OLEFINATION OF ALIPHATIC ALDEHYDES
IN THE SYNTHESIS OF MONO-, DI-, AND TRIENIC
PHEROMONES OF LINEAR STRUCTURE

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This review systematizes information published mainly in the last 15 years on the use of the olefination of aliphatic aldehydes (the Wittig reaction and its modifications) in the synthesis of mono-, di, and trienic pheromones of linear structure.

Linear hydrocarbons, alcohols and their acetates, aldehydes, ketones, and carboxylic acid derivatives containing one or more double bonds with the (Z)- or the (E)- geometry have been identified as pheromones of Lepidoptera — the most numerous order of insects [1—14]. A number of monographs and reviews [1, 2, 8, 10, 15—23] have been devoted to such pheromones. It has been reported that fulfillment of the requirements for the regio- and stereochemical features of the target molecule is necessary for the achievement of a high biological activity of a synthetic pheromone [24—32]. One of the commonest approaches to the construction of a carbon skeleton having a double bond in a definite position is based on the Wittig reaction [17, 33] and its modifications [34—40]. Initially, the stereoselectivity of the formation of a Z-double bond by the Wittig reaction did not exceed 85% [41, 42]. It was later established that a decisive influence of the stereochemistry of the reaction is exerted by the nature of the phosphorus ylide and the reaction conditions [10, 43]. Unstabilized ylides form predominantly (Z)-alkenes with aldehydes [10, 44], while the action of ylides stabilized by electron-accepting substituents on the phosphorus atom or the α-carbon atom leads to reaction products that prove to be the (E)-alkenes [45—48]. It has been found that in the presence of lithium salts the Z/E ratio of the alkenes changes in favor of the (E)- isomer [46, 49]. Numerous examples of the synthesis of pheromones with mono-, di-, and trienic carbon skeletons using the olefination of aliphatic aldehydes are presented in the above-mentioned reviews. However, even the most recent of them refer to work published predominantly before 1983.
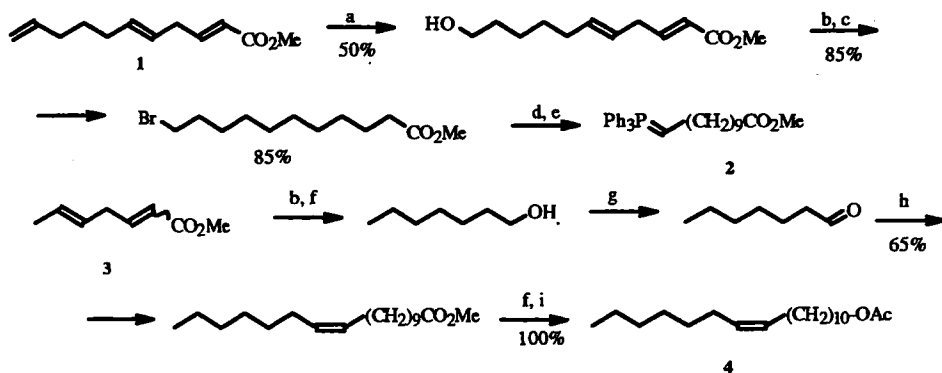
SYNTHESIS OF (Z)-MONOENIC PHEROMONES

The initial compounds used in the approach under consideration for the synthesis of pheromones are ω-functional [50, 51] or ω-unsaturated aldehydes and halogen derivatives [52—54]. One widely used method of synthesizing α,ω-bifunctional aliphatic compounds is the oxidative cleavage of cyclic olefins or functionalized linear unsaturated compounds [10, 55—57]. ω-Hydroxyaldehydes used in the synthesis of pheromones are obtained by the selective oxidation of diols [58—60], while ω-unsaturated alcohols can be obtained by the thermolysis of diols [61] or by the use of the selective hydroalumination of α,ω-dienes [62]. The ozonolysis of cyclic mono-, di-, and trienes has substantially expanded the possibilities of obtaining derivatives of ω-formylcarboxylic acids and pheromones based on them [63—73].

