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Hydroalumination of 3-Butyn-1-ol: Application to a Stereoselective Synthesis of (3*E*,5*Z*)-3,5-Dodecadienyl Acetate, the Sex Pheromone of the Leaf Roller Moth

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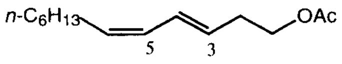
Abstract: Hydroalumination-iodinolysis of 3-butyn-1-ol (**2**) provided *E*-4-iodo-3-buten-1-ol (**4*E***) as the major product. This compound was transformed in three steps into the leaf roller moth sex pheromone **1** with high (>99% de) stereoselectivity and good overall yield (4 steps, 39% from **2**).

Keywords: aluminium and compounds; dienes; pheromones

Introduction

The female sex pheromone of the leaf roller moth *Bonagota cranaodes* Meyrick, an economically important pest of South American apple orchards, was recently identified as (3*E*,5*Z*)-3,5-dodecadienyl acetate (**1**).[1] This compound was originally prepared as a mixture of geometric isomers which were then separated by liquid chromatography on $AgNO_3$-impregnated silica gel.[1] Subsequently, stereoselective syntheses of all four geometric isomers of 3,5-dodecadienyl acetate were reported; however, the (3*E*,5*Z*)-isomer of interest was contaminated with the (3*E*,5*E*)-isomer and had to be purified by $AgNO_3$/silica chromatography.[2] As the natural isomer is the (3*E*,5*Z*)-isomer, and thus this would be the isomer of interest for use in lures, we sought to develop a highly stereoselective route to this compound. Such a synthesis would avoid tedious chromatographic separations. In addition, it is known that with other insect pheromones, isomers (including enantiomers,[3] epimers,[4] and geometric isomers[5]) may be highly inhibitory. Since the biological properties of the other isomers have yet to be fully evaluated, it would be prudent to prepare the natural isomer in high stereochemical purity.



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The route shown in Scheme 1 was envisaged as a viable route to the desired compound. The hydroalumination of simple terminal alkynes followed by iodinolysis of the intermediate vinylalane is known to give highly stereoselectively (>99% de) the *E*-vinyl iodide.[6] Palladium catalyzed coupling of the iodide with a 1-alkyne would then give an enyne which is expected to undergo hydroboration/protonolysis with high (>99% de) syn stereoselectivity. This sequence has been used previously to establish the *E*,*Z* stereochemistry of other diene pheromones with high degrees of stereocontrol.[7,8]

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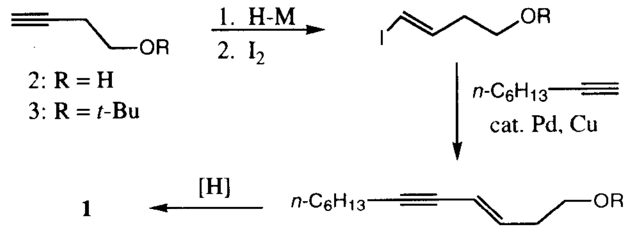
Scheme 1



For this particular synthesis, the hydroalumination reaction presents a special challenge because the alkyne required is a homopropargylic alcohol or ether (*i.e.* 3-butyn-1-ol or a derivative thereof). It has been previously reported that hydroalumination/iodination of *t*-butyl 3-butynyl ether (**3**) gives predominantly (>98% de) the *Z* iodide.[9] The only other report of hydroalumination chemistry of a 3-butyn-1-ol derivative was on the parent alcohol: hydroalumination/iodination of 3-butyn-1-ol (**2**, 2 equiv of DIBAL-H) gives stereoselectively *E*-4-iodo-3-buten-1-ol (**4E**) but in only 65% yield and as a 2:1 mixture with 4-iodobutan-1-ol (**5**).[10] Thus neither of these literature results would be very satisfactory for the intended chemistry. Iodo alcohol **4E** has also been prepared from the corresponding tributylstannane (prepared by hydrostannation of **2**), but chromatographic separation of hydrostannation mixture is required followed by chromatographic removal of Bu_3SnI after iodinolysis.[11] Thus, we decided to investigate the hydroalumination/iodination of 3-butyn-1-ol in more detail as a possible route to **4E**.

