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

XI. CONVENIENT SYNTHESIS OF NONADEC-cis-7-EN-11-ONE AND EICOS-cis-7-EN-11-ONE – COMPONENTS OF THE SEX PHEROMONE OF Carposina niponensis

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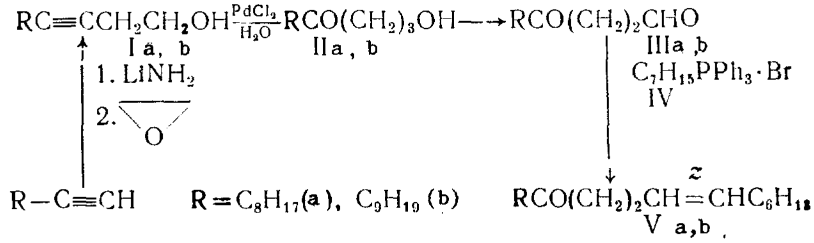
A simple synthesis of the nonadec-cis-7-en-11-one and eicos-cis-7-en-11-one, components of the sex pheromone of the peach moth, has been performed from homopropargyl alcohols.

The sex pheromone of the peach moth Carposina niponensis W., a quarantine pest for the USSR, consists of two components, nonadec-cis-7-en-11-one (Va) and eicos-cis-7-en-11-one (Vb) in a ratio of 1:20, respectively [1]. The ketones (Va) and (Vb) have been obtained by Grignard synthesis starting from undec-4-ynal [1], undec-cis-4-enal [2], and undec-4-ynonitrile [3] or undec-4-enonitrile [4], from β-dicarbonyl compounds [5, 6], by the selective ozonolysis of cycloocta-cis-1,cis-5-diene [7], and via selenoethers [8].

The selective elongation of the ketoaldehyde 4-oxododecanal and 4-oxotridecanal with heptylidenediphenylphosphorane has been widely used [6, 9-11].

We have effected synthesis of the ketones (Va) and (Vb) from homopropargyl alcohols.



The hydration of the β,γ-acetylenic alcohols (Ia, b) [12] in aqueous acetone in the presence of palladous chloride led with a yield of 50-60% to the hydroxyketones (IIa, b), which were readily oxidized to the ketoaldehydes (IIIa, b). The latter were converted with a yield of 60-65% by interaction with heptylidenediphenylphosphorane, generated by the action of sodium bis(trimethylsilyl)bromide on the phosphonium salt (IV) under the conditions of cis-olefination [13], into the final unsaturated ketones (Va) and (Vb), each containing 97-98% of the cis-isomer.*

The isomeric purity of the ketones (Va) and (Vb) was confirmed by the method of their preparation, and also by the presence in the ^{13}C nuclear resonance spectrum of only two signals corresponding to the carbons of double bonds.

The β,γ-acetylenic alcohols were conveniently synthesized with a yield of 60% from ethylene oxide and acetylenic hydrocarbons via the corresponding lithium acetylides which, in contrast to [14], where butyllithium was used as the base, were obtained by the action of lithium amide in phosphoric acid hexamethyltriamide.

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EXPERIMENTAL

The IR spectra of solutions of the substances in CCl_4 were taken on a UR-20 instrument at a layer thickness of 0.121 μm with NaCl and LiF prisms, the cell being of NaCl. PMR spectra were obtained on a BS-467 A spectrometer in CCl_4 at a working frequency of 60 MHz with tetramethyldisiloxane as internal standard. ^{13}C NMR spectra were obtained on a Tesla BS-567a spectrometer in CCl_4 at a working frequency of 25 MHz with tetramethylsilane as internal standard. The isomeric composition of the ketones was determined by the GLC method on a Packard 5880 A instrument with a 0.3 mm × 25 m capillary column, SE-54, temperature 180°C.

