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Synthesis of Sex Pheromones Based on Polyacetal Compounds

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Abstract: *The intensive use of sex pheromones in integrated plant protection systems leads to the need to develop convenient synthesis schemes that make it possible to obtain pheromones of various types of pests with good yield and high isomeric purity from the same starting compounds - synthons.*

Methods have been developed for the synthesis of monoene sex pheromones of insects of the Lepidoptera order based on the Witteg reaction of unstable phosphoranes with polyacetal compounds. A new general method has been developed for the preparation of cis-5-alkenal, cis-5-alken-1-ol, cis-7-alken-1-ol, cis-9-alken-1-ol and their acetates, components of lepidopteran sex pheromones.

Keywords: *Pheromone, Lepidoptera, acetate, components, aldehyde, alcohol, cis-5-decen-1-ol, cis-7-dodecen-1-ol, cis-9-tetradecen-1-ol.*

Introduction

In recent years, a new approach to insect population management has been developing, based on advances in biological science and a deeper understanding of the communication mechanisms of arthropods. It has been established that information exchange in the insect world is mediated by chemical substances known as exohormones. Among these low-molecular-weight bioregulators are pheromones—compounds produced by insects and released into the environment to facilitate intraspecific communication. The ecological advantages of pheromones over other types of pesticides are indisputable: their action is highly species-specific and effective; the required doses are minimal—even compared to pyrethroids and juvenile hormones; and they are non-toxic and leave no harmful residues.

Significant progress has been achieved in the field of insect pheromone chemistry through the efforts of chemists from various countries. Nevertheless, the development of new regio- and stereoselective synthetic routes for these low-molecular-weight bioregulators from readily available raw materials remains a relevant and important challenge.

We have developed general methods for the synthesis of cis-5-alken-1-ol, cis-7-dodecen-1-ol, cis-9-tetradecen-1-ol, and their acetates. Sex pheromones or sex pheromone components of several important agricultural pests have been successfully synthesized. [6,8]

Results and Discussion

Materials and Methods. Pheromone research is carried out in many directions-biological, physiological, chemical, technological, and others. Field testing of sex pheromones is the final stage of many laboratory studies and, along with pheromone screening, serves as the basis for their practical application in plant protection.

This article is devoted to the synthesis of sex pheromones of *Lepidoptera* insects. A large number of cis-monoolefinic alcohols and their acetates were synthesized using the Wittig reaction [1,3].

An advantageous approach to this process involves the reaction of alkylidene triphenylphosphoranes with carbonyl compounds, allowing the formation of olefins as mixtures of *cis* and *trans* isomers. High stereospecificity of this reaction for obtaining the *cis*-isomer is achieved when using aliphatic phosphoranes and aliphatic aldehydes in nonpolar solvents in the absence of lithium salts, or in dipolar solvents. The generation of phosphorus ylides from the corresponding phosphonium salts by treatment with bis(trimethylsilyl)amide of an alkali metal, followed by reaction with aldehydes, leads to *cis*-alkenes with 98% stereochemical purity. This method was applied to the synthesis of attractants containing a single unsaturated bond such as *cis*-7-dodecenyl acetate, *cis*-5-alkenals, *cis*-5-alken-1-ols, and their acetates—components of Lepidoptera sex pheromones. The position and geometry of the double bonds in C_{10}– and C_{14}–alcohol acetates were determined through the study of electroantennographic (EAG) responses in male Lepidoptera antennae to a series of mono-unsaturated acetates with varying double bond positions (*Z-cis*, *E-trans*) in C_{10} and C_{12} one-functional alcohols. Tested compounds included acetates of 5Z-decen-1-ol, 7Z-dodecen-1-ol, and 7Z, 9Z, 11Z-tetradecen-1-ol, as well as two- and three-component mixtures of these substances in various ratios.

The isomeric purity of the synthesized compounds was determined by gas-liquid chromatography using a capillary column with a moderately polar phase (Carbowax, 20 m) and a packed column with a stereospecific phase UF-275, showing *cis*-isomer content of 96–98%.

Mass spectra of the samples were recorded using an Agilent 5977B GC-MSD system operated in SIM, SCAN modes, and electron impact (EI) ionization mode. Analysis conditions included: HP-5ms Ultra Inert analytical column (30 m × 250 µm × 0.25 µm); injection volume of 1.0 µL; splitless injection mode with single taper, gold-plated Ultra Inert glass wool liner with washer; carrier gas – hydrogen at a constant flow of 1.2 mL/min. The transfer line temperature was maintained at 280 °C. For mass spectrometry, a solvent delay of 3.5 minutes was used to eliminate solvent effects. The data acquisition was performed in SCAN mode, with a gain factor of 1.00× and the ion source temperature set to 250 °C.

