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INSECT PHEROMONES AND THEIR ANALOGS.
LI. PRACTICAL SYNTHESIS OF TRIDEC-4E-EN-1-YL ACETATE — A PHEROMONE OF *Keiferia lysopersicella*

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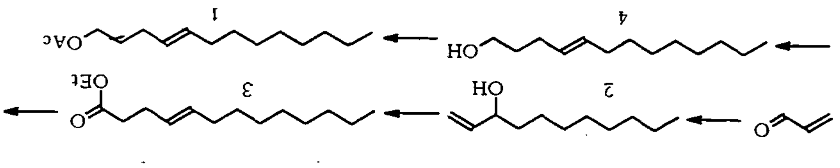
A short practical route to the synthesis of tridec-4E-en-1-yl acetate — the sex pheromone of the tomato pinworm Keiferia lysopersicella *— is proposed which is based on the thermal rearrangement of the readily available undec-1-en-3-ol with the participation of triethyl orthoacetate.*

Tridec-4-en-1-yl acetate (**1**) has been identified as the sex pheromone of the tomato pinworm *Keiferia lysopersicella* [1], and syntheses of it have been described in the literature in which the construction of double bond with the (E)-configuration was achieved via alkyne derivatives [2-4], by the olefination of a carbonyl compound [5, 6], or by opening a cyclopropane ring [7]. We have reported a synthesis of pheromone (**1**) with the use, at the stage of constructing a transoid double bond, of the Claisen rearrangement of the vinyl ether of undec-1-en-3-ol, leading to tridec-4E-enal [8].

In the present paper we present the shortest and most practical of the known methods of synthesizing pheromone (**1**) on the basis of a thermal rearrangement of the initial undec-1-en-3-ol (**2**), taking place smoothly with the participation of triethyl orthoacetate (the Claisen orthoester rearrangement [9]) and giving with good yield ethyl tridec-4-enoate (**3**), the stereochemical individuality of which has been confirmed by chromatographic analysis in a capillary column. The transoid configuration of the double bond formed follows unambiguously from the ^{13}C NMR spectrum of ester (**3**), in which a triplet in the 32.64 ppm region characteristic for the allyl carbon atoms of the H_2C^6 group serves as an evidential signal, while the corresponding signal for olefinic compounds with the (Z)-configuration is characteristically found in a substantially stronger field ($\Delta\delta$ = 4-4.5 ppm [10]).

The reduction of the ester (**3**) with lithium tetrahydroaluminate took place with a high yield of tridec-4E-en-1-ol (**4**), the stereochemical individuality and transoid configuration of which were again confirmed by the results of capillary GLC and the characteristics of its ^{13}C NMR spectrum. In the final stage of the synthesis, the acetylation of alcohol (**4**) gave the desired pheromone (**1**), the overall yield of which was 48.3%, calculated on the initial alcohol (**2**), which was obtained by the interaction of acrolein with *n*-octylmagnesium bromide.



EXPERIMENTAL

IR spectra were taken on a Microlab 620MX spectrometer (in a film), and ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 30 instrument (working frequencies 300 and 75 MHz), with $CDCl_3$ as solvent, chemical shifts being given in the δ scale relative to TMS in the regime of JMOD editing. GLC was conducted on a Chrom-5 instrument with, as the sta-

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tionary phase, SE-30 silicone liquid (5%) on Chromaton N−AW−DMCS (0.16-0.20 mm) at working temperatures of 50-300°C, the carrier gas being helium; compounds (**1**), (**3**) and (**4**) were additionally analyzed on a Carlo Erba instrument with a 0.2 mm × 25 m glass capillary column at working temperatures of 50-200°C. TLC was performed on Silufol plates with a fixed layer of SiO_2. The elementary analyses of the compounds synthesized corresponded to the calculated values.

Undec-1-en-3-ol (2). Dropwise, over 0.5 h, 5.6 g (0.1 mole) of acrolein in 20 ml of abs. Et_2O was added to the Grignard reagent obtained from 19.3 g (0.1 mole) of octyl bromide, 2.43 g (0.1 gram-atom) of magnesium turnings and 100 ml of abs. Et_2O. The mixture was heated to the boil, stirred at this temperature for 5 h, and left for 12 h at room temperature, after which 30 ml of saturated NH_4Cl solution was added, the organic layer was separated off, and the aqueous layer was extracted with diethyl ether (3 × 50 ml). The organic layer was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated, and the residue was distilled in vacuum. This gave 12.25 g (72%) of the alcohol (**2**), bp 126-128°C/20 mm, n_D^{20} 1.4435, cf. [8, 11]. The IR and PMR spectra were identical with those given in [8, 12].

