloride and copper iodide in piperidine proceeded very rapidly (30 min) at room temperature and gave terminal dienyne **2a** (90% isomeric purity) in 85% distillated yield (scheme I). Cis-galbanolene **3** was obtained in 71% yield (90% E purity) by stereoselective reduction with activated zinc.[9, 1c-e] Chlorodiene **1** can also be used as an efficient starting material for the preparation of terminal dienynes **2** by coupling with different 1-alkynes.



2b-c
(E:Z / 90:10)

b	R = Me_3Si	73%
c	R = $(CH_2)_3Cl$	69%

In a similar way, (1Z)-1-chloro-1,3-butadiene **5** (90% Z purity), obtained from (2E)-butene-1,4-diol, was coupled with 1-heptyne under Pd-catalysis to give the terminal (Z)-dienyne **6** in good yield.



In conclusion, the Pd-catalyzed coupling reaction of (E) or (Z)-1-chloro-1,3-butadiene with 1-alkynes has proven to be an efficient and practical route to terminal dienynes and cis-galbanolene.

EXPERIMENTAL

(3E)-1,3-Undecadien-5-yne (2a): Under an argon atmosphere, a suspension of $PdCl_2(PhCN)_2$ (3.5 mmol, 1.34 g), (1E)-1-chloro-1,3-butadiene **1** (70 mmol, 6.16 g) and piperidine (70 ml) was stirred at room temperature. After 15 min, was added successively 1-heptyne (84 mmol, 8.06 g) and CuI (7 mmol, 1.33 g). The reaction was exothermic and the temperature was maintained between 15-20 °C (30 min) by using a water-ice bath. Stirring was continued at room temperature until GLC analysis indicated complete consumption of the chlorodiene **1** (30 min) and the reaction mixture was then treated with a saturated solution of NH_4Cl (60 ml). The aqueous layer was extracted with ether (2 x 50 ml), the combined organic layers were washed successively with aqueous HCl (0.2 M, 15 ml), $NaHCO_3$ (10 ml) and H_2O (2 x 30 ml), dried over $MgSO_4$ and concentrated under vacuum. Purification by distillation through a 10 cm vigreux column bp 60-62 °C (0.1 mmHg) provided **2a** (colorless liquid) 8.81 g (85%) as a mixture (90:10) of E:Z isomers assigned by GLC (SGE 50 QC 2 / BP5 0.25). ^1H NMR (400 MHz, $CDCl_3$) δ 6.45 (1H, dd, J = 15.0, 10.5 Hz), 6.26 (1H, ddd, J = 17.0, 10.0, 10.5 Hz), 5.54 (1H, dt, J = 15.0, 2.2 Hz), 5.15 (1H, dd, J = 17.0, 1.5 Hz), 5.03 (1H, dd, J = 10.0, 1.5 Hz), 2.24 (2H, td, J = 7.0, 2.2 Hz), 1.46 (2H, quint, J = 7.0 Hz), 1.15 to 1.36 (4H, m), 0.89 (3H, t, J = 7.0 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 140.90, 136.35, 118.50, 112.65, 93.65, 79.50, 31.10, 28.45, 22.20, 19.60, 13.95; CIMS (NH_3) m/e (relative intensity) 166 ($(M+NH_4)^+$, 100), 148 (M^+, 18), 105 (18), 91 (21).

The spectral properties of **2a** were in good agreement with those reported in the literature.[10b]

(3E)-1-Trimethylsilyl-3,5-hexadien-1-yne (2b): prepared from **1** and trimethylsilyl acetylene according to the procedure described for **2a**. Yield 73%, bp 85-86 °C (15 mmHg), E isomeric purity 90%. IR (neat) cm^{-1} 2210, 1820, 1620; ^1H NMR (250 MHz, $CDCl_3$) δ 6.64 (1H, dd, J = 15.7, 10.0 Hz), 6.35 (1H, ddd, J = 16.9, 10.0 Hz), 5.64 (1H, dd, J = 15.7, 0.6 Hz), 5.31 (1H, dd, J = 17.0, 1.4 Hz), 5.20 (1H, dd, J = 10.0, 1.4 Hz), 0.21 (9H, s); ^{13}C NMR (250 MHz, $CDCl_3$) δ 143.00, 136.00, 120.00, 111.80, 104.05, 97.25, -0.15; MS m/e 150 (M^+), 135 (M^+ - CH_3); Anal. calcd. for $C_9H_{14}Si$: C, 71.96; H, 9.40 Found: C, 71.64; H, 9.63.

