SUMMARY

1. The addition of anthraquinone leads to an appreciable increase in the yield of low-molecular-weight products of the alkaline hydrolysis of cotton-plant lignin.

2. The monomeric fractions of the hydrolysis products contain a high level of p-coumaryl structures and a very low level of syringyl structures, which may be due to the demethyoxylation of the lignin under the conditions described.

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INSECT PHEROMONES AND THEIR ANALOGS.

XII. SYNTHESIS OF THE ISOMERIC DEC-5-ENYL ACETATES – THE SEX PHEROMONES OF *Anarsia lineatella* AND *Agrotis segetum*

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A new route for the synthesis of dec-5E- and -5Z-enyl acetates – the sex pheromones of the peach-tree borer and of the turnip moth – is proposed which is based on the two-stage hydroxyethylation of hex-1-yne using 2-chloroethyl vinyl ethers and ethylene oxide.

The sex pheromones of the peach-twig borer (*Anarsia lineatella*) and the turnip moth (*Agrotis segetum*), which have been identified as dec-5E- and -5Z-enyl acetates, respectively, have been obtained previously by the use of the allyl rearrangement [1] or the Wittig reaction [2, 3] at the stage of constructing the alkene fragment.

We have developed a new scheme for the synthesis of these pheromones which is based on a two-stage hydroxyethylation, first with 2-chloroethyl vinyl ether (CEVE) and then with ethylene oxide. The starting material was hex-1-yne (I), the lithium derivative of which, under the action of CEVE gave oct-3-yn-1-ol (II), which was converted into 1-bromooct-3-yne (IV) via the tosylate (III). The lithium derivative of the bromide (IV) was converted into dec-5-yn-1-ol (V) by treatment with ethylene oxide. Reduction of the alkynol (V) with the aid of sodium in liquid ammonia or of 9-borabicyclo[3.3.1]nonane (BBN) took place with high selectivity and led to dec-5E-enol (VI) or dec-5Z-enol (VII), respectively, the acetylation of which gave the corresponding acetates (VIII) or (IX) – the desired pheromones (scheme).

It must be mentioned that the use of ethylene oxide in the first stage of hydroxyethylation substantially lowered the yield of the alcohol (II), while the hydroxyethylation of the bromide (IV) took place more smoothly with ethylene oxide. The stereochemical individuality of compounds (VIII) and (IX) was confirmed by capillary GLC. In the ^{13}C NMR spectra the signals of the allyl carbon atom of the acetate with the E configuration (VIII) were shifted downfield substantially as compared with the corresponding signals of the Z isomer (IX) [4].

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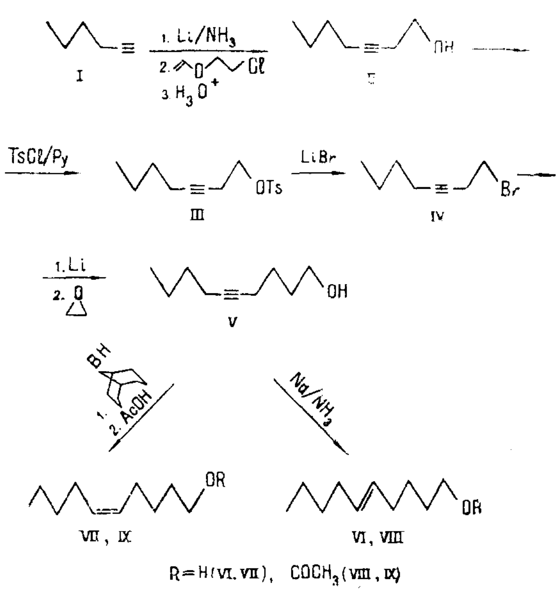

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film). The PMR spectra of the substances were obtained on a Tesla BS-467 spectrometer with a working frequency of 60 MHz using $CDCl_3$ as solvent, δ, 0 — TMS. ^{13}C NMR spectra were recorded on a Jeol FX-90Q instrument with broad-band and partial suppression with respect to protons using $CDCl_3$ as solvent; 0 — TMS.

