INSECT PHEROMONES AND THEIR ANALOGS.

XIII. SYNTHESIS OF DODEC-8E-ENYL AND DODEC-8Z-ENYL ACETATES — COMPONENTS OF THE SEX PHEROMONES OF *Grapholitha funebrana* AND *Grapholitha molesta*

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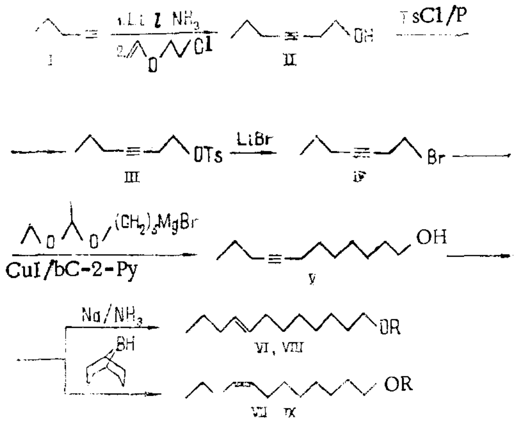
A new route is proposed for the synthesis of dodec-8E-enyl and dodec-8Z-enyl acetates which is based on the reaction of the Grignard reagent from the readily accessible 1-bromo-5-(1-ethoxyethoxy)pentane with 1-bromohept-3-yne — the bromide obtained from product of the β-hydroxyethylation of pent-1-yne with 2-chloroethylvinyl ether, hept-3-yn-1-ol, by a double decomposition reaction of its tosylate with lithium bromide. The key synthon — dodec-8-yn-1-ol — was converted with the aid of sodium in liquid ammonia into the stereochemical individual dodec-8E-enol, while its reduction with the aid of 9-borabicyclo[3.3.1]nonane (BBN) gave the steroisomeric alcohol exclusively with the Z configuration, as followed from the results of capillary GLC and the IR spectra of the corresponding acetates. The PMR spectra of the compounds synthesized are also given.

The geometric isomers of dodec-8-enyl acetate have been identified as components of the sex pheromones of the plum fruit moth (*Grapholitha funebrana*) and the oriental peach moth (*Grapholitha molesta*) [1-3]. In known schemes for the synthesis of these compounds the Wittig reaction [2] is used for the construction of the double bond, or terminal alkyne derivatives are used as the starting materials



We propose a new route to the synthesis of dodec-8E-enyl acetate (VIII) and dodec-8Z-enyl acetate (IX) which is based on the interaction of the Grignard reagent from the readily accessible 1-bromo-5-(1-ethoxyethoxy)pentane with 1-bromohept-3-yne (IV) — the bromide obtained from the product of the β-hydroxyethylation of pent-1-yne (I) with 2-chloroethyl vinyl ether [8] (II) by a double-decomposition reaction of its tosylate (III). The key synthon — dodec-8-yn-1-ol (V) — was converted with the aid of sodium in liquid ammonia into the stereochemically individual dodec-8E-enol (VI) and by reduction with the aid of 9-borabicyclo[3.3.1]nonane (BBN) [9] into the stereoisomeric alcohol (VII) exclusively with the Z configuration, as followed from the results of capillary GLC and the IR spectra of the corresponding acetates (VIII) and (IX). The total yield of the desired compounds (VIII) and (IX) was ~40%, calculated on the initial (I).

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EXPERIMENTAL

The PMR spectrta of the substances were obtained on a Tesla BS-467 spectrometer with a working frequency of 60 MHz using $CDCl_3$ as the solvent, the chemical shifts being given in the δ scale relative to the signal of TMS (internal standard). The IR spectra were taken on a UR-20 spectrometer (in a film) and GLC analysis was performed on a Chrom-4 instrument with the stationary phase SE-30 (15%) on Chromaton N-AW-DMCS (0.16-0.20 mm) at a working temperature of 50-300°C with helium as the carrier gas. The stereochemical individuality of the final products was analyzed on a Chrom-5 instrument with 1,2,3-tris(β-cyanoethoxy)propane as the stationary phase in a 50 m × 0.25 mm stainless-steel capillary column at 146°C with helium as the carrier gas.

Hept-3-yn-1-ol (II). At −30°C, 100 ml of absolute diethyl ether and 0.35 g of iron acetylacetonate, and then, dropwise over 0.5 h, a solution of 32 g (0.3 mole) of 2-chloroethyl vinyl ether in 1 ml of absolute diethyl ether were added to a suspension of lithium pentynide obtained from 2.1 g (0.3 g-atom) of lithium and 21 g (0.31 mole) of pentyne (I) in 400 ml of dry liquid ammonia. The temperature of the reaction mixture was gradually raised to 20°C and it was stirred (argon) for 15 h, after which 100 ml of water was added and then, in drops, over 0.5 h, 100 ml of 10% HCl. The reaction mixture was stirred at 30°C for 2 h, after which 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. The residue was distilled in vacuum, giving 23.2 g (69%) of the heptynol (II), bp 79°–80°C (18 mm) n_D^{20} 1.4562 [10].

1-Tosyloxyhept-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 2.24 g (20 mmole) of the alcohol (II) in 6.5 ml of dry pyridine, and the mixture was poured onto ice (20 g) and extracted with diethyl ether (300 ml). the ethereal solution was washed successively with 10% HCl (to pH 4), 10% $NaHCO_3$ (to pH 8) and with saturated NaCl (to pH 7) and was dried with Na_2SO_4 and evaporated, giving 5.05 g (95%) of the tosylate (III).

