

PHEROMONES OF INSECTS AND THEIR ANALOGS.

XXVIII. PRACTICAL SYNTHESIS OF TETRADECA-9Z,12E-DIEN-1-YL ACETATE - A COMPONENT OF THE SEX PHEROMONES OF INSECTS OF THE ORDER LEPIDOPTERA

V. N. Odinkov, U. M. Dzhemilev,
G. Yu. Ishumuratov, L. P. Botsman,
A. G. Ibragimov, I. M. Ladenkova,
T. A. Kargapol'teva, A. P. Zolotarev,
and G. A. Tolstikov

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Tetradeca-9Z,12E-dien-1-yl acetate, a sex pheromone of the Indian meal moth Plodia interpunctella has been synthesized from the readily available product of the hydrodimerization of butadiene - octa-1,7-diene.

Synthetic pathways via acetylene derivative [2-4] and syntheses based on the Wittig olefination reaction [5-7] and by the fragmentation of a substituted tetrahydropyridine [8] are known for tetradeca-9Z,12E-dien-1-yl acetate (I) - a component of the sex pheromones of many species of insects of the order Lepidoptera [1].

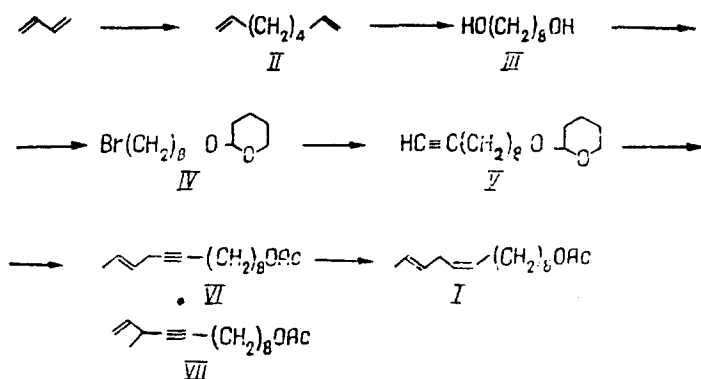
We have developed a convenient preparative synthesis of the pheromone (I) from octa-1,7-diene (II) - the readily available product of the hydrodimerization of butadiene [9]. The pioneering stage in the proposed synthesis consisted of the hydroalumination of the diene (II), which takes place under mild conditions at both double bonds under the action of diisobutylaluminum hydride (DIBAH) catalyzed by zirconium tetrachloride. The oxidation of the organoaluminum intermediate by oxygen followed by hydrolysis led to octane-1,8-diol (III), which was converted as in [10] into the tetrahydropyranyl ether (THPE) of 8-bromooctan-1-ol (IV). The two-stage coupling of the bromohydrin (IV), first with acetylene and then with crotyl bromide gave an enynic alcohol the acetylation of which led to the corresponding acetate (VI). The formation of the THPE of the alkynol (V) took place most smoothly in a mixture of liquid ammonia, DMSO, and THF. The condensation with crotyl bromide was carried out by first treating (V) with an equimolar amount of ethylmagnesium bromide and CuI. Subsequent acid treatment and acetylation gave a mixture (9:1 according to GLC) of the linear (VI) and branched (VII) enynic acetates. The latter was identified after its isolation from the mixture of (VI) and (VII) with the aid of GLC. The formation of this by-product was due to the occurrence of a S_N2' nucleophilic substitution in the crotyl bromide. Selective hydrogenation of the enynic acetate (VI) gave the desired pheromone (I). It must be mentioned that a high attractiveness* for males of the Indian meal moth is possessed by the product obtained by the hydrogenation of the mixture of (VI) and (VII) which contained, according to capillary GLC about 90% of compound (I). The overall yield of the pheromone (I) by the scheme developed amounted to 25%, calculated on the diene (II).