Copolymers of 1,3-dienes and acrylates are of undoubted interest in the synthesis of pheromones [74]. Thus, in the synthesis of octadec-11Z-en-1-yl acetate (4) — the pheromone of *Lycorea ceres ceres* — the initial compounds were methyl undeca-2E,5E,10-trienoate (1), from which the phosphorane (2) was obtained, and methyl hepta-2E/Z,5E-dienoate (3).
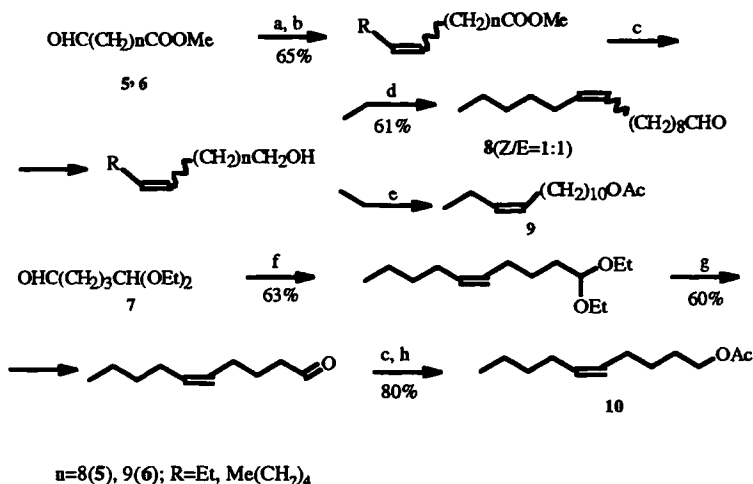

Scheme 1 (compounds 1–4):

1 $\xrightarrow[50\%]{a}$ $\text{HO}\text{—}\text{CO}_2\text{Me}$ $\xrightarrow[85\%]{b,c}$

$\xrightarrow{}$ $\text{Br}\text{—}\text{CO}_2\text{Me}$ (85%) $\xrightarrow{d,e}$ $\text{Ph}_3\text{P}\text{—}(CH_2)_9CO_2Me$ (2)

3 $\xrightarrow{b,f}$ $\text{—}\text{OH}$ $\xrightarrow{g}$ $\text{—}\text{O}$ $\xrightarrow[65\%]{h}$

$\xrightarrow{}$ $\text{—}(CH_2)_9CO_2Me$ $\xrightarrow[100\%]{f,i}$ $\text{—}(CH_2)_{10}\text{-OAc}$ (4)

a) B_2H_6; $H_2O_2/NaOH$; b) H_2/Ni; c) PBr_3; d) PPh_3; e) $^tBuOK/DMF$; f) $LiAlH_4$; h) 2;
g) PCC/CH_2Cl_2; i) Ac_2O/Py

The olefination of methyl 11-oxodecanoate (5) and methyl 11-oxoundecanoate (6) or of the diethyl acetal of pentane-1,5-dial (7) by the appropriate phosphoranes led, after simple transformations of the functional groups, to hexadec-10E/Z-enal (8) [75] and the acetates (9) and (10) of tetradec-11Z-1-ol [76] and of dec-5Z-en-1-ol [77], which are components of the pheromones of *Dichrocis punctiferalis*, the green oak-tortrix *Tortrix viridana*, and the turnip moth *Agrotis segetum*, respectively.

Scheme 2 (compounds 5–10):

$\text{OHC}(CH_2)_nCOOMe$ (5,6) $\xrightarrow[65\%]{a,b}$ $R\text{—}(CH_2)_nCOOMe$ $\xrightarrow{c}$

$\xrightarrow[61\%]{d}$ $\text{—}(CH_2)_8CHO$ 8(Z/E=1:1)

$\xrightarrow{}$ $R\text{—}(CH_2)_nCH_2OH$

$\xrightarrow{e}$ $\text{—}(CH_2)_{10}OAc$ (9)

$\text{OHC}(CH_2)_3CH(OEt)_2$ (7) $\xrightarrow[63\%]{f}$ $\text{—}\overset{OEt}{\underset{OEt}{CH}}$ $\xrightarrow[60\%]{g}$