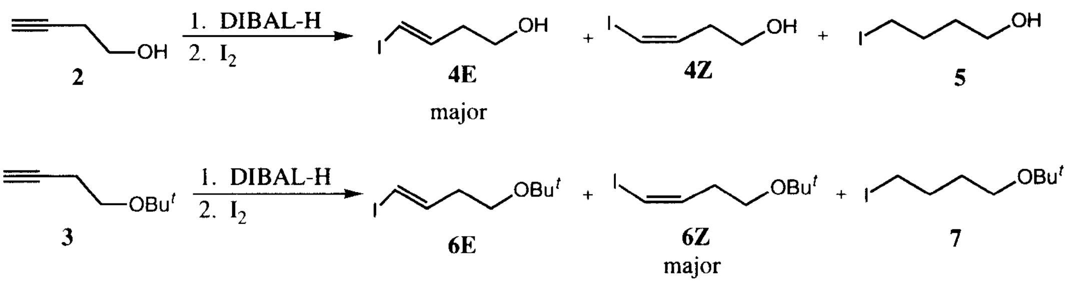
Results and Discussion

Since we were particularly interested in the stereoselectivity of the hydroalumination/iodination of 3-butyn-1-ol, we began our studies by preparing authentic samples of **6Z** and **6E** as standards for GC analysis. The *E* isomer could be easily prepared via hydrostannation of the *t*-butyl ether of 3-butyn-1-ol (**3**); this reaction gave a mixture of products but the *E* stannane could be isolated by flash chromatography. Iodinolysis then gave **6E**. For the *Z* isomer, it had been reported that treatment of **3** with DIBAL-H followed by I_2 provides **6Z** with >99% stereoselectivity. Thus we were surprised to find that in our hands, while **6Z** was the major product formed, **6E** and the saturated iodide **7** were also formed (Scheme 2, **6E** : **6Z**: **7** = 6 : 70 : 24) The isomeric vinyl iodides are formed presumably because the hydroalumination step is not completely stereoselective while the saturated iodide is derived from a bis-hydroalumination intermediate.[12] In any case, **6E**, **6Z**, and **7** were readily separable by GC and thus could serve as useful standards.

Initial studies on the hydroalumination/iodination of 3-butyn-1-ol with DIBAL-H (2 equiv, hexanes, –25 °C) gave modest (ca. 60%) yields of products. Yields were increased substantially (to >85%) by modifying the work-up to include a continuous extraction step to better extract the partially water-soluble alcohols from the aqueous phase. Direct analysis of the crude reaction mixture (as the free alcohols) by GC-MS indicated the presence of 2 principal components: an unsaturated iodobutenol and a saturated iodobutanol. This is consistent with the results reported by Bao *et al.* who isolated a 2:1 mixture of **4E** and

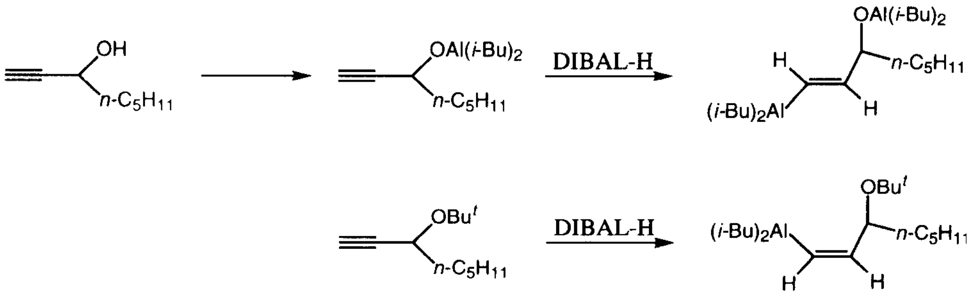
4-iodobutanol (**5**). However, conversion of the crude alcohols to their *t*-butyl ethers followed by analysis by GC-MS revealed a mixture of 3 compounds, **6E**, **6Z**, and **7** in a ratio of 76 : 6 : 18. Thus it seems that the *Z* iodoalcohol **4Z** is also formed in small amounts in the hydroalumination of 3-butyn-1-ol but is not readily detected unless the alcohols are derivatized.

