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INSECT PHEROMONES AND THEIR ANALOGS

LV. SYNTHESIS OF TRIDECA-4E,7Z-DIEN-1-YL ACETATE — COMPONENT OF THE SEX PHEROMONE OF *Phthorimaea opercucella*

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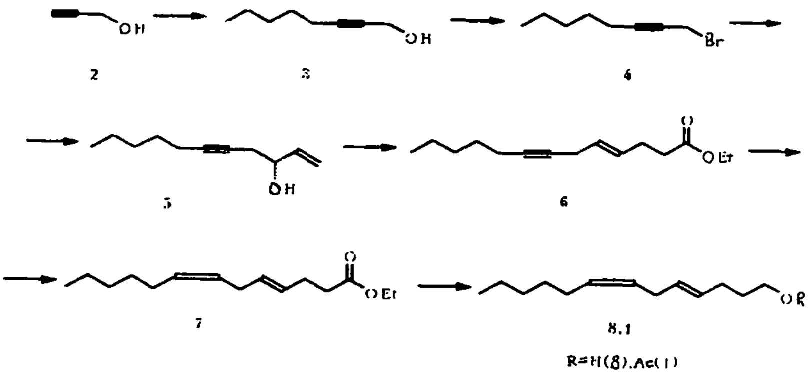
542.91+547.473+632.936.2

Starting from propargyl alcohol and using the thermal Claisen rearrangement at the stage of constructing the (E)- double bond, we have synthesized trideca-4E,7Z-dien-1-yl acetate — a component of the sex pheromone of the potato moth Phthorimaea opercucella *(Zeller).*

Trideca-4E,7Z-dien-1-yl acetate (**1**) has been identified as a component of the sex pheromone of the potato moth *Phthorimea opercucella* (Zeller) — a pest of potatoes [1]. A number of syntheses of compound (**1**) have been described [2-11] of which the most attractive are syntheses based on the construction of the (E)- double bond with the aid of the Claisen rearrangement [8-11]. In these cases the substance involved in the rearrangement is the secondary enynic alcohol (**5**) [8, 9] or the product of the *cis*-hydrogenation of its acetylenic fragment [10, 11], obtained from propargyl bromide.

In the scheme for the synthesis of pheromone (**1**) that we are proposing, in place of propargyl bromide as the initial compound we have used the more accessible propargyl alcohol (**2**); this, in liquid ammonia in the presence of lithium amide or in a mixture of tetrahydrofuran and HMPT under the action of butyllithium, was converted into its dianion, which reacted with bromopentane at the carbanionic center to form oct-2-yn-1-ol (**3**). The bromination of the latter and the condensation of the resulting 1-bromooct-2-yne (**4**), in the form of the magnesium derivative, with acrolein led to the key synthon undec-1-en-5-yn-3-ol (**5**). A Claisen rearrangement conducted with compound (**5**) in the presence of triethyl orthoacetate under conditions given in the literature [9, 12] led with a yield of about 70% to ethyl tridec-4E-en-7-ynoate (**6**). GLC analysis in a capillary column showed that compound (**6**) was a single geometric isomer, while the presence of intense absorption at 965 cm^{-1} (*trans*- double bond) and the absence of absorption in the 700-740 cm^{-1} region (*cis*- double bond) of its IR spectrum confirmed the assignment of (**6**) to the (E)- series. Selective *cis*-hydrogenation of the triple bond in the enynic ester (**6**) over an Ni-2P catalyst in the presence of ethylenediamine took place stereospecifically, leading to a 90% yield of ethyl trideca-4E,7Z-dienoate (**7**). The concluding stages — the hydride reduction of the ester (**7**) and acetylation of the resulting trideca-4E,7Z-dien-1-ol (**8**) — led smoothly to the desired compound (**1**).



