INSECT PHEROMONES AND THEIR ANALOGUES.
IX. STEREOSPECIFIC SYNTHESIS OF (Z)-DODECA-9,11-DIENYL ACETATE, A COMPONENT OF THE SEX PHEROMONE OF THE COTTON BOLLWORM MOTH *Diparopsis castanea*

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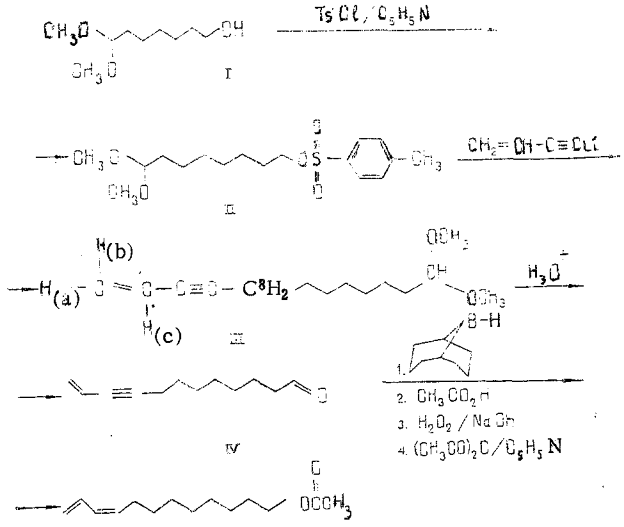
A method has been developed for the stereospecific synthesis of (Z)-dodeca-9,11-dienyl acetate, a component, together with the corresponding (E) isomer, of the sex pheromone of the red cotton bollworm moth, that is based on the coupling of vinylacetylene with either 8-hydroxyoctanal or 8-bromooctan-1-ol to form a C_{12} enynic compound in which the acetylenic bond is then reduced stereospecifically with 9-borabicyclo[3.3.1]nonane.

A whole series of stereospecific methods for obtaining one of the components of the sex pheromone of the red cotton bollworm moth (*Diparopsis castanea* Hmps), namely (E)-dodeca-9,11-dienyl acetate is known, a review of them being given in [1]. Methods for the synthesis of another component of this pheromone, the geometric isomer of the diene acetate just mentioned, have been studied to a far smaller extent. The methods described for the preparation of (Z)-dodeca-9,11-enyl acetate are based on the linkage of 1-(2-tetrahydropyranyloxy)dec-9-yne with vinyl bromide catalyzed by tetrakis(triphenylphosphine)palladium followed by the conversion of the double bond into a (Z)-olefinic bond by hydrogenation with the aid of di(sec-isoamyl)borane [1-3].

We have developed a new method for the stereospecific synthesis of (Z)-dodeca-9,11-dienyl acetate (V) which is based on the use of but-1-en-3-yne (vinylacetylene), obtained by the dehydrochlorination of 1,3-dichlorobut-2-ene [4]. The addition of lithium vinylacetylide, generated by the action of lithium amide on vinylacetylene, to 1,1-dimethoxy-8-tosyloxyoctane (II) obtained by the tosylation of 1,1-dimethoxyoctan-8-ol (I), which has



Scheme I.

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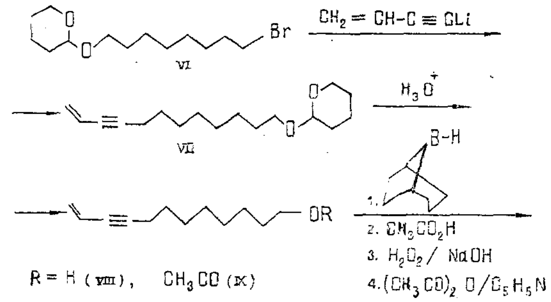
become an accessible compound thanks to the selective ozonolysis of cycloocta-1,5-diene [5], leads with a high yield to 1,1-dimethoxydodec-11-en-9-yne (III) — the key synthon for the desired compound (V).

