

## AN IMPROVED STEREOSPECIFIC SYNTHESIS OF (Z,E)-9,11-TETRADECADIENAL. SEX PHEROMONE COMPONENT OF *STENOMA CECROPIA*

JORGE A. CABEZAS\* AND ALLAN C. OEHLISCHLAGER\*\*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada, V5A 1S6

\* Present Address: Escuela de Química, Universidad de Costa Rica, San José, 2060, Costa Rica.

\*\* Present Address: Chem Tica Internacional S. A. Apdo. 159-2150, San José, Costa Rica.

**ABSTRACT:** (Z,E)-9,11-Tetradecadienal, a sex pheromone component of *Stenoma cecropia*, has been synthesized in 7 steps and 61% overall yield. The synthesis utilized a palladium catalyzed coupling between 9-decynyl *tert*-butyldimethylsilyl ether and *trans*-1-iodo-1-butene, followed by reduction of triple bond of enyne with disiamylborane. Deprotection of silyl ether and oxidation afforded the desired aldehyde.

Compounds containing stereodefined conjugated polyenes occur widely in nature and several exhibit biological activity. *Stenoma cecropia* is a defoliator of oil palm that causes serious economic damage in South America. Female pheromone glands of this insect contain (Z,E) 9,11-tetradecadien-1-yl acetate and the corresponding aldehyde which have been shown to be two of the main pheromone components.<sup>1</sup> The former compound has also been identified as a component of the sex pheromone of the Egyptian cotton leafworm *Spodoptera littoralis*.<sup>2</sup>

Ramiandrasoa and Tellier reported a 6 step (25% overall yield) synthesis of this dienic acetate.<sup>3</sup> In this approach, the diene system was built by the palladium catalyzed coupling of an iodoalkene with an alkenylzinc. The major drawbacks of this synthetic approach are the preparation of the vinyl iodide *cis*-10-iodo-9-decenyl *tert*-butyl ether, which was prepared in 50% yield from a carbocupration reaction between acetylene and the corresponding cuprate (formed from 8-lithium octyl *tert*-butyl ether and copper iodide) followed by quenching with iodine. The *tert*-butyl ether of

the latter vinyl iodide was converted into an acetate, and reacted with (E)-1-butene zinc bromide under palladium (0) catalysis to afford the coupled product in a crude yield of 70%.

We report herein a more efficient synthetic strategy which gave the desired aldehyde in 61% overall yield from 1-nonyne in 7 steps.

### RESULTS AND DISCUSSION

Our synthetic approach consisted of a palladium catalyzed coupling of 9-decynyl *tert*-butyldimethylsilyl ether, **4**, and *trans*-1-iodo-1-butene **6**, to give the corresponding enyne whose double bond geometry is maintained. The triple bond of enyne **7** was regio- and stereospecifically reduced with disiamylborane to afford the corresponding diene.

The sequence utilized 2-decyn-1-ol (**2**), which was obtained in quantitative yield (97% isolated yield) by low temperature reaction of 1-nonyne **1**, with *n*-BuLi and paraformaldehyde. Alcohol **2** was isomerized in 97% to **3** by a zipper reaction using potassium



3-aminopropyl-amide (KAPA) in 1,3-diaminopropane (APA).<sup>4</sup> The alcohol of **3** was protected (95%) as a *tert*-butyl dimethyl silyl ether. This protecting group was very stable under subsequent conditions used to build the diene and was easily removed under non acidic conditions without diene isomerization.

Stereochemistry of the C<sub>11</sub>-C<sub>12</sub> double bond was achieved by palladium catalyzed coupling of acetylene **4** and *trans*-iodo alkene **6**. The latter was stereospecifically obtained by *cis*-hydroalumination<sup>5</sup> of 1-butyne with diisobutylaluminum hydride (DIBAL-H), followed by reaction of the intermediate vinyl alane with iodine (Figure 1).

Palladium catalyzed cross-coupling of *trans*-1-iodo-1-butene **6** with acetylenic silyl ether **4** (but not with the butenylzinc bromide as used in Tellier's strategy) was performed according to the procedure of Ratovelomana and Linstrumelle,<sup>6</sup> using diethylamine instead of *n*-propylamine. Analysis of the cross-coupled product revealed quantitative transformation of **4** into **7**, which was separated from catalyst and triphenylphosphine oxide by filtration of the cold pentane solution (92% isolated yield).