$\xrightarrow{}$ $\text{—}\text{O}$ $\xrightarrow[80\%]{c,h}$ $\text{—}OAc$ (10)

n=8(5), 9(6); R=Et, Me(CH$_2$)$_4$

a) n=8, $EtCH=PPh_3(Z)$; b) n=9, $Me(CH_2)_5PPh_3/BuLi$ (Z/E=1:1); c) $LiAlH_4$;
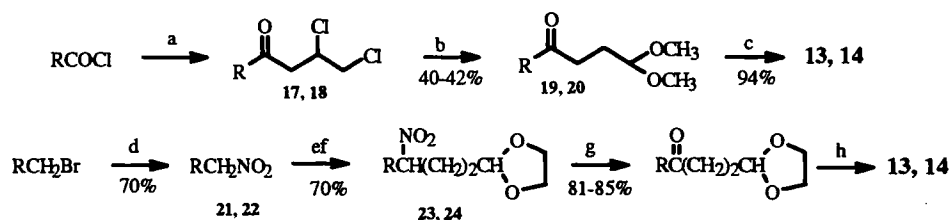d) PCC/CH_2Cl_2; e) Ac_2O/Py; f) $Me(CH_2)_3CH=PPh_3$; g) H_3O^+; h) AcCl

Alkyl-branched analogs of pheromone (10) have been obtained with the aid of the Wittig reaction [78]. Nonadec-12Z-en-9-one (15) and eicos-13Z-en-10-one (16) — components of the sex pheromone of the peach fruit moth *Carposina niponensis* — were synthesized with a yield of about 55% by the selective olefination of 3-oxododecanal (13) or of the trioxotridecanal (14) with heptylidenetriphenylphosphorane [79—84]. The ketoaldehydes (13) and (14) were obtained by the interaction of the corresponding (p-tolylsulfonyl)alkanes (11) with methyl 4,4-dimethoxybutanoate, followed by desulfonation of the resulting coupling product (12) under the action of aluminum amalgam [79].

Scheme (top):

$$RCH_2Br \xrightarrow{a} RCH_2Ts \xrightarrow{b, c} \underset{11}{} \underset{\substack{Ts \ O}}{RCH-C(CH_2)_2CH(OMe)_2} \xrightarrow{d}{70\%} \underset{}{RCH_2C(CH_2)_2CH(OMe)_2} \xrightarrow{e}{75-81\%}$$

$$\longrightarrow \underset{13,14}{RCH_2C(CH_2)_2CHO} \xrightarrow{f}{55\%} \underset{15,16}{RCH_2C(CH_2)_2} \diagup(CH_2)_5Me$$
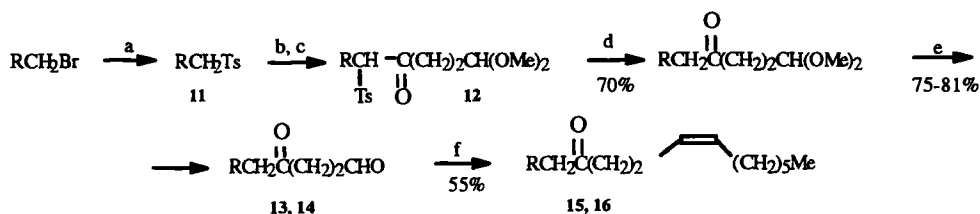
R=Me(CH₂)₆ (13, 14), Me(CH₂)₇ (15, 16)

a) TsONa · 4H₂O/MeOH; b) LDA; c) (MeO)₂CH₂CH₂COOMe; d) Al/Hg/THF-H₂O; e) HCl;
f) Me(CH₂)₅CH=PPh₃

Synthesis of the ketoaldehydes (13) and (14) has also been effected by the acylation of allyl chloride with the subsequent methanolysis of the corresponding allyl dichlorides (17) and (18) to form the ketoacetals (19) and (20) [82]. Condensation of the nitroalkanes (21) an (22) with acrolein followed by the electrochemical oxidation at a platinum electrode of the corresponding nitroacetals (23) and (24) led, after elimination of the acetal protection, to the same ketoaldehydes (13) an (14) [83].