GLC analysis was performed on a Chrom-4 instrument [stationary phase SE-30 (15%) on Chromaton NAW-DMCS (0.16-0.20 mm), working temperature 50-300°C] or a Chrom-5 instrument [stationary phase 1,2,3-tris(2'-cyanoethoxy)propane, stainless-steel capillary column (50 m × 0.25 mm), working temperature 146°C], with the carrier gas helium.

Oct-3-yn-1-ol (II). At −30°C, 100 ml of absolute diethyl ether and 0.5 g of iron acetonylacetonate, and then, dropwise over 0.5 h, a solution of 42.5 g (0.4 mole) of CEVE in 100 ml of absolute diethyl ether were added to a suspension of lithium hexynide obtained from 2.8 g (0.4 g-atom) of lithium and 33 g (0.4 mole) of (I) in 400 ml of dry liquid ammonia. The temperature of the reaction mixture was gradually raised to 20°C with stirring (15 h, Ar), and then 100 ml of water was added, followed by, dropwise over 0.5 h, 100 ml of 10% HCl, the mixture was stirred (30°C, 2 h), 1 liter of diethyl ether was added, and the organic layer was separated off, washed with saturated NaCl, dried with Na_2SO_4, and evaporated, and the residue was distilled giving 32.4 g (65%) of oct-3-yn-1-ol (II), bp 93-95°C (14 mm), n_D^{20} 1.4565 [5].

1-Tosyloxyoct-3-yne (III). At −5 to 0°C, 4.2 g (22 mmole) of p-toluenesulfonyl chloride was added in portions to a solution of 2.52 g (20 mmole) of the alcohol (II) in 6.5 ml of dry pyridine and the mixture was stirred (at −5°C for 0.5 h and then at 0°C for 6 h) and was poured onto ice (20 g). After extraction with diethyl ether (300 ml) the extract was washed successively with 10% HCl (to pH 4), with 10% $NaHCO_3$ (to pH 8), and with saturated NaCl (to pH 7) and was dried with Na_2SO_4 and evaporated, giving 5.2 g (93%) of the tosylate (III), $C_{15}H_{20}O_3S$. IR spectrum (ν, cm^{-1}): 560 m, 583 m, 670 m, 1600 m, 2230 w. PMR spectrum (ppm); t 0.8 (3 H, CH_3, J = 7 Hz); m 1.25 (4 H, CH_2); m 1.98 (2 H, $C^5H_2C{\equiv}C$); m 2.31 (2 H, $C^2H_2C{\equiv}C$); s 2.35 (3 H, CH_3Ar); t 3.96 (2 H, CH_2O, J = 7 Hz); d 7.28 (2 H, H—Ar, J = 7.5 Hz); d 7.75 (2 H, H—Ar, J = 7.5 Hz).

1-Bromooct-3-yne (IV). A solution of 5.6 g (20 mmole) of the tosylate (III) in 30 ml of absolute acetone was treated with 2.61 g (30 mmole) of lithium bromide and the mixture was boiled for 6 h and evaporated; the residue was extracted with diethyl ether (300 ml) and the extract was dried with $MgSO_4$ and evaporated. After chromatography (SiO_2, n-hexane) 3.2 g (85%) of the bromide (IV) was obtained, with bp 90-93°C (22 mm), n_D^{20} 1.4650 [6].

IR spectrum (ν, cm^{-1}): 577 m, 645 m, 223 w. PMR spectrum (ppm): t 0.8 (3 H, CH_3, J = 7 Hz); m 1.25 (4 H, CH_2); m 2.06 (2 H, $C^2H_2C{\equiv}C$); m 2.6 (2 H, $C^2H_2C{\equiv}C$); t 3.3 (2 H, CH_2Br, J = 7 Hz).