Scheme 2



The difference in stereochemical outcomes in the hydroalumination of alcohol **2** and *t*-butyl ether **3** is initially counter-intuitive. Since unfunctionalized alkynes typically undergo syn hydroalumination (which, after iodinolysis, would provide *E* vinyl iodides), it might be expected that the *t*-butyl ether **3** with a relatively non-coordinating functionality would give rise to the *E* vinyl iodide **6E**. If anti hydroalumination occurs due to intramolecular coordination effects, one would expect the alcohol **2** to be more likely than *t*-butyl ether **3** to exhibit this phenomenon and hence give rise to alcohol **4Z**. In practice, the alcohol **2** undergoes predominantly syn hydroalumination while the *t*-butyl ether **3** gives mostly the anti hydroalumination product. This apparent anomaly may be reconciled by considering that it is not the free alcohol which is undergoing hydroalumination but rather the derived diisobutylaluminum alkoxide; this alkoxide would then be less effective at coordinating to the DIBAL-H. In fact, this difference has been previously observed in propargylic systems (Scheme 3).[13,14] These results imply that *t*-butyl ethers, although sterically encumbered, may be coordinating if they are in close proximity to the site of reaction.

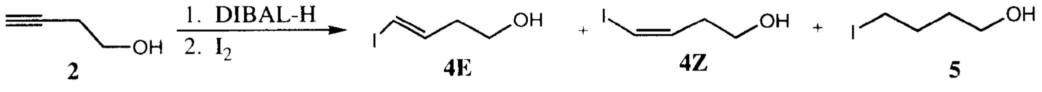
Scheme 3



It is also interesting to note that the relatively large amounts of saturated compounds (**5** and **7**, ca. 20% vs <5% with unfuctionalized alkynes) formed are likely also due to coordination effects: bis-hydroalumination is commonly observed when THF is used as solvent.[15]

With a good isolation procedure and analytical method in hand, we examined various reaction conditions to optimize the yield of **4E** (Table). Since the major by-product was saturated alcohol **5**, less DIBAL-H was tried (entry 3). As hoped for, the product distribution improved in favour of alcohol **4E**; however, the overall yield suffered. A lower temperature was also employed in an attempt to increase selectivity (Entry 4); however, the amount of undesired saturated alcohol increased. With CH_2Cl_2 as solvent, the reaction was very poor, providing a low yield of predominantly saturated alcohol **5**. Thus, somewhat ironically, the best conditions for the preparation of **4E** were those originally used (entry 2).

Table. Hydroalumination-iodinolysis of **2**



Entry	Temp (°C)	Solvent	DIBAL-H (eq.)	Yield[a] (%)	Product Distribution[b] (%)		
					4E	**4Z**	**5**
1[c]	-20	Hexane	2.0	65	66	0	34
2	-25	Hexane	2.0	88	76	6	18
3	-25	Hexane	1.5	40	86	4	10
4	-60	Hexane	2.0	55	56	3	41
5	-60	CH_2Cl_2	2.0	13	21	0	79

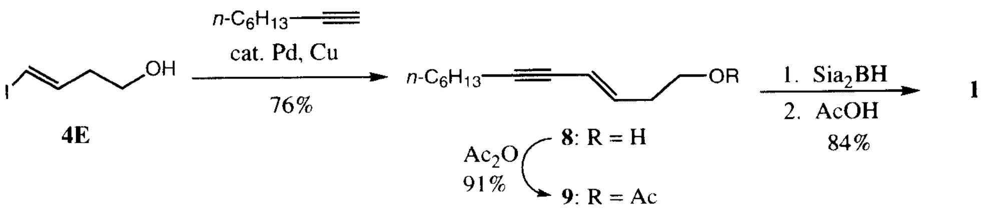
[a] Isolated yields of product mixture

[b] Product distributions were determined by GC-MS of the derived *t*-butyl ethers