Scheme (middle):

$$RCOCl \xrightarrow{a} \underset{17,18}{R} \xrightarrow{b}{40-42\%} \underset{19,20}{R\text{—}OCH_3/OCH_3} \xrightarrow{c}{94\%} 13, 14$$

$$RCH_2Br \xrightarrow{d}{70\%} \underset{21,22}{RCH_2NO_2} \xrightarrow{ef}{70\%} \underset{23,24}{RCH(CH_2)_2CH} \xrightarrow{g}{81-85\%} \underset{}{RC(CH_2)_2CH} \xrightarrow{h} 13, 14$$

R=Me(CH₂)₇ (13, 17, 19, 21, 23), Me(CH₂)₈ (14, 18, 20, 22, 24)

a) H₂C=CHCH₂Cl/AlCl₃/CH₂Cl₂; b) MeONa/MeOH; c) HCOOH; d) KNO₂/DMSO;
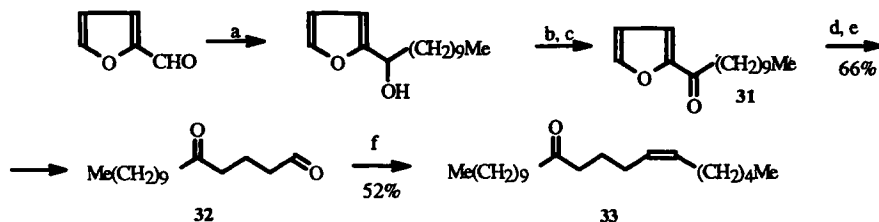e) H₂C=CHCHO/Bu₃P; f) (CH₂OH)₂/TsOH; g) e⁻ (Pt anode); h) HCl

The key synthons for the component of the peach fruit moth pheromone — the ketoaldehydes 13) and (14) — have also been obtained by the carbethoxylation of the acetylpropyl alcohol derivative (25) with the subsequent alkylation of the resulting ketoester (26). Decarboxylation of the β-ketoesters (27) and (28) and oxidation of the hydroxyketones (29) and (30) led to the desired compounds (13) and (14) [84].

Scheme (bottom):

$$\underset{25}{OTHP} \xrightarrow{a} \underset{26}{EtO_2C\text{—}OTHP} \xrightarrow{b} \underset{\substack{CO_2Et \ 27,28}}{R\text{—}OTHP} \xrightarrow{c,d}$$

$$\longrightarrow \underset{29,30}{R\text{—}OH} \xrightarrow{e} 13, 14$$
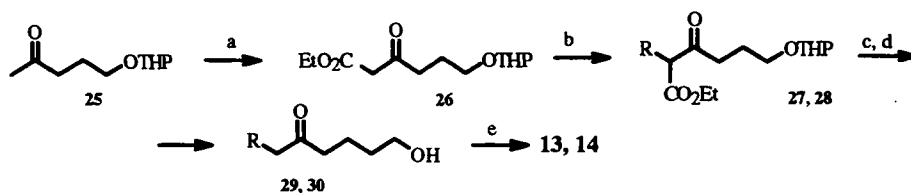
R=Me(CH₂)₆ (27, 29), Me(CH₂)₇ (28, 30)

a) (EtO)₂CO/NaOH/EtOH; b) RBr/NaOEt-EtOH; c) KOH-H₂O; d) H₃O⁺; e) PCC/CH₂Cl₂

The pheromone of the Douglas fir tussock moth *Orgyia pseutsugata*, having the structure of heneicos-6Z-en-11-one (33) has been synthesized by the olefination of 5-oxopentadecanal (32) with hexylidenetriphenylphosphorane [85—92]. The ketoaldehdye (32) can be obtained from furfural through the intermediate 2-acetyltetrahydrofuran (31) [85, 92].

The mixture of the Z- and E-isomeric alkenols obtained on the Wittig olefination of the corresponding aldehydes in the presence of lithium salts was separated into individual isomers after epoxidation. The preparative separation of the cis- and trans-epoxides was readily achieved by column chromatography. Subsequent deoxygenation of the transoid epoxide (34), for example with the aid of LiPPh$_2$—MeI led (after hydrolysis) to non-6Z-en-1-ol (35), while P$_2$I$_4$ led (after acetylation) to non-6E-en-1-yl acetate (36) — the pheromones of Dacus olae and Dacus curbitae, respectively [93].