Dec-5-yn-1-ol (V). To 1.59 g (0.228 g-atom) of finely cut lithium in 175 ml of absolute diethyl ether (Ar, −15°C) was added 21.6 g (0.114 mole) of the bromide (IV) in 75 ml of absolute diethyl ether and, after being stirred (at −10°C for 2 h and at 0-5°C for 1 h), the mixture was diluted with 75 ml of absolute diethyl ether, after which a solution of 6.5 ml (0.13 mole) of ethylene oxide in 10 ml of absolute diethyl ether was added dropwise (−5 to 0°C), and the mixture was stirred for 2 h and was left at room temperature for 12 h. Then 100 ml of saturated NH_4Cl solution and 500 ml of diethyl ether were added and the organic layer was separated off, washed with saturated NaCl, dried with Na_2SO_4, and evaporated. The residue was chromatographed (SiO_2, hexane—diethyl ether (7:3)), giving 9.7 g (55%) of the alcohol (V) with n_D^{20} 1.4576 [2].

Dec-5E-enol (VI). A solution of 1.54 g (10 mmole) of the decynol (V) in 50 ml of absolute diethyl ether was added dropwise to a solution of 2.3 g (0.1 g-atom) of sodium in 500 ml of dry liquid ammonia. The reaction mixture was stirred (−35°C for 15 h), and then 400 ml of diethyl ether and 50 ml of water (0.5°C) were added. The ethereal layer was separated off, washed with 50 ml of saturated NaCl, dried with Na_2SO_4, and evaporated. The residue was chromatographed (SiO_2, $n\text{-}C_6H_{14}\text{—}Et_2O$ (7:3)), giving 1.48 g (95%) of the (E)-enol (VI) with n_D^{20} 1.4520 [1, 2].

Dec-5E-enyl Acetate (VIII). A mixture of 0.77 g (5 mmole) of the alcohol (VI) and 10 ml of a 2:3 mixture of acetic anhydride and pyridine was stirred and left at room temperature for 24 h. Then 100 ml of methylene chloride was added to the reaction mixture and it was washed with 10% HCl and then with 10% $NaHCO_3$ and saturated NaCl, dried with $MgSO_4$, evaporated, and chromatographed (SiO_2, $n\text{-}C_6H_{14}\text{—}Et_2O$ (15:1)), giving 0.95 g (96%) of the acetate (VIII) with n_D^{20} 1.4417 [2].

^{13}C NMR spectrum (δ, ppm): O—C^1 64.52; C^2 25.90; C^3 28.09 C^4 32.29; =C^5 131.08; =C^6 129.49; C^7 32.14; C^8 31.79; C^9 22.21; C^{10} 13.98; O=C 171.17; CH_3 21.00.

Dec-5Z-enyl Acetate (IX). A solution of 1.54 g (10 mmole) of the decynol (V) in 5 ml of absolute THF (Ar, 0°C) was treated dropwise with 44 ml (22 mmole) of a 0.5 M solution of BBN [7] in absolute THF. The reaction mixture was kept at 0°C for 24 h, and then 10 ml of glacial AcOH was added and it was boiled for 9 h, after which 300 ml of diethyl ether was added at 20°C and the mixture was washed with 40 ml of 6M NaOH and 20 ml of saturated NaCl and dried with $MgSO_4$, and evaporated, giving the alcohol (VII) which was converted into the acetate described above for the E isomer (VIII). The yield of the acetate (IX) was 1.6 g (81%), n_D^{20} 1.4424 [3]. ^{13}C NMR spectrum (δ, ppm): O—C^1 64.47; C^2 26.96; C^3 28.24; C^4 26.74; =C^5 130.53; =C^6 129.02; C^7 26.05; C^8 31.94; C^9 22.37; C^{10} 14.00; O=C 171.13; CH_3 20.98.

SUMMARY

A new route to the synthesis of dec-5E-enyl and dec-5Z-enyl acetates — the sex pheromones of the peach-twig borer Anarsia lineatella and the turnip moth Agrotis segetum — has been developed which is based on the two-stage hydroxyethylation of hex-1-yne using 2-chloroethyl vinyl ether and ethylene oxide.

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