(3E)-9-Chloro-1,3-nonadien-5-yne (2c): prepared from **1** and 5-chloro-1-pentyne according to the procedure described for **2a**. Yield 69%, bp 82-83 °C (0.5 mmHg), E isomeric purity 90%. IR (neat) cm^{-1} 3090, 3010, 2210, 1820, 1620, 1000; ^1H NMR (250 MHz, $CDCl_3$) δ 6.34 (1H, dd, J = 15.0, 11.0 Hz), 6.16 (1H, ddd, J = 16.7, 10.0 Hz), 5.42 (1H, dt, J = 16.0, 2.0 Hz), 5.08 (1H, dd, J = 17.0, 1.3 Hz), 5.01 (1H, dd, J = 10.0, 1.3 Hz), 3.47 (2H, t, J = 6.5 Hz), 2.34 (2H, td, J = 7.0, 2.0 Hz), 1.49 (2H, quint, J = 6.5 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 141.25, 136.00, 118.80, 112.00, 90.95, 80.25, 43.45, 31.24, 16.85; MS m/e 156 (M^+ ^{37}Cl), 154 (M^+ ^{35}Cl); Anal. calcd. for $C_9H_{11}Cl$: C, 70.10; H, 7.20 Found: C, 70.54; H, 7.33.

(3Z)-1,3-Undecadien-5-yne (6): prepared from **5** and 1-heptyne according to the procedure described for **2a**. Yield 90%, bp 60-61 °C (0.1 mmHg), Z isomeric purity 90%. IR (neat) cm^{-1} 3080, 3020, 2205, 1825, 1620, 1430, 1000, 730, 675; ^1H NMR (250 MHz, $CDCl_3$) δ 6.80 (1H, ddd, J = 17.0, 10.0 Hz), 6.25 (1H, t, J = 10.0 Hz), 5.38 (1H, dt, J = 10.0, 2.0 Hz), 5.30 (1H, br d, J = 17.0 Hz), 5.16

(1H, br d, J = 10.0 Hz), 2.30 (2H, td, J = 7.0, 2.3 Hz), 1.39 (2H, quint, J = 7.0 Hz), 1.29 to 1.01 (4H, m), 0.80 (3H, t, J = 7.0 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 139.05, 134.10, 119.25, 110.60, 97.10, 77.40, 31.05, 28.45, 22.15, 19.60, 13.90; MS m/e 148 (M^+), 119 ($M^+ - C_2H_5$), 105 ($M^+ - C_3H_7$), 91 ($M^+ - C_4H_9$), 77 (M^+ C_5H_{11}); Anal. calcd. for $C_{11}H_{16}$: C, 89.11; H, 10.89 Found: C, 89.64; H, 10.68.

(3E,5Z)-1,3,5-Undecatriene (3): Activated zinc dust was prepared from zinc Merck (zinc powder for analysis > 230 mesh ASTM, 60 μm) as previously described.[9,1c-e] A solution of compound **2a** (2 mmol, 297 mg) in 10 ml H_2O-MeOH (1/1) was added to the suspension of activated Zn (1 g) and stirred at 35 °C. After 2 h, the mixture was filtered on a pad of celite and concentrated. Ether was added (20 ml) and the organic layer washed with H_2O (2 x 10 ml), dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification by flash chromatography (R_f (pentane) 0.60) afforded cis-galbanolene **3** in 71% yield (213 mg) as a mixture (90:10) of 3E:3Z isomers assigned by GLC analysis (SGE 50 QC 2 / BP5 0.25). IR (neat) cm^{-1} 3080, 3020, 2960-2860, 1620, 1575, 1005, 940, 900, 760; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.49 (1H, dd, J = 14.9, 11.0 Hz), 6.42 (1H, ddd, J = 16.8, 11.0, 10.6 Hz), 6.21 (1H, dd, J = 14.9, 10.6 Hz), 6.03 (1H, dd, 11.0 Hz), 5.50 (1H, dt, J = 11.0, 7.0 Hz), 5.20 (1H, d, J = 16.8 Hz), 5.09 (1H, d, J = 11.0 Hz), 2.20 (2H, q, J = 7.0 Hz), 1.45 to 1.20 (6H, m), 0.90 (3H, t, J = 6.7 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 137.25, 133.60, 132.90, 128.70, 128.25, 116.80, 31.45, 29.30, 27.85, 22.55, 14.05; CIMS (NH_3) m/e (relative intensity) 151 ($(M+H)^+$, 100), 150 (M^+, 23), 92 (19), 93 (34), 80 (83), 79 (33).