a) Me(CH$_2$)$_9$MgBr;   b) H$_2$/Ph-C;   c) CrO$_3$;   d) Li/HMPA-THF, -78 °C;   e) PCC/CH$_2$Cl$_2$;
f) Me(CH$_2$)$_4$CH=PPh$_3$
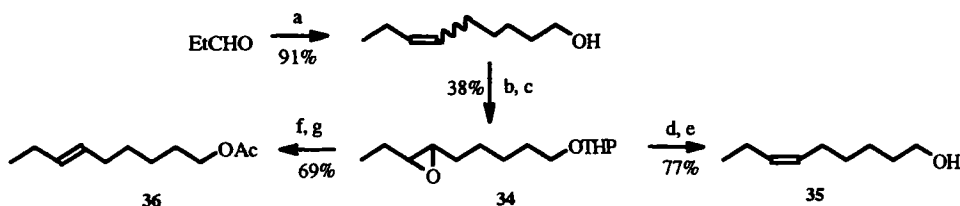
a) HO(CH$_2$)$_6$PPh$_3$/BuLi-THF;   b) DHP/HCl;   c) MCPBA/CH$_2$Cl$_2$;   d) Ph$_2$Li/MeI;   e) H$_3$O$^+$;   f) P$_2$I$_4$;
g) AcCl/AcOH

Hexadec-11Z-en-1-ol — the pheromone of Chilo infuscatellus [94] — and octadec-11Z-enal — the pheromone of the wax moth Achroia grisella [95] — have been synthesized by the use of a Wittig reagent from undec-10-enal and methyl undec-10-enoate, respectively.
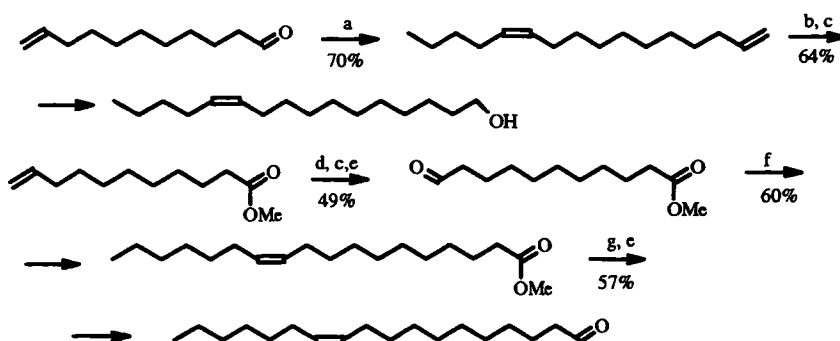
a) Me(CH$_2$)$_3$CH=PPh$_3$/THF-HMPA, -20 °C → 0 °C; b) Ca(BH$_4$)$_2$/THF; c)H$_2$O$_2$/NaOH; d) B$_2$H$_6$/THF;
e) PCC/AcONa/CH$_2$Cl$_2$; f) Me(CH$_2$)$_5$CH=PPh$_3$/THF; LiAlH$_4$/Et$_2$O

Routes to the synthesis of tricos-9Z-ene (37) [96] and heneicos-9Z-ene — components of the pheromone of the house fly Musca domestica — including those making use of the Wittig reaction, have been given in a special review devoted to this pheromone [97].

The fluorine-containing analogs (42) and (43) of components of the pheromones of a number of insect species belonging to the Lepidoptera order were synthesized by the olefination of the polyfluorinated aldehydes (38) and (39) with undecylidenetriphenylphosphorane, followed by hydroboration of the resulting dienes (40) and (41) [98, 99].

n = 1 (38, 40, 42), 3 (39, 41, 43)   42 (E/Z = 53:47), 43 (E/Z = 70:30)
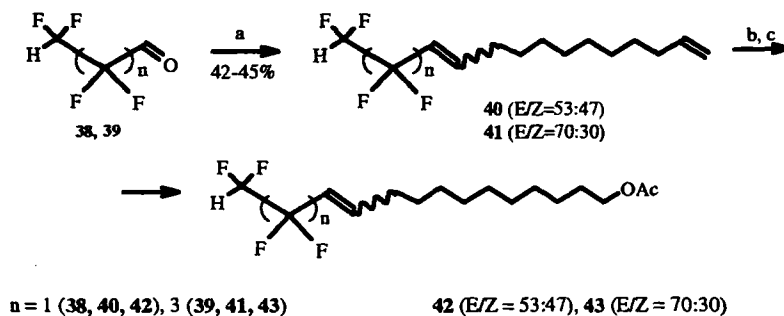
a) CH₂=CH(CH₂)₈CH=PPh₃/THF; b) 9-BBN, H₂O₂/NaOH; Ac₂O/Py