TIC (Total Ion Current) in the range of 50–1100 m/z. MS conditions: drying gas flow rate – 4 L/min, gas temperature – 320 °C, nebulizer gas pressure – 20 psi, evaporator temperature – 250 °C, capillary voltage – 4500 V [4].

We have developed a synthesis of mono-diethyl acetals of glutaraldehyde and pimelic aldehyde based on the currently available diethyl acetal of glutaconaldehyde (III). The latter is reliably obtained in acceptable yields by the addition of orthoformates to 1-trimethylsilyloxy-1,3-butadiene (II), which, in turn, is prepared in good yields from commercially available crotonaldehyde (I).

$$CH_3CH{=}CHCHO \xrightarrow{(CH_3)_3SiCl} CH_2{=}CHCH{=}CHOSi(CH_3)_3 \xrightarrow{CH(OC_2H_5)_3,ZnCl_2}$$

I II

$$(C_2H_5O)_2CHCH_2CH{=}CHCHO \xrightarrow{H_2/PtO_2} (C_2H_5O)_2CH(CH_2)_3CHO$$

III IV

Catalytic hydrogenation of acetal (III) yielded the mono-diethyl acetal of glutaraldehyde (IV). We have studied the hydrogenation conditions (catalyst type, solvent) of acetal (III) in more detail. When hydrogenating over palladium catalysts using 0.5–5% catalyst in ether or hexane, the reaction does not proceed to completion, and alongside the acetal of glutaraldehyde (IV), the reaction mixture contains the starting material (I). When hydrogenation is carried out in ethanol with more than 5% catalyst, we observed the formation of a significant amount of hydroxyl-containing compounds, the structure of which was not investigated. Satisfactory results were obtained using 0.2–2% palladium oxide in ether, yielding the diethyl acetal of glutaraldehyde (IV) with an 80% yield.

The mono-diethyl acetal of pimelic aldehyde (IX) was obtained according to the following scheme:

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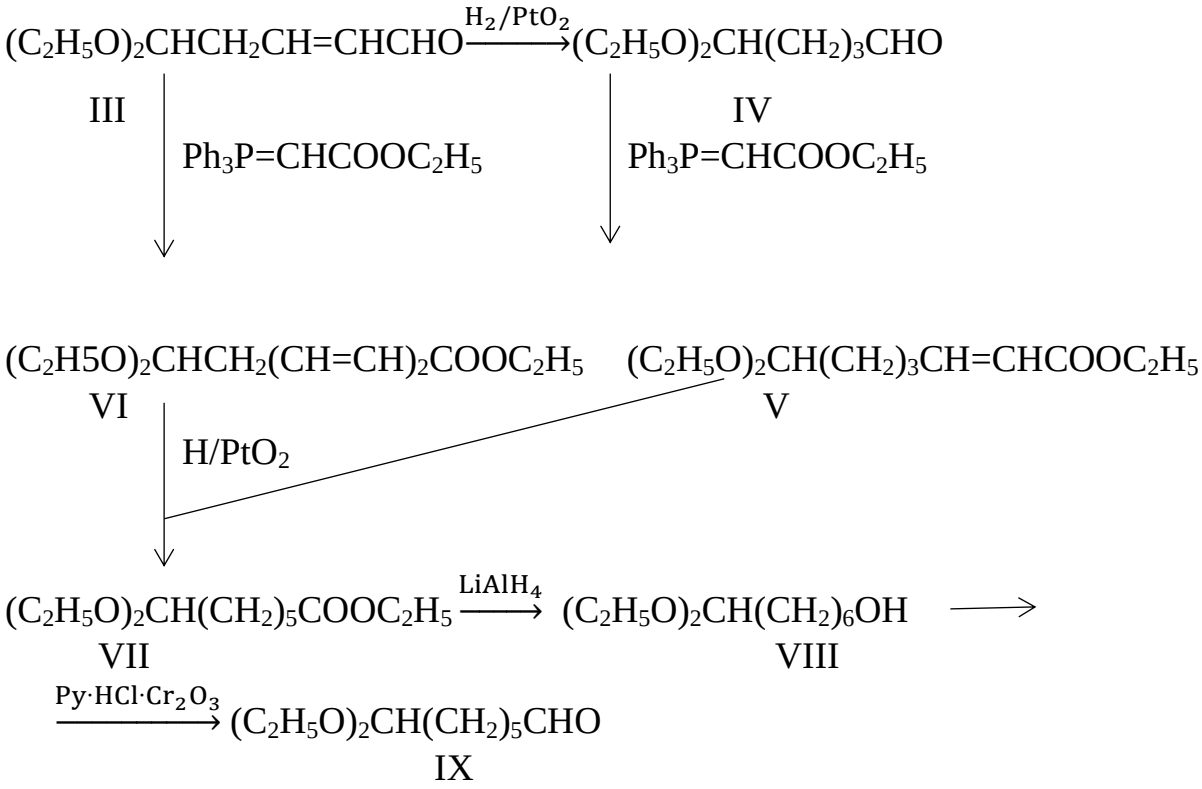
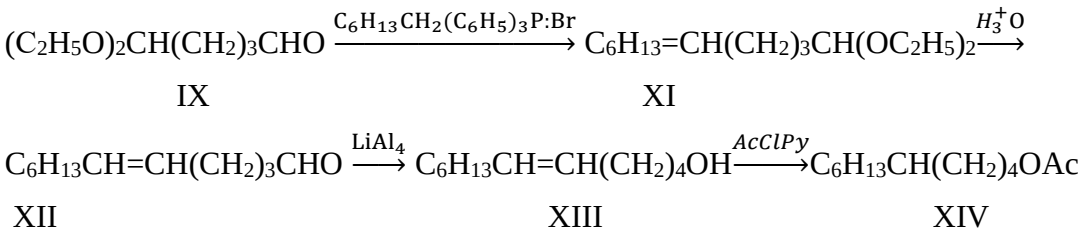