The spectral properties of **3** were in good agreement with those reported in the literature.[7a,8c,10]

References and notes.

1. (a) Ratovelomanana, V.; Linstrumelle, G. Tetrahedron Lett. 1981, 22, 315. (b) Ratovelomanana, V.; Linstrumelle, G. Tetrahedron Lett. 1984, 25, 6001. (c) Chemin, D.; Linstrumelle, G. Tetrahedron 1992, 48, 1943. (d) Chemin, D.; Alami, M.; Linstrumelle, G. Tetrahedron Lett. 1992, 33, 2681. (e) Alami, M.; Crousse, B.; Linstrumelle, G.; Lengo, M.; Larchevêque, M. Syn. Lett. 1993, 217.
2. Alami, M.; Linstrumelle, G. Tetrahedron Lett. 1991, 32,.6109.
3. (a) Chrétien-Bessière, Y.; Garnero, J.; Benezet, L.; Peyron, L. Bull. Soc. Chim. Fr. 1967, 97. (b) Naves, Y. R. Bull. Soc. Chim. Fr. 1967, 3152. (c) Teisseire, P.; Corbier, B.; Plattier, M. Recherches (Paris), 1967, 16, 5.
4. (a) Pettus, Jun. J. A.; Moore, R. E. J. Am. Chem. Soc. 1971, 93, 3087. (b) Moore, R. E.; Mistysyn, J.; Pettus, Jun. J. A. J. Chem. Soc. Chem. Commun. 1972, 326. (c) Moore, R. E.; Pettus, Jun. J. A.; Mistysyn, J. J. Org. Chem. 1974, 39, 2201. (d) Moore, R. E. Acc. Chem. Res. 1977, 10, 40.
5. Müller, D. G.; Clayton, M. N.; Gassmann, G.; Boland, W.; Marner, F. J.; Schotten, T.; Jaenicke, L. *Naturwissenschaften* 1985, 97.
6. Ohloff, G. in Riechstoffe und Geruchssinn, Springer-Verlag, Berlin, Heidelberg 1990, 175.
7. (a) Solladié, G.; Urbano, A.; Stone, G. B. Syn. Lett. 1993, 548 and references therein. (b) Hodgetts, K. J.; Saengchantara, S. T.; Wallis, C. J.; Wallace, T. W. Tetrahedron Lett. 1993, 34, 6321.
8. (a) Kalaidzhydan, A. E.; Rastomyan, I. M.; Kurginyan, K. A.; Chukhadzhyan, G. A. Arm. Khim. Zh. 1980, 31, 57. (b) Keegstra, M. A.;

Verkruijsse, H. D.; Andringa, H.; Brandsma, L. Synth. Comm. 1991, 21, 721. (c) Alexakis, A.; Barthel, A. M.; Normant, J. F.; Fugier, C.; Leroux, M. Synth. Comm. 1992, 22, 1839.

9. Boland, W.; Schroer, N.; Sieler, C.; Feigel, M. Helv. Chim. Acta. 1987, 70, 1025.

10. (a) Ratovelomanana, V.; Linstrumelle, G. Bull. Soc. Chim. Fr. 1987, 174. (b) Andreini, B. P.; Benetti, M.; Carpita, A.; Rossi, R. Tetrahedron 1987, 43, 4591. (c) Tellier, F.; Descoins, C.; Sauvêtre, R. Tetrahedron 1991, 47, 7767.

(Received in the UK 10 February 1994)