[c] Taken from Reference 10

Although conditions could not be developed to prepare **4E** as the exclusive product, it was still felt that a stereoselective synthesis of **1** could be accomplished since the vinyl iodide would be next coupled with an alkyne (Scheme 4). It is known that *Z* vinyl halides are less reactive than the corresponding *E* compounds[16,17] and that saturated iodides do not participate in coupling reactions with copper acetylides;[18] thus **4Z** and **5** should not interfere with the Pd/Cu Stephens-Castro type coupling. In fact, coupling of the crude hydroalumination product (a mixture of **4E**, **4Z**, and **5**) with 1-octyne [PhH, cat. CuI, $(Ph_3P)_4Pd$, rt, 18 h] as described in the literature[7] gave a 95:5 mixture of *E* and *Z* enynes, respectively. Fortunately, when the reaction was stopped after 2 h, no *Z* enyne was detected and the desired *E* enyne **8** could be isolated in good yield.[19] Thus it seems that **4E** reacts considerably more quickly than **4Z**; the *Z* enyne is formed after extended reaction times but its formation may be completely suppressed simply by stopping the reaction when **4E** has been consumed. Acetylation (Ac_2O, pyr) of **8** and reduction (Sia_2BH; AcOH) of acetate **9** then furnished the desired 3*E*,5*Z*-diene acetate **1**. This compound exhibited ^{1}H and ^{13}C NMR spectra essentially identical to those previously reported.[2] The stereochemical purity of **1** was judged to be >99.5% since none of the other isomers were detected by GC.[20]

Scheme 4



Thus we have shown that hydroalumination/iodination of **2** is a practical route to vinyl iodide **4E**. This compound served as a key intermediate in a short, practical (4 steps, 39% overall yield from **2**) stereoselective synthesis which affords the leaf roller moth sex pheromone **1** in high stereochemical purity without tedious $AgNO_3$ chromatography. It is likely that other structurally related diene pheromones[21] could also be prepared using this approach.

Experimental

All reactions involving air or moisture sensitive reagents were carried out in a fumehood with oven or flame-dried glassware under argon. Reactions performed at −78°C employed a CO_2 (dry ice)-acetone bath; at -60 °C, a dry ice-$CHCl_3$ bath; at −25°C, a water-ethylene glycol (75:25 v/v)-dry ice bath; and −10°C, acetone-ice bath. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AM-250 spectrometer. Chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane (TMS). The ^{1}H and ^{13}C NMR samples were run in $CDCl_3$ containing 0.01% TMS as an internal standard (δ = 0.0); $CDCl_3$ (δ = 77.0) was the standard for ^{13}C-NMR samples. Gas chromatography – mass spectrometry (GC-MS) data was obtained using a HP5890 gas chromatograph coupled to a HP5973 mass spectrometer detector using a 30 m x 0.25 mm HP5 column. The oven was programmed at 70 °C for 2.5 minutes then ramped at 20 °/min to 250 °C; retention times are given in minutes (min). Mass spectral data are reported in the form *m/z* (intensity relative to base = 100). Infrared (IR) spectra were recorded on a Bomem MB-100 infrared spectrometer. Absorption positions are given in cm^{-1}. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Reaction progress was followed (where practical) by thin-layer chromatography (TLC) using Merck pre-coated silica gel 60 F_{254} sheets. Developed plates were viewed under ultraviolet light and/or by staining with a 4% solution of phosphomolybdic acid in ethanol. Flash chromatography was carried out with silica gel 60 (35-75 µm) from EM Science. Tetrahydrofuran (THF) and methylene chloride were dried by distillation in the presence of sodium metal under a nitrogen atmosphere with benzophenone ketyl as indicator. Hexane was dried over calcium hydride in a similar manner.