Ethyl Tridec-4E-enoate (3). A mixture of 7.92 g (46.6 mmole) of the alcohol (**2**), 12.66 g (82.8 mmole) of triethyl orthoacetate, and 0.3 ml of acetic acid was stirred and heated in an oil bath at 110°C for 6 h, with the distillation of the ethanol liberated. Then the reaction mixture was distilled in vacuum, giving 7.9 g (71% of the ester **3**, bp 160-162°C (17 mm), n_D^{21} 1.4431. IR spectrum (ν_{max}, cm^{-1}): 975, 1670 (E−CH=CH), 1730 (C=O), see [13]. PMR spectrum (ppm): 0.88 (m, 6H, CH_3), 1.26 (m, 12H, CH_2), 1.96 (q, 2H, J = 6 Hz, H-3), 2.33 (m, 4H, H-2, H-6), 4.12 (1, 211; J = 7 Hz, OCH_2), 5.44 (m, 2H, H-4, H-5). ^{13}C NMR spectrum (δ, ppm): 178.27 (s, C-1), 131.89 (d, C-4), 127.96 (d, C-5), 60.25 (t, OCH_2), 34.46 (t, C-2), 32.64 (t, C-6), 32.00 (t, C-11), 29.60, 29.56, 29.43, 29.43, 29.26 (t, C-7, C-8, C-9, C-10), 28.05 (t, C-3), 22.79 (t, C-12), 14.30 (q, $OCH_2\underline{C}H_3$), 14.18 (q, C-13).

Tridec-4E-en-1-ol (4). Over 10 min, 7.9 g (32.9 mmole) of (**3**) in 20 ml of abs. Et_2O was added to a suspension of 1.25 g (32.9 mmole) of $LiAlH_4$ in 120 ml of abs. Et_2O at 0°C (Ar). The mixture was stirred at room temperature for 5 h and, after the addition of 30 ml of saturated NH_4Cl solution at 0°C, it was extracted with Et_2O (3 × 30 ml), and the extract was dried with Na_2SO_4 and evaporated. This gave 5.41 g (83%) of the alcohol (**4**), n_D^{21} 1.4562. IR spectrum (ν_{max}, cm^{-1}): 970, 1660 (E−CH=CH), 3350 (OH). PMR spectrum (δ, ppm): 0.88 (t, 3H, J = 6.5 Hz, H-13), 1.21 (br.s, 14H, CH_2), 1.61 (quint., 2H, J = 7 Hz, H-2), 1.97-2.06 (m, 4H, H-3, H-6), 2.72 (s, 1H, OH), 3.61 (t, 2H, J = 7 Hz, H-1), 5.42 (m, 2H, H-4, H-5) (see [4, 5]). ^{13}C NMR spectrum (δ, ppm): 131.18 (d, C-4), 129.41 (d, C-5), 62.26 (t, C-1), 32.67 (t, C-6), 32.47 (t, C-11), 31.99, 29.66, 29.58, 20.40, (t, C-7, C-8, C-9, C-10), 29.29 (t, C-3), 28.97 (t, C-2), 22.76 (t, C-12), 14.17 (q, C-13).

Tridec-4E-en-1-yl Acetate (1). A mixture of 4.82 g (24 mmole) of the alcohol (**4**), 48 ml of abs. pyridine, and 20.8 ml of Ac_2O was kept at room temperature for 24 h, and was then diluted with 100 ml of Et_2O, washed with 10% HCl and with saturated NaCl solution, and dried with $MgSO_4$. The residue after evaporation was chromatographed [SiO_2, hexane−diethyl ether (9:1)]. This gave 4.64 g (82%) of the acetate (**1**), n_D^{18} 1.4438. The ^{13}C NMR spectrum was analogous to that given in [8]. PMR spectrum (δ, ppm): 0.88 (t, 3H, J = 7 Hz, H-13), 1.26 (br.s, 14H, CH_2), 1.68 (quint., 2H, J = 7 Hz, H-2), 1.99 and 2.04 (m, 4H, H-3, H-6), 4.06 (t, 2H, J = 7 Hz, H-1), 5.41 (m, 2H, H-4, H-5).

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