SYNTHESIS OF (E)-MONOENIC PHEROMONES

The synthesis of monoenic pheromones with the (E)- configuration usually makes use of Schlosser's β-oxido ylide method [100—102]. We must also mention the (E)-selective olefination of aldehydes with the aid of gem-dichromium reagents formed on the reduction of gem-diiodoalkanes with divalent chromium chloride [103]
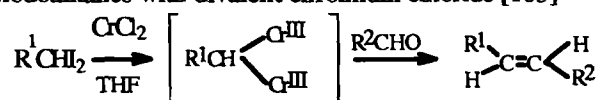
Derivatives of α,β-unsaturated carboxylic acids formed by the Wittig—Horner—Emmons reaction have the (E)-configuration [104—107]. The synthesis of 10-hydroxydec-2E-enoic acid (46) and of 9-oxodec-2E-enoic acid (55), which are components of the royal jelly and queen substance of the honeybee *Apis mellifera* [108—112] and are used in preparations for attracting bee swarms [113, 114], is usually achieved with the aid of Knoevenagel reaction by the interaction of 8-hydroxyoctanal (45) [115, 116] and 7-oxooctanal (54) [117], respectively, with malonic acid. The key compound (45) in the synthesis of the hydroxy acid (46) was obtained by the selective oxidation of octane-1,8-diol after its conversion into the monobromide (44) [115]. The hydroxyaldehyde (45) has also been synthesized by condensing the bromoacetal (47) with 5-(tetrahydropyran-2-yloxy)pentylmagnesium bromide [116] and by the ozonolysis of cyclooctadiene or the product of its partial hydrogenation [118], followed by reduction of the ester group in methyl 8,8-dimethoxyoctanoate (48) [63].
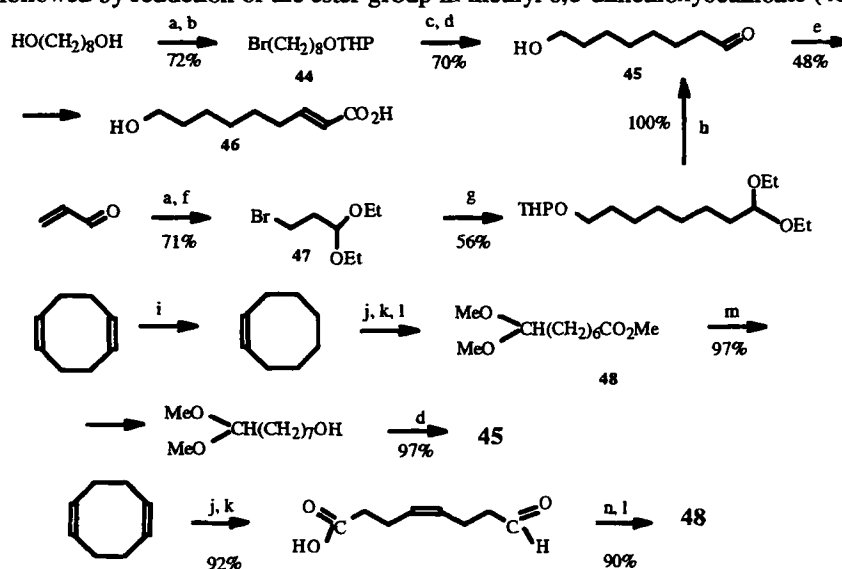

a) HBr;   b) DHP/H⁺;   c) pyridine N-oxide;   d) H₃O⁺;   e) CH₂(COOH)₂/Py;   f) EtOH/TsOH;
g) THPO(CH₂)₅MgBr/Li₂CuCl₄;   h) TsOH/SiO₂;   i) H₂/P-2Ni;   j) O₃/ᶜC₆H₁₂/AcOH;   k) Ac₂O/AcONa;
l) MeOH₂⁺;   m) DIBAH/THF;   n) H₂/Pd-C