1-t-Butoxy-3-butyne (3)[22]

To a 500 mL, 2-neck round bottom flask (RBF) was condensed isobutene (65 g) at −78°C. Methylene chloride (180 mL) and 3-butyn-1-ol (10.15 g, 0.145 mol) were added and the mixture was warmed to room temperature. Sulphuric acid (30 drops) was added and the flask was sealed. The solution was stirred at room temperature for 14 h. The flask was carefully vented. Sodium bicarbonate (500 mg) was added to the reaction mixture and the volatiles were removed under reduced pressure. The crude material was taken up in ether (50 mL), washed with $NaHCO_3$ (10% aq., 3 x 70 mL), and dried over Na_2SO_4. After solvent removal under reduced pressure and purification by distillation (130 °C, 1 atm) **3**

(14.4 g, 79%) was obtained as a colourless liquid. ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 9H), 1.93 (t, 1H, J = 2.7 Hz), 2.37 (td, 2H, J = 7.3, 2.7 Hz), 3.45 (t, 2H, J = 7.3 Hz). MS (EI): *m/z* 87 (38), 81 (41), 59 (50), 57 (100).

Z-1-butoxy-4-Iodo-3-butene (6Z)[9]

To a 500 mL, 2-neck round bottom flask (RBF) was added 1-*t*-butoxy-3-butyne (**3**) (560 mg, 4.44 mmol, 1 eq.) and hexane (4 mL). Diisobutylaluminum hydride (1 M in hexane, 5.33 mL, 5.33 mmol, 1.2 eq.) was added dropwise over 10 min with the temperature maintained at 22°C. The reaction was then warmed to 50°C for 4 h and cooled to room temperature and stirred for 14 h. Volatiles were removed *in vacuo*, maintaining an inert atmosphere throughout. The resulting material was cooled to 0°C and THF (4 mL) was added. After stirring for 5 min, the reaction mixture was cooled to –78°C. An iodine solution (1.354 g, 5.33 mmol, 1.2 eq. in 3 mL THF) was added dropwise over 15 min and the reaction was stirred for 2 h. The reaction was then warmed to 0°C and transferred to an ice-cold, stirred solution of HCl (6 M, 25 mL) and pentane (5 mL) by canula. The aqueous phase was separated and was extracted with pentane (2 x 15 mL). The combined organic phases were washed with NaOH (1 M, 40 mL), Na_2SO_3 (10% aq., 40 mL), and brine (40 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford a light yellow liquid (808 mg, 72%). Thin layer chromatography (TLC) indicated two isomers were present [R_f = 0.28 (minor) and 0.30 (major) in 5% ether / hexane]. Separation was not achieved by flash chromatography. GC-MS indicated the presence of 3 components (min): 6.52 (**6Z**, 70%), 6.60 (**6E**, 6%) and 6.76 (**7**, 24%).

E-1-t-Butoxy-4-iodo-3-butene (6E)

This compound was prepared according to a literature method[11] using **3** as the substrate. ^{1}H-NMR ($CDCl_3$): δ 1.18 (s, 9H), 2.26 (q, 2H, J = 6.9 Hz), 3.38 (t, 2H, J = 6.8 Hz), 6.84 (d, 1H, J = 14.8 Hz), 6.53 (dt, 1H, J = 14.8, 7.0 Hz); MS (EI): *m/z* 254 (M^+, 4), 181 (15), 87 (27), 57 (100).