EXPERIMENTAL

IR spectra were taken on a UR-29 spectrometer (in film). PMR spectra were recorded on a Tesla BS-567 instrument (working frequency 100 MHz) with $CDCl_3$ as solvent and TMS as internal standard. GLC analysis was conducted on a Chrom-5 instrument with the silicone liquid SE-30 (5%) on Chromaton N-Aw-DMCS (0.16-0.20 mm) as stationary phase at a working temperature of 50-300°C

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of 50-300°C with helium as the carrier gas. The stereochemical individuality of pheromone (I) was analyzed on a Chrom-5 instrument with the stationary phase SE-30 in a 0.2 mm × 50 m capillary column at a working temperature of 200°C with helium as the carrier gas. The mixture of compounds (VI) and (V) was separated in a Perkin-Elmer F-21 preparative chromatograph using a 10 mm 5 m column containing the stationary phase SE-30 (10%) on Chromaton N-AW-DMCS (0.20-0.25 mm) at a column temperature of 170°C and an evaporator temperature of 200°C, with helium as the carrier gas. Compound (I) was isolated from the product of the hydrogenation of the mixture of (VI) and (VII) on a Du Pont 8800 instrument with a Zorbax-Sil 4.6 × 250 mm column using hexane-ethyl acetate (100:1) as eluent and a refractometer as the detector.

Octane-1,8-diol (III). To 0.46 g ($2 \cdot 10^{-2}$ mole) of ZrCl_4 was added 40 ml of a 73% solution (0.16 mole) of DIBAH in toluene and the mixture was stirred (20°C, Ar) for 10 min, after which 7.7 g (0.07 mole) of octa-1,7-diene (II), obtained according to [9], was added, stirring was continued for another 6 h, and then the mixture was diluted with 150 ml of dry n-heptane and the product was oxidized successively with dried air (0°C, 0.5 h) and oxygen (0°C, 0.5 h; 20°C, 0.5 h; 20°C, 0.5 h; 50°C, 6 h). Then the reaction mixture was cooled to 0°C, 20 ml of water was added dropwise, stirring was performed at room temperature for 2 h, the product was extracted with diethyl ether (3 × 300 ml), and the extract was dried with Na_2SO_4 and evaporated. The residue was distilled in vacuum. This gave 7.15 g (70%) of the diol (III), bp 118-120°C (1 mm), mp 61-62°C [10].

1-(2-Tetrahydropyranyloxy)dec-9-yne (V). At -4°C, acetylene was bubbled for 2 h at the rate of 1 liter/min through a suspension of lithium amide, obtained from 2.1 g (0.3 g-atom) of lithium in 200 ml of redistilled liquid ammonia in the presence of 0.3 g of ferric chloride at the same temperature, and then a solution of 58.6 g (0.2 mole) of 8-bromo-1-(2-tetrahydropyranyloxy)octane (IV), obtained from the diol (III) according to [10], in 58 ml of absolute THF was added and, immediately after this, over 5 min, 58 ml of absolute DMSO; the mixture was stirred at -40°C for 2 h and then without cooling for 2 h for the complete evaporation of the ammonia, after which 200 ml of water was added and the mixture was extracted with hexane (3 × 300 ml). The combined extract was washed successively with 10% HCl and with saturated NaHCO_3 and NaCl solutions and was dried with MgSO_4 and evaporated. The residue was chromatographed on Al_2O_3 (with hexane-diethyl ether (9:1) as eluent). This gave 40 g (84%) of compound (V), n_D^{25} 1.4598 [11]. Its IR and PMR spectra were identical with those described in the literature [12].

Tetradec-12E-en-9-yn-1-yl Acetate (VI) and 11-Methyltridec-12-en-9-yn-1-yl Acetate (VII). At 20°C, under Ar, a solution of 11.9 g (0.05 mole) of the THP ether (V) in 50 ml of absolute THF was added to a solution of Grignard reagent prepared from 1.2 g (0.05 g-atom) of magnesium, and 5.45 g (0.05 mole) of ethyl bromide in 50 ml of absolute diethyl ether, and the reaction mixture was boiled for 3 h and was then cooled to 0°C, after which 9.52 g (0.05 mole) of CuI was added, and the resulting mixture was stirred for 0.5 h; then 9.45 g (0.07 mole) of crotyl bromide was added dropwise, the temperature was raised to 20°C and stirring was carried out at this temperature for 4 h and, after the addition of 100 ml of saturated NH_4Cl solution, the product was extracted with diethyl ether (3 × 200 ml) and the combined extract was evaporated. The residue (13 g) was dissolved in a mixture of 120 ml of ethanol, 12 ml of water, and 3 g of TsOH and the solution was stirred at room temperature for 20 h, after which the solvent was evaporated off, the residue was extracted with diethyl ether (3 × 200 ml), and the combined extract was washed successively with saturated NaHCO_3 and NaCl solutions and was dried with Na_2SO_4 and evaporated.