Extension of the mono-diethyl acetals of aldehydes (III) and (IV) with **carboethoxymethylenetriphenylphosphorane** yielded the **ethyl esters of 7,7-diethoxy-2E-heptenoic acid (V)** and **7,7-diethoxy-E,E-2,4-heptadienoic acid (VI)** in good yields. Hydrogenation over **palladium oxide** converted both esters into the **ethyl ester of 7,7-diethoxyheptanoic acid (VII)**.

Subsequent **aluminum hydride reduction** of (VII) afforded the **diethyl acetal of 7-hydroxyheptanal (VIII)**. Oxidation of (VIII) with **pyridinium chlorochromate (PCC)** produced the **mono-diethyl acetal of pimelic aldehyde (IX)**, the next homologue in the series of monoacetals of dialdehydes with an odd number of carbon atoms. [7]

We have developed general synthetic routes for 5-cis-alkenals, 5-cis-alkenols, and their acetates. The synthesis of acetals and their acetates was accomplished through a Wittig reaction of unstable phosphoranes with mono-diethylacetal of glutaraldehyde, according to the following scheme:



Condensation of aldehyde (IV) with heptylidenetriphenylphosphorane under cis-olefination conditions yields ethyl 7-cis-dodecenoate (XI). Mild acid hydrolysis of this compound produces 7-cis-dodecen-1-ol (XIII), which is subsequently converted to acetate 7-cis-dodecenyl acetate (XIX) - a component of the sex pheromone of the gamma moth (Autographa gamma).

The reaction of aldehyde (IX) with n-octylmethylenetriphenylphosphorane proceeds smoothly to form 5-cis-tetradecenal. The acetals (XV) were converted to 5-cis-tetradecenal (XVI) by acid hydrolysis, which was then reduced with lithium aluminum hydride to yield 5-cis-tetradecen-1-ol (XVII).

$(C_2H_5O)_2CH(CH_2)_5CHO \xrightarrow{C_8H_{17}CH_2(C_6H_5)_3P/Br} C_8H_{17}CH{=}CH(CH_2)_5^{CH}(OC_2H_5)_2 \xrightarrow{H_3^+O}$

IX XV

$C_8H_{17}CH{\equiv}CH(CH_2)_5CHO \xrightarrow{LiAlH_4} C_8H_{17}CH{=}CH(CH_2)_5OH \xrightarrow{AcCl\cdot Py}$

XVI XVII

$C_8H_{17}CH{=}CH(CH_2)_5Oac$. 7-cis-tetradecenyl acetate.

XVIII

Yield, physicochemical and spectral characteristics of the compounds.