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EXPERIMENTAL

IR spectra were taken on a Microlab 620 MX spectrometer (in a film). PMR spectra were recorded on a Tesla BS-587A instrument (working frequency 80 MHz), solvent $(CD_3)_2CO$. Chemical shifts are given on the δ-scale, with HMDS as internal standard. GLC analysis was conducted on a Chrom-5 instrument with the stationary phase silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm), working temperature 50-300°C, carrier gas helium. Compounds (**1**), (**6**), and (**8**) were analyzed on a Carlo Erba instrument with a glass capillary column 0.2 mm × 20 m, working temperature 50-200°C. TLC was conducted on Silufol plates with a fixed layer of SiO_2. The elementary analyses of the compounds synthesized agreed with the calculated values.

Oct-2-yn-1-ol (3). A. With stirring, 0.1 g of $FeCl_3$ and then, over 30-40 min, 1.4 g (0.2 g-atom) of lithium were added to 150 ml of liquid NH_3. After the disappearance of the blue color of the solution, 5.6 g (0.1 mmole) of the alcohol (**2**) was added in drops. The mixture was stirred for 1 h, after which 13.6 g (0.09 mmole) of bromopentane in 70 ml of absolute diethyl ether was added dropwise, and it was stirred for three hours and was left overnight. Then 50 ml of water was added, the ethereal layer was separated off, and the aqueous layer was extracted with ether (3 × 30 ml). The combined ethereal layers were washed with water, dried with Na_2SO_4, and evaporated. The residue was distilled in vacuum, giving 5.90 g (51%) of the alcohol (**3**), bp 105-107°C (12 mm Hg), n^{20} 1.4632. IR spectrum (ν, cm^{-1}): 3350 (OH), 2230 (C≡C), 1120, 1080, 1060, 1040 (C–O). The PMR spectrum was identical with that given in the literature [13].

B. With stirring (Ar, 4-6°C), 134 ml (0.11 mole) of a solution of BuLi in hexane (0.82 M) was added dropwise to a solution of 2.8 g (0.05 mole) of the alcohol (**2**) in 60 ml of abs. THF and 10 ml of abs. HMPT, the mixture was stirred for 1 h, and then a solution of 7.55 g (0.05 mole) of bromopentane in 20 ml of abs. HMPT was added dropwise. After the reaction mixture had been brought to room temperature, it was stirred for another 4 h and was left overnight. Then 50 ml of a 25% solution of NH_4Cl was added, the organic layer was separated off, and the aqueous layer was extracted with hexane (3 × 30 ml). The combined organic layers were washed with saturated NaCl solution, dried with Na_2SO_4, and evaporated. The residue was chromatographed (SiO_2; pentane, and then pentane–ether (1:1)). This gave 4.0 g (64%) of the alcohol (**3**), identical with that obtained in the preceding experiment.

1-Bromooct-2-yne (4). At −10 to −15°C, 11.6 g (40.4 mmole) of PBr_3 in 20 ml of abs. diethyl ether was added dropwise over 0.5 h to a mixture of 4.46 g (36.8 mmole) of the alcohol (**3**) and 1.6 g of pyridine in 50 ml of abs. diethyl ether. The mixture was kept at −15°C for 2 h and was stirred for another 3 h at room temperature and for 45 min at 30°C, after which it was treated with cooled water (3 × 50 ml). The organic layer was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $CaCl_2$, and evaporated. The residue was distilled under vacuum, giving 5.36 g (77%) of the bromide (**4**), bp 87°C (16 mm Hg), n_D^{20} 1.4805. Its IR spectrum was identical with that given in [13].

Undec-1-en-5-yn-3-ol (5). After the dropwise addition (Ar, −15°C, 0.5 h) of 0.78 g (15 mmole) of acrolein in 10 ml of abs. diethyl ether to a solution of the Grignard reagent obtained from 2.82 g (15 mmole) of the bromide (**4**) and 0.32 g (15 mg-atom) of magnesium turnings in 30 ml of abs. diethyl ether, the mixture was warmed to 0°C over 0.5 h, and 20 ml of ice-cooled water was added. The ethereal layer was separated off and the aqueous layer was extracted with ether (3 × 20 ml). The combined ethereal layers were washed with saturated NaCl solution, dried with Na_2SO_4, and evaporated. The residue was chromatographed on silica gel (pentane, then pentane–ether (1:1)), giving 1.69 g (68%) of the enynic alcohol (**5**), n_D^{20} 1.4365. IR spectrum (ν, cm^{-1}): 3350 (OH), 2220 (C≡C), 1645, 995, 930 ($CH=CH_2$). Its PMR spectrum was identical with that given in [9].