E-4-Iodo-3-buten-1-ol (4E)

To a 100 mL, 2-neck round bottom flask (RBF) was added 3-butyn-1-ol (**2**) (1.093 g, 15.6 mmol, 1 eq.) and hexane (2 mL). The mixture was cooled to –25 °C for 10 min and diisobutylaluminum hydride (1 M in hexane, 31.2 mL, 31.2 mmol, 2 eq.) was added dropwise over 40 min with the temperature maintained below -20°C. The reaction was stirred for 0.5 h at -20 °C then at room temperature for 14 h. Volatiles were removed *in vacuo*, maintaining an inert atmosphere throughout. The resulting material was cooled to 0 °C and THF (20 mL) was added. After stirring for 5 min, the reaction mixture was cooled to –78 °C. An iodine solution (4.77 g, 18.8 mmol, 1.2 eq. in 25 mL of THF) was added dropwise over 30 min and the reaction was stirred for 1 h. The reaction was then warmed to 0°C and transferred to an ice-cold, stirred solution of HCl (6 M, 20 mL) and ether (10 mL) by canula. Sodium hydroxide (1 M) was added until pH ~ 4. Sodium chloride was added until the solution was saturated and the aqueous phase was continuously extracted with ether for 15 h. The solvent was removed under reduced pressure resulting in a light yellow oil (2.721 g, 88%). ^{1}H NMR spectra indicated the presence of **4E** and 4-iodo-1-butanol (**5**) and agrees well with the literature[10] data; (**4E**) ($CDCl_3$): δ 2.11 (s, 1H, exch D_2O), 2.28 (dq, 2H, J = 1.1, 7.4 Hz), 3.63 (t, 2H, J = 7.4 Hz), 6.11 (dt, 1H, J = 14.4, 1.1 Hz), 6.50 (dt, 1H, J = 14.4, 7.4 Hz). The mixture was used in the next step without further purification. The product distribution was determined by GC-MS of the derived (excess isobutene, cat. H_2SO_4, CH_2Cl_2) *t*-butyl ethers; retention times were 6.52 (**6Z**, 6%), 6.60 (**6E**, 76%), and 6.76 (**7**, 18%) min. Thus the ratio of alcohols formed was **4Z** : **4E** : **5** = 6 : 76 : 18.

E-Dodec-3-en-5-yn-1-ol (8)

The procedure of Rossi and Carpita was used.[7] Thus a solution of NaOH (1 M, 56 mL) was degassed by bubbling N_2 through it for 30 min. In a separate flask with degassed benzene (13 mL) was added benzyltriethylammonium chloride (53 mg, 0.23 mmol), copper (I) iodide (76 mg, 0.40 mmol), *tetrakis*(triphenylphosphine)palladium (227 mg, 0.2 mmol), *trans*-4-iodo-3-buten-1-ol (**4E**) (3.90 g, 9.8 mmol, mixed with **4Z** and **5**), and 1-octyne (1.09 g, 9.9 mmol, 1 eq.). The degassed NaOH solution was added dropwise over 40 min and the reaction was stirred for 2 h. Water (20 mL) and saturated ammonium chloride (40 mL) were added. The reaction was extracted with hexane (2 x 40 mL) and ether (40 mL). The combined organic extractions were washed with saturated ammonium chloride (3 x 40 mL), water (2 x 40 mL) and brine (40 mL) and dried over Na_2SO_4. Solvent was removed under reduced pressure. Flash chromatography (R_f = 0.17 in 50% ether / hexane) provided **8** as a yellow oil (1.37 g, 76%). ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H, J = 6.6 Hz), 1.08 (m, 8H), 2.01 (s, 1H, exch D_2O), 2.21 – 2.42 (m, 4H), 3.66 (t, 2H, J = 6.2 Hz), 5.57 (d, 1H, J = 15.7 Hz), 6.02 (dt, 1H, J = 15.7, 7.3 Hz); ^{13}C NMR ($CDCl_3$): δ 13.9, 19.3, 22.4, 28.5, 28.6, 31.3, 36.2, 61.5, 78.8, 89.6, 112.8, 138.5; MS (EI): *m/z* 180 (M^+, 12), 107 (29), 93 (60), 91 (68), 79 (100), 77 (70), 67 (58); IR (neat): 3354, 2929, 2858, 2216, 1040, 955 cm^{-1}. Anal. calcd for $C_{12}H_{20}O$: C 79.94, H 11.18; Found: C 80.06, H 10.99.

