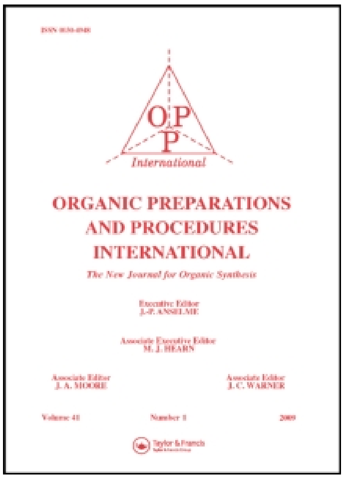

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A NEW ROUTE FOR THE SYNTHESIS OF Z-11-HEXADECEN-1-OL, A SEX PHEROMONE OF *CHILO INFUSCATELLUS* (SNELL)

S. Narasimhan[a]; K. Ganeshwarprasad[a]
[a] Centre for Agrochemical Research, SPIC Science Foundation, Madras, India

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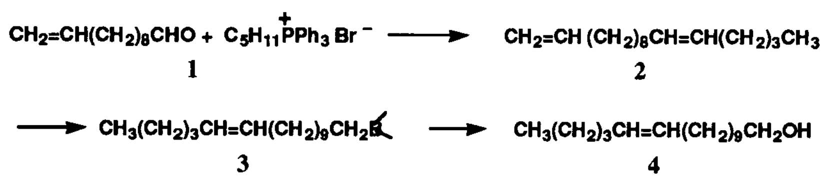
A NEW ROUTE FOR THE SYNTHESIS OF Z-11-HEXADECEN-1-OL, A SEX PHEROMONE OF *CHILO INFUSCATELLUS* (SNELL)

Submitted by S. Narasimhan* and K. Ganeshwarprasad
(06/17/92)

Centre for Agrochemical Research, SPIC Science Foundation
110, Mount Road, Madras - 600 032, INDIA

Chilo infuscatellus Snell (Crambidae; Lepidoptera), the early shoot borer of sugar cane, affects the shoots during germination stages prior to internode formation resulting in the drying up of the entire clump and hence decrease in yield and quality.[1] There have been a few reports on the utility of pheromone technology to control this insect.[2,3] However, the composition of the pheromone components recommended varied from a mixture of Z-11- hexadecen-1-ol and Z-11-hexadecenal to Z-11-hexadecen-1-ol alone as an attractant. These reports could lead to the use of varying compositions in the lures which would be less effective and inferior to the virgin females. In order to establish the effective composition, pure components were needed. We report here a new route for the synthesis of Z-11-hexadecen-1-ol in high purity(>98%):



(Z-11)-1,11-Hexadecadiene (**2**) was obtained from the Wittig reaction of 10-undecenal with *n*-pentyltriphenylphosphonium bromide. Selective hydroboration of the terminal double bond was achieved by a new hydroborating procedure, the *ester-induced* hydroboration by $Ca(BH_4)_2$.[4] This method offers a simple work-up procedure and uncontaminated product.

EXPERIMENTAL SECTION

Reactions were performed in all glass apparatus, flame-dried and colored under nitrogen. Triphenylphosphine (Aldrich), *n*-pentyl bromide (Aldrich) and 10-undecenal (Perfumery grade, Bush-Boake and Allen) were used as received.. THF was purified by distaillation from LAH. Hexamethylphoramide was purified by distillation and stored over molecule seives (4Å). NMR spectra were recorded on a Joel 400 MHz instrument.