The residue (8 g) was treated at 0°C with 44 ml of a mixture (2:3) of acetic anhydride and pyridine and the resulting mixture was stirred at room temperature for 24 h, after which the solvent was evaporated off and the residue was dissolved in 400 ml of diethyl ether; this solution was washed successively with 10% HCl and with saturated solutions of NaHCO₃ and NaCl and was dried with MgSO₄ and evaporated. The residue was chromatographed on Al₂O₃ (with hexane-diethyl ether (9:1) as eluent). This gave 8.7 g (69%) of a mixture (9:1, respectively, according to GLC) of the acetates (VI) and (VII). The individual compounds (VI) and (VII) were isolated by preparative GLC.

Compound (VI). IR spectrum (ν , cm⁻¹): 970, 1640, 3020 (E, CH=CH), 2210 (C≡C), 1240 (C-O-C), 1740 (C=O). PMR spectrum (100 MHz, CDCl₃): 1.25-1.50 (m 12H, CH₂), 1.60-1.73 (m, 3H, H-14), 2.05 (s, 3H, CH₃CO), 2.08-2.44 (m, 2H, H-8), 2.76-2.93 (m, 2H, H-11), 4.06 (t, 2H, J = 6.5 Hz, H-1), 5.45-5.95 (m, 2H, CH=CH). Found, %: C 76.69; H 10.42. C₁₆H₂₆O₂. Calculated, %: C 76.75; H 10.47. M 250.37.

Compound (VII). IR spectrum (ν , cm⁻¹): 920, 1000, 1670 (CH=CH₂), 2210 (C≡C), 1245 (C-O-C), 1740 (C=O). PMR spectrum (100 MHz, CDCl₃): 1.23 (d, 3H, J=7 Hz, CH₃-11), 1.25-1.52 (m, 12H, CH₂), 2.05 (s, 3H, CH₃CO), 2.0-2.42 (m, 2H, H-8), 2.93-3.19 (m, 1H, H-11), 4.05 (t, 2H, J = 6.5 Hz H-1), 4.90-5.30 (m, 2H, H-13), 5.53-5.94 (m, 1H, H-12). Found, %: C 76.67; H 10.43. C₁₆H₂₆O₂. Calculated, %: C 76.75; H 10.47. M 250.37.

Tetradeca-9Z,12E-dien-1-yl Acetate (I). a) With stirring, a solution of 0.015 g (0.0004 mole) of sodium tetrahydroborate in 50 ml of ethanol and then 0.13 ml of ethylenediamine were added to a solution of 0.1 g (0.0004 mole) of nickel acetate in 1.1 ml of 95% ethanol, after which 0.5 g (0.002 mole) of the enyne (VI) was also added, and hydrogenation was carried out at room temperature in an atmosphere of hydrogen. The course of hydrogenation was monitored with the aid of GLC. After the end of hydrogenation, the reaction mixture was filtered, the solvent was distilled off, the residue was dissolved in diethyl ether (50 ml), and the solution was washed successively with 10% HCl and saturated NaCl solution and was dried with MgSO₄ and evaporated. The residue was chromatographed on Al₂O₃ (with hexane-diethyl ether (9:1) as eluent). This gave 0.43 g (85%) of the acetate (I) containing, according to capillary GLC, 97-98% of the main substance, n_D^{20} 1.4570 [6]; the IR and PMR spectra were identical with those described previously [7].

b) As described in the preceding experiment, 5.0 g (0.02 mole) of the mixture of (VI) and (VII) was hydrogenated. This gave 4.23 g (84%) of the acetate (I), containing, according to the capillary GLC, 88-89% of the main substance. The individual acetate (I) was isolated by preparative HPLC with spectral characteristics coinciding with those given previously [7].

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