SYNTHETIC STUDIES IN THE FIELD OF ATTRACTIVE SUBSTANCES (SEX ATTRACTANTS) OF INSECTS.

SYNTHESIS OF NONADECA-1,cis-3,cis-6,cis-9-TETRAENE – THE SEX PHEROMONE OF Operophtera brumata (LEPIDOPTERA; GEOMETRIDAE)

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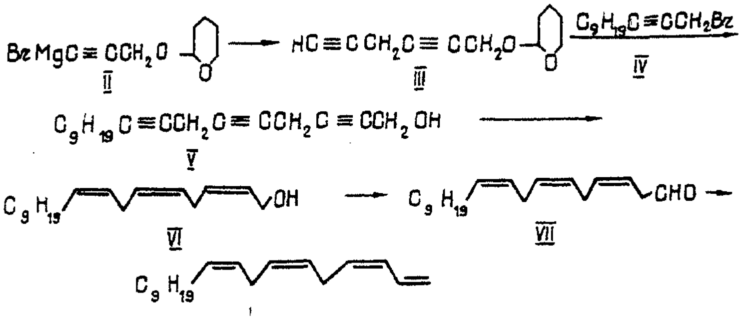
A new synthesis of nonadeca-1,cis-3,cis-6,cis-9-tetraene, the sex pheromone of the winter moth Operophtera brumata, has been developed which involves the alkylation of bromomagnesium derivatives of tetrahydropyranyl ethers of mono- and diacetylenic alcohols by a monoacetylenic bromide, followed by hydrogenation of the resulting triynol to a trienol, oxidation of the latter to an aldehyde, and interaction of the latter with methylenetriphenylphosphorane.

The winter moth Operophtera brumata is a serious pest – a polyphage of deciduous trees of forests [1] and orchards [2]. Its sex pheromone has been identified as nonadeca-1,cis-3,cis-6,cis-9-tetraene (I) [1, 3, 4] and can be used for the development of new environment-friendly approaches to the fight against this pest. Several schemes for obtaining the pheromone (I) have been described: $C_{12} + C_4 + C_3$ [3, 5], $C_{11} + C_3 + C_2 + C_5$ [4], $C_4 + C_3 + C_{12}$ [6], $C_3 + C_2 + C_{14}$ [7].

We have synthesized nonadeca-1,cis-3,cis-6,cis-9-tetraene (I) by a new $C_3 + C_3 + C_{12} + C_1$ scheme:



The alkylation of the bromomagnesium derivative of 1-(2-tetrahydropyranyloxy)prop-2-yne (II) with propargyl bromide gave a moderate yield of 1-(2-tetrahydropyranyloxy)hexa-2,5-diyne (III), the alkylation of which under the same conditions with the bromide (IV), followed by elimination of the tetrahydropyranyl protection, led with satisfactory yield to octadeca-2,5,8-triyn-1-ol (V). The bromide (IV) was obtained from dodec-2-yn-1-ol by the method of [9].

It is known that the hydrogenation of methylene-separated triynic systems analogous to the triynic alcohol (V) on the catalysts P-2Ni, $Pd/BaSO_4$ in methanol, and $Pd/CaCO_3$ in hexane with additions of Et_3N takes place nonselectively, with the formation in approximately equal proportions of several components the structures of which have not been studied [6]. Only the Lindlar catalyst in ethyl alcoholic solution gave satisfactory results.

The product of the hydrogenation of the acetylenic alcohol (V) over Lindlar catalyst under our conditions was represented on GLC by three peaks, 1, 2, and 3, in a percentage ratio of 62.21:28.98:5.79, respectively. A comparison of the retention times of linoleyl and linolenyl alcohols with those for the components of the hydrogenation product showed that peaks 1 and 2 can be assigned to the trienic alcohol (VI) and a dienic alcohol, respectively.

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Oxidation of the mixture of octadecatrienic alcohols obtained was carried out at room temperature with MnO_2 in absolute methylene chloride [8]. On GLC, the oxidation product was represented by two peaks. The trienic aldehyde (VII) was isolated by column chromatography with a purity of 93%.

The aldehyde (VII) was converted by the Wittig reaction with methylenetriphenylphosphorane into nonadeca-1,cis-3,cis-6,cis-9-tetraene (I) – the sex pheromone of the winter moth. The overall yield of hydrocarbon (I) was 4.0%.

