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SYNTHESIS OF HEXADEC-9Z-ENAL – ONE OF THE COMPONENTS OF THE SEX PHEROMONE OF Heliothis armigera

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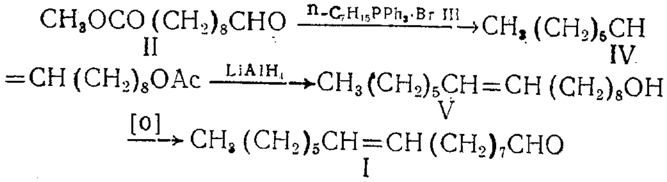
Hexadec-9Z-enal – a component of the sex pheromone of the cotton bollworm Heliothis armigera – has been obtained by a three-stage synthesis from 9-acetoxynonanal and n-heptyltriphenylphosphonium bromide followed by reduction and oxidation.

Hexadec-9Z-enal (I) is one of the components of the pheromone of the cotton bollworm – the principal pest of the cotton plant [1]. The traditional methods for synthesizing the aldehyde (I) are based on the alkylation of lithium octynylide with 2-(8-chlorooctyloxy)- or 2-(8-bromooctyloxy)tetrahydropyran, followed by hydrolysis and then the hydrogenation of the resulting hexadec-9-yn-ol to hexadec-9Z-en-1-ol and the conversion of the latter into (I) [2].

We have carried out a three-stage synthesis of the aldehyde (I) that permits the performance of the successive reactions in one flask, including the condensation of 9-acetoxynonanal (II) with n-heptyltriphenylphosphonium bromide (III) under the conditions given in [3].



$$\underset{\text{II}}{CH_3OCO(CH_2)_8CHO} \xrightarrow{n\text{-}C_7H_{15}PPh_3\cdot Br\ \text{III}} \underset{\text{IV}}{CH_3(CH_2)_5CH}$$
$$=CH(CH_2)_8OAc \xrightarrow{LiAlH_4} \underset{\text{V}}{CH_3(CH_2)_5CH=CH(CH_2)_8OH}$$
$$\xrightarrow{[0]} \underset{\text{I}}{CH_3(CH_2)_5CH=CH(CH_2)_7CHO}$$

The initial 9-acetoxynonanal (II) was obtained by the oxidation of 9-acetoxynonan-1-ol with pyridinium chlorochromate in methylene chloride [4]. The reaction of aldehyde (II) with the phosphonium salt (III) gave hexadec-9Z-enyl acetate (IV), which was reduced with lithium tetrahydroaluminate to hexadec-9Z-en-1-ol (V). Oxidation of the latter with pyridinium chlorochromate gave hexadec-9Z-enal (I).

The isomeric purity of the aldehyde (I), determined by gas-liquid chromatography (GLC), was not less than 97%.

EXPERIMENTAL

IR spectra were taken on a Specord 75 spectrometer in CCl_4. The PMR spectra of the substances under investigation in CCl_4 were obtained relative to HMDS on a Varian MAT 311 in-

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strument. GLC analysis was conducted on a Chrom-5 instrument with the stationary phase E301 (10%) on Chromaton N-AW-HMDS at a temperature of the 3 × 3500 mm glass column of 160°C, the carrier gas being helium.

Hexadec-9Z-en-1-yl Acetate (IV). In an atmosphere of nitrogen, a solution of 3.2 g (0.018 mole) of sodium bis(trimethylsilyl)amide in 10 ml of tetrahydrofuran (THF) was added to a stirred suspension of 7.4 g (0.017 mole) of the phosphonium salt (III) in 20 ml of THF. The mixture was kept at 50-55°C for 60 min and was then cooled to −78°C, a solution of 1.7 g (0.0085 mole) of the acetate (II) in 6 ml of THF was added, and the mixture was stirred at this temperature for 30 min and then at 20°C for 12 h. The solvent was evaporated off, the residue was extracted with hexane–ether (4:1) (6 × 30 ml), the extract was evaporated, and the residue was distilled. This gave 1.6 g (61%) of the acetate (IV), bp 111-113°C (3 mm), n_D^{22} 1.4402. PMR spectrum: 0.85 (3H, t, CH_3), 1.10 (6H, t, CH_3), 1.25 (6H, br. s, CH_2), 2.00 (4H, m, $CH_2C{=}CCH_2$), 3.45 (4H, m, $-OCH_2$), 4.30 (1H, t, $-OCHO-$), 5.30 (2H, m, $CH{=}CH$). IR spectrum, cm^{-1}: 1100 s, 1120 s, 3010 w.

Hexadec-9Z-en-1-ol (V). A solution of 1.6 g (0.0057 mole) of the acetate (IV) in 10 ml of absolute ether was added dropwise to a suspension of 0.065 g (0.0017 mole) of lithium tetrahydroaluminate in 40 ml of absolute ether. The mixture was stirred at 20°C for 5 h and was decomposed by the addition of ethyl acetate and then of water. The ethereal layer was separated off, dried over sodium sulfate, filtered, and evaporated, and the residue was distilled. This gave 1.4 g (82%) of the alcohol (V), bp 130-133°C (2 mm), n_D^{20} 1.4595. Its IR and PMR spectra were identical with those described in the literature [2].

Hexadec-Z-enal (I). A solution of 1.4 g (0.0057 mole) of the alcohol (V) was treated with 0.46 g (0.006 mole) of pyridinium chlorochromate in 10 ml of methylene chloride. The mixture was stirred at 20°C for 40 min. The organic layer was separated off and it was washed with 10% hydrochloric acid and with water, dried over sodium sulfate, and evaporated, and the residue was distilled. The yield was 0.42 g (67%), bp 110-113°C (2 mm), n_D^{20} 1.4503.

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