The triple bond of enyne **7** was regio- and stereospecifically reduced by hydroboration of the alkyne followed by protonolysis of the intermediate vinylborane with acetic acid. Diene **8** was obtained in 95% yield from **7** without alkene isomerization. Silyl ether **8** was treated with Bu<sub>4</sub>NF in THF at 0 °C, to remove the protecting group again without alkene isomerization. Silyl impurities present in the crude reaction mixture were removed by Kugelrohr distillation and the residue was purified by filtration through a small pad of silica gel. The alcohol thus obtained was oxidized using PDC to give aldehyde **9** (78% yield from **8**). <sup>1</sup>H-NMR and G.C. analysis revealed aldehyde **9** was produced in high stereoisomeric purity.

This route allowed stereospecific generation of dienic aldehyde **9** in 61% yield from 1-nonyne. Formation of the enyne system via palladium cross coupling of *trans*-1-iodo-1-butene with the corresponding acetylene proved to be an improved strategy for formation of the enyne system. For this reaction, use of the terminal acetylene (CuI, Et<sub>2</sub>NH) rather than the corresponding alkenylzinc halide<sup>3</sup>, clearly seems to be the method of choice to achieve high coupling yields. The use of disiamylborane to stereospecifically reduce

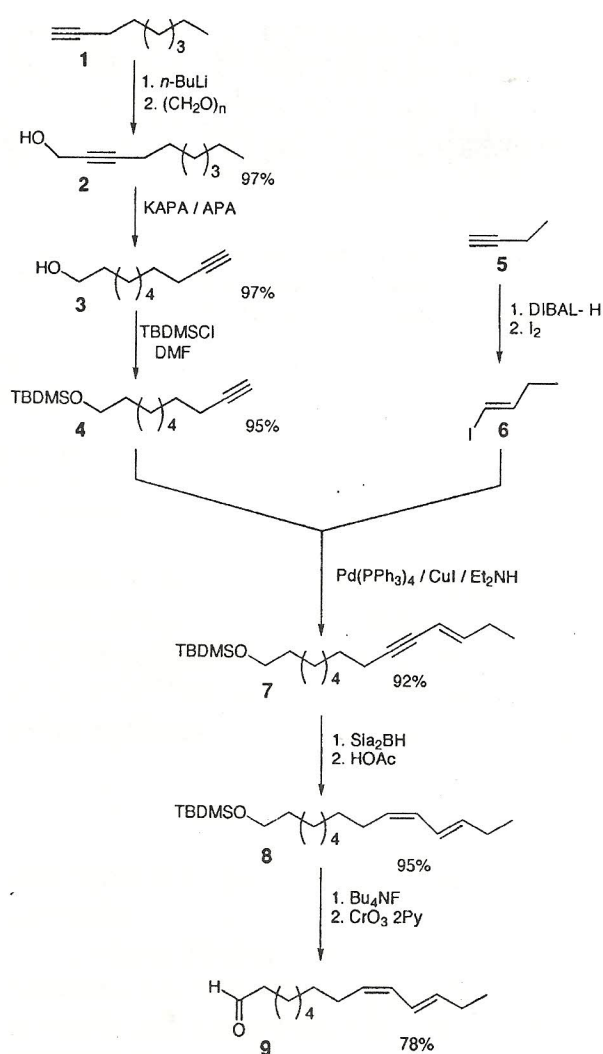


Figure 1

the triple bond of enyne **7** proved to be highly effective and the diene was cleanly obtained.

## EXPERIMENTAL SECTION

Glassware and syringes were dried in an oven overnight at 140 °C and flushed with argon immediately prior to use. Transfers of liquids were performed with syringes equipped with stainless-steel needles. CrO<sub>3</sub>, KH, TBDMSCl, CuI and Pd(PPh<sub>3</sub>)<sub>4</sub> were weighed in a glove bag under nitrogen. Reactions were carried out under positive pressure of argon. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker AMX-400 spectrometer, operating at 400.13 MHz and 100.62 MHz respectively. Gas chromatographic analyses were conducted on a Hewlett-Packard 5892 instrument equipped with a flame ionization detector.

Alcohol **3** was transformed to silyl ether **4** according to the procedure of Corey and Venkateswarlu.<sup>7</sup>

All the products gave satisfactory <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopic properties.

#### ACKNOWLEDGMENTS

We wish to thank the Natural Sciences and Engineering Research Council of Canada for a Research Grant to A.C.O. and the University of Costa Rica for a stipend to J.A.C.

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