Field trials of the nonadecatetraene (I) in doses of 10, 100, 1000, and 10,000 μg showed that doses of 1000 and 10,000 μg are attractive for winter moth males.

EXPERIMENTAL

The IR spectra of solutions of the substances in CCl_4 were taken on a Specord 75IR instrument with NaCl and KBr prisms and a NaCl cell. High-resolution PMR spectra were obtained on a Tesla BS-467 spectrometer in CCl_4 at a working frequency of 60 MHz, with tetramethylsilane as internal standard. The gas-chromatographic investigation of the compounds obtained was conducted on a Chrom-5 chromatograph using glass columns (3 mm × 1.2 m) filled with 5% of SE-30 on the support Chromaton 100-120 mesh or with 5% of bishydroxymethylcyclohexane succinate on the same support. Isomeric purities were determined on a Vista 6000 chromatograph with a quartz capillary column (0.3 mm × 25 m) and SE-54.

1-(2-Tetrahydropyranyloxy)hexa-2,5-diyne (III). To the Grignard reagent obtained from 4.13 g of Mg and 18.5 g of ethyl bromide in 60 ml of absolute THF was slowly added 23.4 g of the tetrahydropyranyl ether of propynol in 60 ml of absolute THF, and the mixture was stirred at 20°C for 1 h and at 55°C for 1 h and was then cooled to room temperature; 0.15 g of CuCl and, after 20 min, 14.6 g of propargyl bromide were added and the resulting mixture was stirred in a current of dry argon at 20°C for 12 h and at 55°C for 2 h. It was then decomposed with 25 g of NH_4Cl in 75 ml of H_2O and was extracted with ether; the extract was dried with anhydrous Na_2SO_4, the solvent was evaporated off, and the residue was distilled. This gave 11.3 g (59.5%) of the acetal (III), bp 134-136°C (3 mm), n_D^{20} 1.4758.

IR spectrum (cm^{-1}): 3300, 1312, 1130, 1030, 910. PMR spectrum (δ, ppm): 1.49 br.s (6H, $(C\underline{H}_2)_3$), 2.12 (1H, $C{\equiv}C\underline{H}$), 3.26 d (2H, $\equiv CC\underline{H}_2C\equiv$, J = 4 Hz), 3.69 m (2H, $OC\underline{H}_2$), 4.26 t (2H, $\equiv CC\underline{H}_2O$, J = 6 Hz), 4.83 s (1H, $OC\underline{H}O$).

1-Bromododec-2-yne (IV) was synthesized by a method described in the literature [9]; yield 61%, bp 136°C (6 mm), n_D^{20} 1.4892.

Octadeca-2,5,8-triyn-1-ol (V). In drops, 9.0 g of the protected hexadiynol (III) in 25 ml of absolute THF was added to the Grignard reagent prepared from 2.8 g of Mg and 15.0 g of ethyl bromide in 50 ml of absolute THF. The mixture was stirred in a current of dry argon at 20°C for 2 h, and then 0.3 g of anhydrous CuCl and, after 20 min, 12.0 g of 1-bromodec-2-yne in 10 ml of absolute THF were added. The reaction mixture was stirred in a current of dry argon at 20°C for 24 h and was then decomposed with NH_4Cl and extracted with ether; the extract was dried with anhydrous Na_2SO_4, and the solvent was evaporated off. The residue was stirred with 1.2 N HCl in methanol for 1 h and was then extracted with saturated NaCl solution and with ether, and the ethereal solution was dried with $MgSO_4$. The product was purified on a column of SiO_2 (40/100 mesh) with elution by ether–n-hexane (1:4). This gave 4.0 g (56%, calculated on the bromide that had reacted) of the trienol (V), mp 52°C.

IR spectrum (cm^{-1}): 3360, 1390, 1311. PMR spectrum (δ, ppm): 0.86 t (3H, $C\underline{H}_3$, J = 6 Hz), 1.23 br.s (14H, $(C\underline{H}_2)_7$), 2.1 m (2H, $C\underline{H}_2C\equiv$), 3.16 s (4H, $2{\equiv}CC\underline{H}_2C\equiv$), 4.2 s (1H, $O\underline{H}$).