Ethyl Tridec-4E-en-7-ynoate (6). A mixture of 1.40 g (8.4 mmole) of the alcohol (**5**), 8.05 g (42 mmole) of triethyl orthoacetate, and 0.7 g of propionic acid was heated at 136-139°C for 2 h, with the elimination by distillation of the ethanol liberated. After cooling to room temperature, the reaction mixture was diluted with diethyl ether (30 ml) and was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with Na_2SO_4, and evaporated, the orthoester being distilled off under vacuum. The residue was chromatographed (SiO_2; pentane–ether (8:2)), giving 1.34 g (68%) of the ester (**6**), n_D^{20} 1.4245. IR spectrum (ν, cm^{-1}): 2220 (C≡C), 1640, 965 (*trans*-HC=CH). Its PMR spectrum was similar to that given in [9].

Ethyl Trideca-4E,7Z-dienoate (7). A suspension of 0.93 g (24.6 mmole) of $NaBH_4$ and 1.2 ml (2.4 mmole) of a 2 N solution of NaOH in 24 ml of ethanol was stirred at room temperature for 15 min and was filtered. Then, over 10 min, 7.2 ml of the filtrate was added to a suspension of 1.44 g (5.7 mmole) of $Ni(OAr)_2 \cdot 4H_2O$ in 30 ml of ethanol being stirred in an atmosphere of H_2. The resulting mixture was treated with 1 ml (15.3 mmole) of ethylenediamine and, after 5 min, with a solution of 1.05 g (4.4 mmole) of compound (**6**) in 9 ml of ethanol. The reaction mixture was stirred at room temperature for 6 h, left overnight, and then diluted with saturated NaCl solution and extracted with diethyl ether (3 × 30 ml). The ethereal extract was washed with 10% HCl and then with water (to pH 7), dried with Na_2SO_4, and evaporated, giving 0.95 g (90%) of the ester (7). IR spectrum (ν,cm^{-1}): 1730 (C=O), 1640, 965 (E-CH=CH). Its PMR spectrum was identical with that given in [9].

Trideca-4E,7Z-dien-1-ol (8). A solution of 0.80 g (3.6 mmole) of the dienoate (7) in 10 ml of abs. diethyl ether was added to a suspension of 0.14 g (3.7 mmole) of $LiAlH_4$ in 5 ml of diethyl ether cooled in an ice bath, the mixture was stirred for 2 h, and then 0.5 ml of water was added, followed by 0.5 ml of 10% NaOH solution and another 1.5 ml of water. The ethereal layer was separated off, washed with NaCl solution, dried with Na_2SO_4, and evaporated, giving 0.63 g (89%) of the dienone (**8**), n_D^{20} 1.4670. IR spectrum (ν, cm^{-1}): 3350 (OH), 1635, 965 (E-CH=CH), 730 (Z-CH=CH). Its PMR spectrum was identical with that given in [6].

Trideca-4E,7Z-dien-1-yl Acetate (1). After the addition of 1 ml of pyridine and 1 ml of acetic anhydride to 0.52 g (2.025 mmole) of the alcohol (**8**), the mixture was stirred at room temperature for 12 h and was then evaporated; the residue was dissolved in 10 ml of diethyl ether, and the solution was washed successively with 10% HCl and saturated NaCl solution, dried with Na_2SO_4, and evaporated. The residue was chromatographed (SiO_2; pentane−ether (8:2)), giving 0.50 g (80%) of the acetate (**1**), n_D^{20} 1.4530. IR spectrum (ν, cm^{-1}): 1745 (C=0), 1635, 960 (E-CH=CH), 730 (Z-CH=CH). Its PMR spectrum was identical with that given in [6].

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