№	Connections	Yield	π_D^{20}	R	X	^{1}H NMR
1	$C_6H_{13}CH{=}CH(CH_2)_3CH(OC_2H_5)_2$	52	1.4420	6H 3H 4H 1H	CH_2 CH_2CO $HOCCH_2$ C_2H_5CO	1.43 (m, 2H) 2.10 (s, 3H) 2.20 (m, 2H) 9.71 (t, J = 2.1 Hz, 1H)
2	$C_6H_{13}CH{=}CH(CH_2)_3CHO$ 5z-$C_{19}CHO$	73	1.4566	3H 8H 4H 2H 2H 1H	CH_3 CH_2 $CH_2CH{=}CHCH_2$ CH_2CHO CH=CH CHO	0.84 (t, J = 7.2 Hz, 3H) 1.25 (br. s, 1H) 2.00 (m, 2H) 2.10 (m, 2H) 5.20 (m, 1H) 9.55 (t, J = 2.0 Hz, 1H)
3	$C_6H_{13}CH{=}CH(CH_2)_4OH$ 5z-$C_{12}OH$	37	1.4542	12H 4H 2H 2H	CH_2 CH_2CCCH_2 CH_2O CHCH	1.25 (br. s, 1H) 0.50 (m, 2H) 5.25 (m, 1H) 3.50 (t, *J* = 6.8 Hz, 2H)
4	$C_6H_{13}CH{=}CH(CH_2)_4OCOCH_3$	81	1.4426	12H 4H 2H 2H	CH_2 CH_2COCH_2 CH_2O $CH_2OC_2H_5$	1.25 (br. s, 1H) 1.50 (m, 2H) 3.50 (t, J = 6.5 Hz, 2H) 5.15 (t, J = 5.8 Hz, 1H)
5	$C_8H_{17}CH{=}CH(CH_2)_3CH(OC_2H_5)_2$	52	1.4431	3H 6H 14H 4H 4H 1H 2H	CH_3 CH_3 CH_2 CH_2CCCH_2 OCH_2 OCHO CHCH	0.85 (t, J = 7.0 Hz, 3H) 1.50 (t, J = 7.0 Hz, 3H) 1.25 (br. s, 1H 2.00 (m, 2H) 3.50 (m, 2H) 4.45 (m, 1H) 5.30 (m, 1H)
6	$C_8H_{17}CH{=}CH(CH_2)_3CHO$ 5z-$C_{14}HO$	53	1.4525	3H 14H 4H 2H	CH_3 CH_2 CH_2CCCH_2 CH_2CO	0.85 (t, J = 7.0 Hz, 3H) 1.20 (br. s, 1H) 2.00 (m, 2H)

				2H 1H 3H	CHCH CHO CH_3	2.45 (m, 2H) 5.45 (m, 1H) 9.85 (t, J = 2.0 Hz, 1H)
7	$C_8H_{17}CH=CH(CH_2)_4OH$ 5z-$C_{14}OH$	91	1.4550	16H 4H 2H 2H	CH_2 CH_2CCCH_2 CH_2O CHCH	1.23 (br. s, 1H) 2.00 (m, 2H) 3.50 (t, J = 6.5 Hz, 2H) 5.30 (m, 1H)

Thus, through the conducted research, we have developed general methods for obtaining the bases of hemiacetals of 5Z-alkenals, 5Z-alken-1-ols and their acetates, 7Z-alken-1-ols and acetates, and synthesized sex pheromones or components of sex pheromones of a number of agricultural pests.

Components of sex pheromones of the order Lepidoptera.

№	Compound	Ratio of sex pheromone components (%)	view
1	7z-$C_{12}OAc$	-	Ypsilon moth Scotia ipsilon
2	5z-$C_{12}OAc$/5z-$C_{14}OAc$	60:40	Goat Moth Cossus cossus
3	7z-$C_{14}OAc$/5z-$C_{14}OAc$	70:30	Black Cutworm Amathes C-nigrum
4	5z-$C_{14}OAc$/9z-$C_{14}OAc$	80:20	Black Cutworm Skotia excplaionis
5	7z-$C_{12}OAc$/7z-$C_{12}OH$	90:10	Scoop gamma Skotia segetum

From the results of field trials of various pheromone trap designs, the most attractive composition for the dispenser-based formulation was identified and recommended for practical use in plant protection.

Conclusion

This article is dedicated to the synthesis of sex pheromones of Lepidoptera insects. Cis-monoolefinic alcohols and their acetates were synthesized using the Wittig reaction. A favorable version of this process — the reaction of alkylidenetriphenylphosphoranes with carbonyl compounds — makes it possible to obtain olefins as mixtures of cis- and trans-isomers. Based on the Wittig reaction with mono-diethyl acetal of glutaric dialdehyde, a method was developed for the synthesis of 5-cis-alkenal, 5-cis- and 7-cis-alken-1-ols and their acetates. The synthesis of 5-cis-tetradecene, 7-cis-tetradecene, 7-cis-dodecen-1-ol, and 9-cis-tetradecen-1-yl acetate — components of the sex pheromones of Lepidoptera — was successfully carried out.

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