Octadeca-cis-2,cis-5,cis-8-trien-1-ol (VI). In a hydrogenation flask, 2.5 g of the triynol (V) was dissolved in 50 ml of absolute alcohol, and 100 mg of Lindlar catalyst and three drops of quinoline were added. The hydrogenation reaction was monitored by the GLC method. After the absorption of an equivalent amount of hydrogen and the disappearance of the acetylenic alcohol, the reaction mixture was filtered and the ethyl alcohol was distilled off. The trienol was purified on a column of SiO_2 (40/100 mesh), with elution by CH_2Cl_2–ether (18:1). This yielded 2.0 g (79%) of the trienol (VI) (containing 29% of an octadienol according to capillary chromatography). Rechromatography under the same conditions gave the trienol with a purity of 95%, n_D^{20} 1.4769.

IR spectrum (cm^{-1}): 3360, 3012, 1645, 1010. PMR spectrum (δ, ppm): 0.88 t (3H, $C\underline{H}_3$, J = 6 Hz), 1.23 br.s (14H, $(C\underline{H}_2)_7$), 2.16 m (2H, $C\underline{H}_2\overset{|}{C}{=}$), 2.82 t (4H, $2{=}C\overset{|}{C}H_2\overset{|}{C}{=}$), J = 6 Hz), 3.06 s (2H, $CC\underline{H}_2$), 4.16 s (1H, $O\underline{H}$), 5.32 m (6H, $C\underline{H}{=}C\underline{H}$). Found, %: C 82.12; H 12.63. $C_{18}H_{32}O$. Calculated, %: C 81.75; H 12.20.

Octadeca-cis-2,cis-5,cis-8-trienal (VII). To a suspension of 16.0 g of MnO_2 in 30 ml of absolute CH_2Cl_2 was added 1.3 g of the trienol with the dienol impurity. The reaction mixture was stirred in an atmosphere of argon at 20°C for 24 h. The course of the oxidation reaction was monitored by TLC. This gave 0.7 g (58%) of oxidation product the column chromatography of which on SiO_2 (40/100 mesh) [eluent: either–n-hexane (1:9)] yielded the aldehyde (VII) with a purity of 93%.

IR spectrum (cm^{-1}): 3012, 2735, 1685, 1645. PMR spectrum (δ, ppm): 0.86 t ($3H_3$, $C\underline{H}_3$, J = 6 Hz), 1.23 br.s (14H, $(C\underline{H}_2)_7$), 2.0 m (2H, $C\underline{H}_2\overset{|}{C}{=}$), 2.72 m (4H, $2{=}C\overset{|}{C}\underline{H}_2\overset{|}{C}{=}$), 6.2-6.48 m (6H, $C\underline{H}{=}C\underline{H}$), 9.49 d (1H, $C\underline{H}O$, J = 8 Hz.

Nonadeca-1,cis-3,cis-6,cis-9-tetraene (I). Over 30 min (Ar, −10°C), 0.7 g of the octadecatriene (VII) in 10 ml of absolute THF was added to a solution of the methylenetriphenylphosphorane obtained from 0.9 g of methyltriphenylphosphonium bromide and 3.1 ml of a 0.85 N hexane solution of butyllithium in 15 ml of absolute THF. The mixture was stirred at 20°C for 4 h, the solvent was evaporated off, the residue was deposited on a column of SiO_2 (40/100 mesh), and elution was conducted with n-hexane. The purity of the hydrocarbon was monitored by GLC. The yield was 0.4 g (44.9%), n_D^{20} 1.4645.

IR spectrum (cm^{-1}): 3065, 3015, 1645, 990, 900. PMR spectrum (δ, ppm): 0.86 t (3H, $C\underline{H}_3$, J = 7 Hz), 1.23 br.s (14H, $(C\underline{H}_2)_7$), 2.03 m (2H, $C\underline{H}_2\overset{|}{C}{=}$), 2.8 m (4H, $2{=}\overset{|}{C}{-}CH_2\overset{|}{C}{=}$), 5.20 m (2H, $CH{=}C\underline{H}_2$), 5.40 m (5H, $C\underline{H}{=}C\underline{H}$), 6.0 m (1H), 6.33 m (1H).

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