IR spectrum (ν, cm^{-1}): 560 m, 580 m , 670 m, 1600 m, 2230 w. PMR spectrum (δ, ppm): t 0.85 (3 H, CH_3, J = 7 Hz), m 1.3 (2 H, CH_2); m 1.95 (2 H, $C^5H_2C{\equiv}C$); m 2.3 (2 H, $C^2H_2\,C{\equiv}C$); s 2.33 (3 H, CH_3–Ar); t 3.95 (2 H, CH_2O, J = 7 Hz); d 7.25 (2 H, H–Ar, J = 7.5 Hz); d 7.72 (2 H, H–Ar, J = 7.5 Hz). Found, %: C 62.98; H 6.78; S 11.83. $C_{14}H_{18}O_3S$. Calculated, %: C 63.16; H 6.76; S 12.04.

1-Bromohept-3-yne (IV). A mixture of 5.32 g (20 mmole) of the tosylate (III), 2.61 g (30 mmole) of lithium bromide, and 30 ml of absolute acetone was boiled for 6 h and was then evaporated and the residue was extracted with ethyl ether (300 ml) and the extract was dried with $MgSO_4$ and evaporated. The residue was chromatographed (SiO_2, n-hexane), giving 3.1 g (90%) of the bromide (IV) with bp 100°C (65 mm), n_D^{20} 1.4785 [11]. IR spectrum (ν, cm^{-1}): 580 m, 645 m, 2230 w. PMR spectrum (δ, ppm): t 0.85 (3 H, CH_3, J = 7 Hz); m, 1.3 (2 H, C^6H_2); m 2.08 (2 H, $C^5H_2C{\equiv}C$); m 2.63 (2 H, $C^2H_2C{\equiv}C$); t 3.33 (2 H, CH_2CH_2Br, J = 7 Hz).

Dodec-8-yn-1-ol (V). To 1.56 g (8.2 mmole) of CuI in 40 ml of absolute THF was added 1.3 g (8.2 mmole) of bi-2-pyridyl, adn the mixture was stirred at 20°C for 0.5 h (argon) and was then cooled to 2°C, after which a solution of 7.35 g (42 mmole) of the bromide (IV) in 40 ml of absolute THF was added and the resulting mixture was stirred for 10 min. Then the Grignard reagent obtined from 2.4 g (0.1 g-atom) of magnesium and 14.3 g (60 mmole) of 5-bromo-1-(1-ethoxyethoxy)pentane in 40 ml of absolute THF was added and the reaction mixture was stirred at 2°C for 2 h, after which 30 ml of 10% HCl and, after stirring (20°C, 12 h), 600 ml of diethyl ether were added and the organic layer was washed successively with 10% $NaHCO_3$ (to pH 8) and with saturated NaCl (to pH 7) and was dried with Na_2SO_4 and evaporated. The residue was chromatographed (SiO_2, n-hexane–diethyl ether (7:3)), giving 6.0 g (78%) of the alcohol (V), with n_D^{20} 1.4598 [4].

Dodec-8E-enol (VI). A solution of 1.82 g (10 mmole) of the alkynol (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 at −35°C for 15 h, and then 400 ml of diethyl ether and 50 ml of water were added successively (0-5°C). The ethereal layer was washed with 50 ml of saturated NaCl, dried, and evaporated. The residue was chromatographed (SiO_2, n-hexane–diethyl ether (7:3)), giving 1.76 g (96%) of the alcohol (VI) with n_D^{20} 1.4545 [4].

Dodec-8E-enyl Acetate (VIII). A mixture (2:3) of acetic anhydride in pyridine (10 ml) was used to treat 0.92 g (5 mmole) of the alcohol (VI), and after 24 h (~25°C) 100 ml of methylene chloride was added to the reaction mixture which was then washed successively with 10% HCl, 10% $NaHCO_3$, and saturated NaCl, dried with Na_2SO_4, and evaporated, and the residue was chromatographed (SiO_2, n-hexane–diethyl ether (15:1)), giving 1.08 g (95%) of the acetate (VIII) with n_D^{20} 1.4435 [4, 5]. IR spectra (ν, cm^{-1}): 975 m, 1045 m, 1245 s, 1742 s, 3012 m.

Dodec-8Z-enyl Acetate (IX). A 0°C in an atmosphere of argon, 44 ml (22 mmole) of a 0.5 M solution of BBN in absolute THF was added dropwise to a solution of 1.82 g (10 mmole) of the alkynol (V) in 5 ml of absolute THF and the mixture was kept for 24 h, after which 10 ml of glacial acetic acid was added and it was boiled for 9 h. After cooling to 20°C, 300 ml of diethyl ether was added and the resulting mixture was washed successively with 40 ml of 6 M NaOH and 20 ml of saturated NaCl, and it was dried with Na_2SO_4 and evaporated. The residue was treated at 0.5°C with 4.4 ml of acetic anhydride and 6 ml of pyridine and the mixture was kept at 20°C for 15 h and was then worked up as described above for the acetate (VIII), which yielded 1.85 g (82%) of the acetate (IX) with n_D^{29} 1.4453 [4]. IR spectrum (ν, cm^{-1}): 730 w, 1050 w, 1242 s, 1742 s, 3010 m.

SUMMARY

A new route to the synthesis of the Z and E isomers of dodec-8-enyl acetate – the components of the sex pheromones of teh peach-twig borer and the oriental fruit moth – have been developed starting from hept-3-ynol, the product of the hydroxyethylation of pent-1-yne with 2-chloroethyl vinyl ether.

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