Preparation of (11-Z-)-1,11-Hexadecadiene (2).- A pre-dried flask equipped with a side-arm and a magnetic stirring bar was charged with *n*-pentyltriphenylphosphonium bromide (4.13 g, 10 mmol) and THF (10 mL). To the stirred suspension, sodamide (0.585 g, 15 mmol.) was added followed by HMPA (2.5 mL). The yellow-orange solution was stirred at room tempera- ture for 1 hr, then cooled in an ice-salt bath for 15 min. 10-Undecenal (2.28 mL, 11 mmol) was added over a period of five minutes. The reaction mixture was stirred for 1 hr at the ice bath tempe- rature and water was added whereupon a clear solution was obtained. The solvent was removed under reduced pressure and the residue was extracted with hexane(5 x 20 mL) . The organic layer was washed with saturated brine (2 x 10 mL), dried over anhyd. $NaSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2,12"x 2",hexane) to obtain 1.55 g (70%) of (11-Z-)1,11-hexadecadiene, bp 156°/1 torr., lit.[5] bp. 95°/0.01 torr. ^1H NMR ($CDCl_3$, 400MHz): δ 0.89 (t, 3H), 1.33 (m, 16 H), 2.03 (m, 6H), 4.92 (d, d, J = 10.25 Hz, 1H), 4.98 (d, d, J = 17.09 Hz, 1H), 5.34 (t, J = 5.88 Hz, 2H), 5.80 (d, d, t, J = 17.09, 10.25, 6.84 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.02 (q, 1C), 22.39 (t, 1C), 26.96 (t, 1C, 27.23 (t, 1C), 29.0 to 32.03 (t, 7C) 33.88 (t, 1C), 114.13 (t, 1C), 129.89 (d, 2C), 139.21 (d, 1C).

Preparation of Z-11-Hexadecen-1-ol (4).- A predried side-armed flask fitted with a septum, equipped with a magnetic stirring bar was charged with **2** (1.38 mL, 5 mmol) and $Ca(BH_4)_2$ (5.25 mL of 0.375 M solution in THF,15.75 mmol of H^-). The reaction mixture was brought to reflux and ethyl acetate(0.49 mL, 5 mmol) was added dropwise (1 min.). After refluxing for 6 hrs the reaction mixture was cooled to room temperature, quenched with methanol and made alkaline by dropwise addition of 3 M NaOH (3 mL) and H_2O_2(1.1 mL of 30% solution). The solution was stirred for 1 hr, aqueous layer was saturated with anhyd. K_2CO_3 and the product was extracted with THF. The solvent was removed under reduced pressure to yield 0.71 g (64%) of **4** (bp. 160-162°/0.5 torr., lit.[5] bp 140°/0.15 torr.[5]

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.9 (t, 3H), 1.25- 1.35 (m, 18H), 1.55 (q, 2H), 2.05 (m, 4H), 3.65 (t, *J* = 6.64 Hz, 3H, CH_2O, OH), 5.35 (t, *J* = 4.89, 2H).

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SYNTHESIS OF C-24 THIAZOLIDINONE AND OXAZOLIDINONE DERIVATIVES OF BILE ACIDS

Submitted by
(06/22/92)

A. U. Siddiqui*†, A. H. Siddiqui and T. Sundara Ramaiah

Department of Chemistry, Nizam College,
Osmania University, Hyderabad-500001, INDIA

The chemistry[1] and wide spectrum of pharmacolgical activities of thiazolidinone[2] and oxazolidinone[3] derivatives have been cited in the literature. This paper describes the synthesis of C-24 thiazolidinone and oxazolidinone derivatives of bile acids, lithocholic acid (**1a**) and deoxycholic acid (**1b**). The present work was stimulated by reports that C-24 derivatives of bile acids possess useful biological activities.[4]

The methyl ester of bile acids, methyl-3α-hydroxy-5β-cholan-24-oate (**1c**) and methyl-3α,12α-dihydroxy-5β-cholan-24-oate (**1d**) on reaction with hydrazine afforded acid hydrazides **2a** and **2b**. The ^{1}H NMR spectra of **2a** and of **2b** exhibited broad singlets at δ 5.9 and δ 8.1, exchangeable with deuterium for NH_2 and CO<u>NH</u> protons , and IR spectra showed absorptions at 3250, 3100 (NH_2, NH) and 1660 cm^{-1} (CONH). Reaction of **2a** and **2b** with phenyl isocyanate[5] afforded 24-N-