However, the selective hydrogenation of the conjugated enyne (III) could not be performed over Lindlar catalyst [6] or zero-valent nickel [7]. Hydrolysis of the acetal (III) and reduction of the resulting dodec-11-en-9-ynal (IV) by the action of di(iso-butyl)-aluminum hydride followed by acylation of the hydroxy group permitted the production of (Z)-dodeca-9,11-dienyl acetate (V) with a yield of about 30%.

We have found that the desired dienic acetate (V) exclusively with the (Z) configuration is obtained with far higher yield (of the order of 70%) if the reduction of the enynal (IV) is carried out with the aid of 9-borabicyclo[3.3.1]nonane (9-BBN) [8]. Thus, the overall yield of (Z)-dodeca-9,11-dienyl acetate (V) in a five-stage synthesis amounted to 52% calculated on the initial hydroxyacetal (I) (scheme 1).

We have also used vinylacetylene in condensation with 8-bromo-1-(2-tetrahydropyranyloxy)octane (VI), obtained by the reaction of octane-1,8-diol with 48% HBr and 2,3-dihydropyran [1]. The 1-(2-tetrahydropyranyloxy)dodec-11-en-9-yne (VII), obtained with a yield of about 80%, was subjected to hydrolysis, and the resulting dodec-11-en-9-yn-1-ol (VIII), identified in the form of the acetate (IX), was converted by the hydroboration reaction with the aid of 9-BBN into (Z)-dodeca-9,11-dien-1-ol, the acylation of which gave the desired acetate (V) with an overall yield of the order of 60%, calculated on compound (VI) (scheme 2).



Scheme 2.

The presence of a conjugated enynic system in compound (III) was confirmed by adsorption at 234 nm (ε 10,075), 224 (ε 11,250), and 215 nm (ε 7450) [9]. The PMR spectrum of the acetate (III) contained a characteristic singlet of methoxy groups (3.28 ppm), the triplet of an acetal proton (4.32 ppm, J = 5 Hz), a poorly resolved triplet of the C^8H_2 group (2.25 ppm), a multiplet of the protons of a vinyl group (5.15-5.7 ppm region), and the multiplet of methylene protons with an intensity ratio of 6:1:2:3:12. It was established by the double magnetic resonance method that the protons of the vinyl group did not interact through a triple bond with the protons of the C^8H_2 methylene group, since the multiplet in the 5.15-5.7 ppm region did not change when the protons resonating in the 2.25 cm region were decoupled. Consequently, the multiplicity of the vinyl group is due only to the interaction of its three protons with one another. It follows from an analysis of this multiplet that all three protons $H_{(a)}$, $H_{(b)}$, and $H_{(c)}$, are nonequivalent and give two doublets (H_a 5.57 ppm, J = 4 Hz; H_b 5.74 ppm, J = 10 Hz), and a quartet (H_c 5.28 ppm, J_1 = 4 Hz, J_2 = 10 Hz) in the spectrum. The mass spectrum of the acetal (III) contains peaks of the corresponding molecular ion (m/z 224) and of ions (m/z 193, 161, and 160) confirming the direction of fragmentation of M^+ at C—O bonds that is characteristic for acetals. As was to be expected, the strongest peak was that of an ion with m/z 75 having the structure $CH(OCH_3)_2^+$.

EXPERIMENTAL

GLC analysis was performed on a Chrom-5 instrument with a flame-ionization detector using as stationary phase 1,2,3-tri(β-cyanoethoxy)propane (10%) on Chromosorb G-AW-DMCS (0.2-0.25 mm) modified with $AgNO_3$ (2%); column 2.5 m × 3 mm; temperature 146°C; carrier gas helium. IR spectra were taken on a UR-20 spectrometer in a thin layer. The UV spectrum was obtained on a Specord UV-VIS instrument (with hexane as solvent). PMR spectra were taken on a Tesla BS-487B spectrometer with a working frequency of 80 MHz using $CDCl_3$ or CCl_4 as solvent, the chemical shifts being given in the δ scale relative to the signal of HMDS (internal standard). Mass spectra were measured on an MKh-1306 instrument at a temperature of the ionizing chamber of 120°C and an ionizing voltage of 70 V.