E-Dodec-3-en-5-ynyl Acetate (9)

To a 25 mL, 1-neck RBF was added alcohol **8** (0.112 g, 0.64 mmol), acetic anhydride (91 μL, 0.96 mmol), pyridine (155 μL, 1.92 mmol) and 4-dimethylaminopyridine (cat.) which were stirred for 3 h at room temperature. The reaction was diluted with ether (20 mL) and washed with HCl (1 M, 2 x 20 mL), water (20 mL) and brine (20 mL) and dried over Na_2SO_4. Solvent was removed under reduced pressure yielding a colourless oil, **9** (129 mg, 91%). ^1H NMR ($CDCl_3$): δ 0.77 (t, 3H, J = 6.8 Hz), 1.07 - 1.45 (m, 8H), 1.91 (s, 3H), (dt, 2H, J = 1.8 Hz, J = 6.9 Hz), 2.28 (q, 2H, J = 6.6 Hz), 3.96 (t, 2H, J = 6.6 Hz), 5.42 (d, 1H, J = 15.7 Hz), 5.86 (dt, 1H, J = 15.7 Hz); ^{13}C NMR ($CDCl_3$): δ = 13.9, 19.2, 20.7, 22.4, 28.5, 28.7, 31.2, 32.1, 63.1, 78.6, 89.8, 112.7, 137.4, 170.7; MS (EI): *m/z* 207 (M^+ - CH_3), 162 (25), 105 (64), 92 (45), 91 (100), 79 (30). IR (neat): 2932, 2218, 1742, 1237, 1039, 957 cm^{-1}. This compound (unlike the parent alcohol **8**) decomposed on storage and thus was used immediately in the next step.

3E,5Z-Dodecadienyl Acetate (1)

To a solution of *trans*-dodec-3-en-5-ynyl acetate (**9**) (200.4 mg, 0.90 mmol, 1.0 eq.) in THF (10 mL) at –10°C was added a freshly prepared solution of disiamylborane [2-methyl-2-butene (0.56 mL, 5.29 mmol), THF (40 mL), BH_3•THF (1.0 M in THF, 4.4 mL, 4.4 mmol), 0 °C, 30 min] over 30 min. The reaction was stirred for 20 min at –10°C then warmed to 0°C for 4 h. Acetic acid (1.17 mL) was added and the reaction was heated to 60°C for 6 h and then cooled to room temperature and stirred for an additional 12 h. The reaction was quenched by the addition of NaOH (6 M, 4.7 mL) at 0°C, followed by dropwise addition of hydrogen peroxide (30% aq., 1 mL) and warming to 40°C for 40 min. The reaction was cooled to room temperature and diluted with ether (20 mL) and water (40 mL). The phases were separated and the aqueous phase was extracted with ether (3 x 20 mL). The combined organic extractions were washed with brine (2 x 40 mL) and dried over Na_2SO_4. The solvent was removed by reduced pressure. After purification by flash chromatography (R_f = 0.27 in 10:1 hexane:ether), **1** was obtained as a colourless oil (168 mg, 84%). ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H, J = 6.6 Hz), 1.22 - 1.44 (m, 8H), 2.07 (s, 3H), 2.16 (q, 2H, J = 6.9 Hz), 2.43 (q, 2H, J = 7.0 Hz), 4.11 (t, 2H, J = 6.9 Hz), 5.37 (dt, 1H, J = 11.0 ,7.3 Hz), 5.60 (dt, 1H, J = 15.0, 7.0 Hz), 5.95 (dd, 1H, J = 11, 11 Hz), 6.39 (ddd, 1H, J = 15.2, 11.0, 1.3 Hz); ^{13}C NMR ($CDCl_3$): δ 14.1, 20.9, 22.6, 28.9, 29.6, 31.6, 31.7, 32.1, 63.8, 128.0, 128.2, 128.6, 131.5, 171.0. Of note is the close agreement between the ^{13}C chemical shifts for the alkene carbons and the literature[2] data for **1**: δ 128.1, 128.2, 128.6, 131.6.

Acknowledgements

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