<u>Dodec-3-yn-1-ol (Ia)</u>. Lithium amide was obtained from 0.42 g (0.06 mole) of lithium and 30 ml of liquid ammonia, after which the ammonia was evaporated off to dryness. Then 40 ml of phosphoric acid hexamethyltriamide (hexametapol) was added and the mixture was stirred at 20°C for 1 h, after which a solution of 6.9 g (0.05 mole) of dodec-1-yne in 10 ml of hexametapol was run in and it was stirred at 20-25°C for another 1 h. Then it was cooled to −45°C, a solution of 2.64 g (0.06 mole) of ethylene oxide in 20 ml of ether was added and the resulting mixture was stirred at the same temperature for 1 h. After this, it was allowed to warm up to room temperature and was stirred for 10 h and, after the addition of 100 ml of water, with product was extracted with ether (3 × 50 ml) and the extract was washed with 10% hydrochloric acid and with water and was dried with anhydrous Na_2SO_4, the solvent was evaporated off, and the residue was distilled. This gave 5.46 g (60%) of the alcohol (Ia), bp 105-110°C (1 mm Hg), n_D^{20} 1.4582. IR spectrum (cm^{-1}): 1050, 3630. Found, %: C 78.79, H 12.10. $C_{12}H_{22}O$. Calculated, %: C 79.06, H 12.16.

<u>Tridec-3-yn-1-ol (Ib)</u>. This was obtained by a procedure similar to that for the preparation of the alcohol (Ia) from 0.4 g (0.055 mole) of lithium, 7.65 g (0.05 mole) of undec-1-yne, and 2.86 g (0.065 mole) of ethylene oxide in 40 ml of hexametapol. This gave 5.53 g (56.4%) of the alcohol (Ib), bp 115-121°C (1 mm Hg), n_D^{20} 1.4601. IR spectrum (cm^{-1}): 1050, 3630. Found, %: C 79.25, H 12.56. $C_{13}H_{24}O$. Calculated, %: C 79.52, H 12.32.

<u>1-Hydroxydodecan-4-one (IIa)</u>. A mixture of 0.91 g (0.005 mole) of the alcohol (Ia), 26 mg (0.0014 mole) of palladous chloride, 0.03 ml of water, and 5 ml of acetonitrile was heated to the boiling point of the solvent and was stirred for 30 min. Then it was cooled and the product was isolated by column chromatography on 30 g of silica gel with elution by ether—hexane (1:1). This gave 0.55 g (55%) of the ketol (IIa), mp 38-39°C. IR spectrum (cm^{-1}): 1050, 1710, 3630. PMR spectrum (δ, ppm): 0.83 t (3 H, CH_3, J = 6 Hz), 1.22 br.s (14 H, CH_2), 2.2-2.5 m (4 H, CH_2COCH_2), 3.5 t (2 H, $C\underline{H}_2OH$, J = 6 Hz), 3.6 s (1 H, OH). ^{13}C NMR spectrum (δ, ppm): 212.1 $(-\overset{|}{C}=O)$, 62.03 ($-CH_2OH$), 42.98 and 39.43 (CH_2COCH_2). Found, %: C 72.21, H 12.17. $C_{12}H_{24}O_2$. Calculated, %: C 71.94, H 12.07.

<u>1-Hydroxytridecan-4-one (IIb)</u>. This was obtained by a procedure similar to that for the ketol (IIa) from 0.98 g (0.005 mole) of the alcohol (Ib), 26 mg (0.0014 mole) of palladous chloride, 0.03 ml of water, and 5 ml of acetonitrile. Yield 0.53 g (50%) of ketol (IIb) with mp 41-43°C. IR spectrum (cm^{-1}): 1050, 1710, 3630. PMR spectrum (δ, ppm): 0.83 t (3 H, CH_3, J = 6 Hz), 1.22 br.s (16 H, CH_2), 2.2-2.5 m (4H, CH_2COCH_2), 3.49 t (2 H, CH_2OH, J = 6 Hz), 3.15 s (1 H, OH). ^{13}C NMR spectrum (δ, ppm): 212.1 $(-\overset{|}{C}=O)$, 61.84 (CH_2OH), 42.95 and 39.36 (CH_2COCH_2). Found, %: C 72.56, H 12.39. $C_{13}H_{26}O_2$. Calculated, %: C 72.84, H 12.28.