1,1-Dimethoxy-8-tosyloxyoctane (II). At —5 to 0°C, 8.4 g of p-toluenesulfonyl chloride was added in portions to a solution of 7.6 g of 8,8-dimethoxyoctan-1-ol (I) in 13 ml of dry pyridine. The mixture was stirred at 0°C for 6 h and was then poured on to ice and extracted with diethyl ether (3 × 150 ml). The ethereal solution was washed with 10% HCl to pH 4 and then with 10% $NaHCO_3$ to pH 8 and was dried over Na_2SO_4, after which the solvent was evaporated off. This gave 13.5 g (98%) of the tosylate (II) $C_{17}H_{28}O_5S$. IR spectrum (ν, cm^{-1}): 565 m, 585 m, 825 m, 940 infl., 975 m, 1135 m, 1185 s, 1195 s, 1370 s, 1600 w. PMR spectrum (ppm): m 1.03-1.52 (12 H, 6 × CH_2); s, 2.35 (3 H, CH_3-Ar), s 3.23 (6 H, 2 × OCH_3); t 3.90 (2 H, CH_2O, J = 6 Hz, t 4.23 (1 H, OCHO, J = 5 Hz), d 7.23 (2 H, 2 × H-Ar, J = 7.5 Hz), d 7.72 (2 H, 2 × H - Ar, J = 7.5 Hz).

1,1-Dimethoxydodec-11-en-9-yne (III). To the lithium amide obtained from 0.72 g of metallic lithium in 200 ml of liquid ammonia was added 5.5 g of vinylacetylene, and the mixture was stirred for 5 h. Then the ammonia was evaporated off, the residue of lithium vinylacetylide was dissolved in 150 ml of HMPTA, and to this solution at —5 to 0°C was added a solution of 34.4 g of the tosylate (II) in 50 ml of THF over 30 min. The mixture was stirred at 5-10°C for 8 h, after which 200 ml of water was added and it was extracted with pentane (3 × 500 ml). The extract was washed with water and dried with Na_2SO_4. After the solvent had been eliminated, the residue was chromatographed [Al_2O_3, activity grade II, hexane—diethyl ether (9:1)]. This gave 17.08 g (75.5%) of the enynic acetal (III), $C_{14}H_{24}O_2$, n_D^{20} 1.4825. IR spectrum (ν, cm^{-1}): 915 m, 970 m, 1605 s, 1135 s, 1615 w, 2230 w. UV spectrum (ν, nm): 234 (ε 10,075), 224 (ε 11,250), 215 (ε 7450). PMR spectrum (ppm): m 1.35 (12 H, 6 × CH_2); t 2.25 (2 H, $CH_2C{\equiv}C$, J = 6 H); s 3.28 (6 H, 2 × OCH_3); t 4.25 (1 H, OCHO, J = 5 Hz); q 5.28 ($CH_{(c)}$, J_1 = 4 Hz, J_2 = 10 Hz); d 5.47 ($CH_{(b)}$, J = 10 Hz); d 5.57 ($CH_{(a)}$, J = 4 Hz). Mass spectrum (m/z; I, %): M^+ 224 (0.42%); ($M^+ - OCH_3$), 193 (4.6%), 161 (1.1%), ($M^+ - 2CH_3OH$), 160 (1.5%), 149 (1.0%), 135 (1.6%), 109 (3.2%), 91 (4.5%), $[CH_3OCHOCH_3]^+$ 75 (100%).

Dodec-11-en-9-ynyl Acetate (IX). In drops, at a temperature of —5 to 0°C a solution of 23.5 g of the bromide (VI) in 50 ml of THF was added over 20 min a solution of lithium vinylacetylide in 180 ml of HMPTA obtained, as described above for the synthesis of compound (III), from 5.2 g of vinylacetylene and 0.7 g of metallic lithium. The reaction mixture was stirred at 25-30°C for 10 h, and then 150 ml of water was added and it was extracted with petroleum ether (3 × 500 ml). The combined extract was washed with water and dried with potassium carbonate. After evaporation, 17 g (81%) of compound (VII) was obtained, and this was dissolved in 80 ml of THF. The solution was treated with 20 ml of 10% HCl and stirred at 20-25°C for 10 h. After the usual working up, 11.1 g (97.5%) of the enynic alcohol (VIII) was obtained, the acetate of which (IX) (n_D^{20} 1.4692) was identical (IR, PMR, and mass spectra) with the compound described in [1].

(Z)-Dodeca-9,11-dienyl Acetate (V). A. A solution of 11.2 g of the enynic acetal (III) in 75 ml of THF was treated with 10 ml of 10% HCl and the mixture was stirred at 20°C for 12 h, after which 250 ml of diethyl ether was added and the solution was washed with 10% $NaHCO_3$ and then with saturated NaCl solution and was dried with Na_2SO_4. After evaporation, 8.72 g (98.5%) of the enynic aldehyde (IV) was obtained, and this was dissolved in 60 ml of absolute THF at 0°C (Ar). Over 15 min, 220 ml of a 0.5 M solution of 9-BBN in absolute THF was added dropwise to the resulting solution. The reaction mixture was left at 0-5°C for 24 h, and then 30 ml of glacial acetic acid was added and it was heated at 60°C for 9 h, after which the solvent was distilled off in vacuum (20 mm). The residue was treated with 180 ml of 30% NaOH and then with 60 ml of 30% H_2O_2. The resulting mixture was stirred at 40°C for 2 h and was then cooled to 20°C, and 200 ml of water and 100 ml of diethyl ether were added. The organic layer was separated off and the aqueous layer was extracted with diethyl ether (3 × 200 ml). The organic layer, combined with the extract, was washed with water and dried with potassium carbonate. After evaporation, 5.93 g (68.3%) of (Z)-dodeca-9,11-dien-1-ol was obtained, and this was treated with a mixture of 15 ml of acetic anhydride and 42 ml of pyridine as described in [8]. This gave 6.72 g (90.5%) of the acetate (V) n_D^{20} 1.4659. According to the results of GLC analysis, the products contained 98-98.5% of the main substance, and the (E) isomer was absent. The IR, PMR, and mass spectra were identical with those given in [1].

B. At 0-2°C, 120 ml of a 0.5 M solution of 9-BBN in absolute THF was added dropwise to a solution of 5.4 g of the alcohol (VIII) in 30 ml of absolute THF. The reaction mixture was stirred at 0-5°C (Ar) for 20 h, after which 30 ml of glacial acetic acid was added and it was heated at 60°C for 7 h and was then evaporated in vacuum (20 mm) at 10-15°C. The residue was treated with 200 ml of 15% NaOH and then with 30 ml of 30% of H_2O_2 and was stirred at 40°C for 1 h, after which the mixture was cooled to 20°C, 250 ml of water was added, the organic layer was separated off, and the aqueous layer was extracted with diethyl ether (3 × 200 ml). The organic layer combined with the ethereal extract was washed with saturated NaCl and dried with potassium carbonate. After the solvent had been evaporated off, 3.8 g (69.5%) of (Z)-dodeca-9,11-dien-1-ol was obtained, and this was converted into the acetate (V) (n_D^{20} 1.4661), which proved to be identical with the product obtained in experiment A.

CONCLUSION

A new stereospecific synthesis of (Z)-dodeca-9,11-dienyl acetate — a component of the sex pheromone of the red cotton bollworm moth — has been developed which is based on the coupling of vinyl acetate with the acetal derivative of 8-tosyloxyoctanal or with 8-bromooctanol with the subsequent reduction of the enynic system with 9-borobicyclo[3,3,1]nonane.

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