<u>3-Oxododecanal (IIIa)</u>. A solution of 1.4 g (0.007 mole) of the ketol (IIa) in 10 ml of methylene chloride was added dropwise to suspension of 2.42 g (0.011 mole) of pyridinium chlorochromate in 20 ml of methylene chloride. The mixture was stirred at 20-25°C until the ketol had been oxidized completely (3 h; TLC monitoring), and then 50 ml of ether was added, the mixture was filtered through a layer of silica gel, and the solvent was evaporated off. This gave 1.05 g (75.9%) of the ketoaldehyde (IIIa), bp 120-122°C (2 mm Hg), mp 26-28 °C. IR spectrum (cm^{-1}): 1730, 2730. PMR spectrum (δ, ppm): 0.80 t (3 H, CH_3, J = 6 Hz), 1.22 br.s (12 H, CH_2), 2.5 m (6 H, $C\underline{H}_2COC\underline{H}_2C\underline{H}_2CHO$), 9.8 t (1 H, CHO, J = 2 Hz). Found, %: C 72.81, H 11.25. $C_{12}H_{22}O_2$. Calculated, %: C 72.68, H 11.18.

<u>3-Oxotridecanal (IIIb)</u>. Under conditions similar to those for the preparation of (IIIa), 1.3 g (0.006 mole) of the ketol (IIb), and 2.0 g (0.0092 mole) of pyridinium chlorochromate in 30 ml of methylene chloride gave 1.16 g (91.7%) of the ketoaldehyde (IIIb), mp 26-28°C.

IR spectrum (cm^{-1}): 1730, 2730. PMR spectrum (δ, ppm): 0.80 t (3 H, CH_3, J = 6 Hz), 1.24 br.s (14 H, CH_2), 2.50 m (6 H, $C\underline{H}_2COCH_2CH_2CHO$), 9.81 t (1 H, CHO, J = 2 Hz). Found, %: C 73.40, H 11.25. $C_{13}H_{24}O_2$. Calculated, %: C 73.53, H 11.39.

Nonadec-cis-7-en-11-one (Va). In a current of nitrogen, 5.1 g (0.011 mole) of the salt (IV) was added to a solution of 2.2 g (0.012 mole) of sodium bis(trimethylsilyl)amide in 35 ml of absolute THF, and the mixture was stirred at 20°C for 20 min and with the boiling of the solvent for 1 h. Then it was cooled to −78°C, and a solution of 2.95 g (0.0148 mole) of the ketoaldehyde (IIIa) in 10 ml of absolute THF was slowly added. The reaction mixture was stirred at −78°C for 1 h and at 20-25°C for 12 h. The THF was evaporated off, the residue was extracted with a 10% solution of ether in hexane, the triphenylphosphine oxide that deposited was filtered off, and the filtrate was washed with 40% $NaHSO_3$ solution, $NaHCO_3$ solution, and water, and was dried with sodium sulfate. After the solvent had been evaporated, the residue was distilled. This gave 2.68 g (65%) of the ketone (Va), mp 162-164°C (1 mm Hg), n_D^{20} 1.4525. IR spectrum (cm^{-1}): 1730, 3020. ^{13}C spectrum (δ, ppm): 210.8 $(-\overset{|}{C}=O)$, 131.28 and 127.96 (CH=CH), 43.02 and 42.8 (CH_2COCH_2). Found, %: C 81.21, H 12.81. $C_{19}H_{36}O$. Calculated, %: C 81.36, H 12.93.

Eicos-cis-7-en-11-one (Vb). Under the conditions described for the synthesis of the ketone Va, 1.86 g (0.01 mole) of sodium bis(trimethylsilyl)amide, 4.19 g (0.0095 mole) of the salt (IV), and 2.0 g (0.0094 mole) of the ketoaldehyde (IIIb) in 50 ml of absolute THF gave 1.69 g (61%) of the ketone (Vb) with bp 159°C (0.7 mm Hg), n_D^{20} 1.4545. IR spectrum (cm^{-1}): 1725, 3015. ^{13}C NMR spectrum (δ, ppm): 210.8 $(-\overset{|}{C}=O)$, 131.3 and 128.1 (CH=CH), 43.05 and 42.9 (CH_2COCH_2). Found, %: C 81.51, H 13.35. $C_{20}H_{38}O$. Calculated, %: C 81.63, H 13.01.

CONCLUSIONS

A simple synthesis of the components of the sex pheromone of the peach moth *Carposina niponensis* W. by the hydration of homopropargyl alcohols to 1-hydroxyalkan-4-ones, their oxidation to 1,4-ketoaldehydes, and the interaction of the latter with heptylidenetriphenylphosphorane has been developed.

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