The oxoaldehyde (54), later converted into the oxodecenoic acid (55), has been obtained by the ozonolysis of the readily available tetrahydropyran-2-yl ether of 7-methyloct-7-en-1-ol (49), followed by oxidation of the hydroxyketone (50) [117].
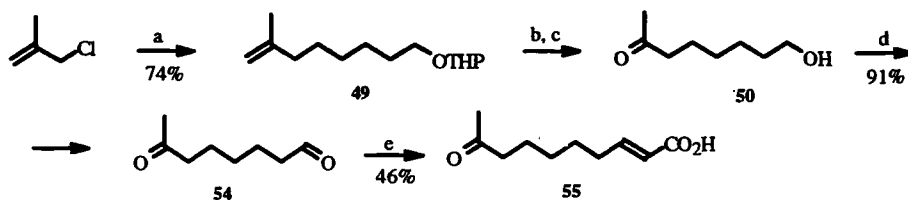

a) THPO(CH$_2$)$_5$MgBr/CuI-bipy; b) O$_3$; c) H$_3$O$^+$; d) PCC/CH$_2$Cl$_2$; e) H$_2$C(COOH)$_2$/Py

The oxoaldehyde (54) can be obtained from aleuritic acid (51) by its oxidative cleavage followed by methylation of the hydroxyaldehyde (52) and oxidation of the diol (53) [119]. If the hydroxyaldehyde (52) is used in a Knoevenagel reaction, oxidation of the primary and secondary hydroxy groups, combined into one operation in the preceding scheme, is carried out in two steps with the intermediate methylation of a formyl acid [119].
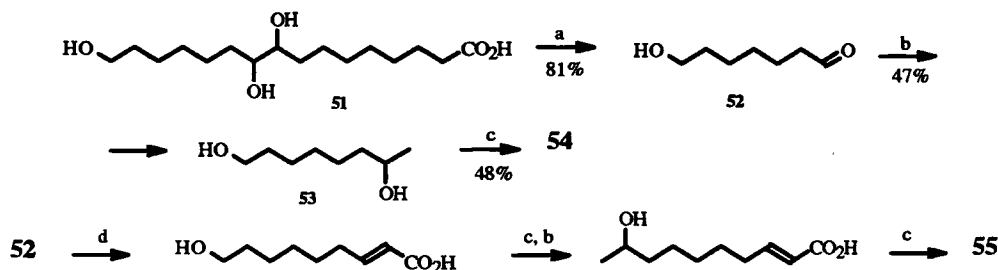

a) NaIO$_4$/MeOH; b) MeMgI; c) PCC/CH$_2$Cl$_2$; d) H$_2$C(COOH)$_2$/Py

The ketoaldehyde (54) has also been obtained by reducing 7-oxooctanoic acid [120]. In place of the ketoaldehyde (54), its synthetic equivalent — the 7-octenal (56) - has been used in the synthesis of acids (46) and (55) [121].
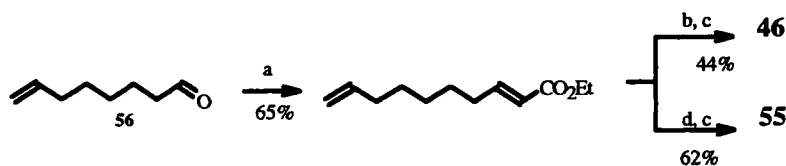
a) (MeO)$_2$P(O)CH$_2$CO$_2$Et/NaH, THF, 20C, 3h; b) O$_2$/PdCl$_2$-CuCl/DMF-H$_2$O, 20°C, 10h; c) NaOH/MeOH-H$_2$O; d) 9-BBN/THF, 20°C; 30% H$_2$O$_2$/3M NaOH, 20°C, 1h

Tetradec-11E-en-1-ol (57) and its acetate (58) and tetradec-11E-enal (59) have been synthesized [123] by a modified Knoevenagel reaction [122].
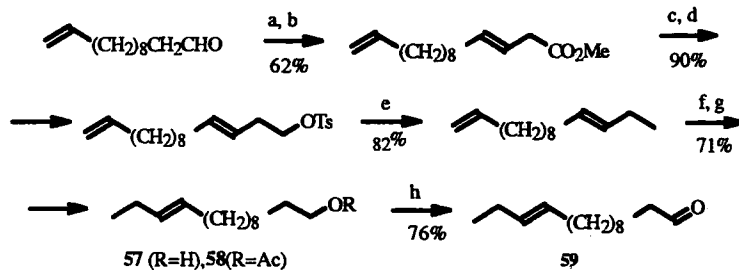
a) CH$_2$(CO$_2$H)$_2$/Pip; b) MeOH/TsOH; c) DIBAH/PhMe; d) TsCl/Py; e) LiAlH$_4$/Et$_2$O, 0°C; f) DIBAH/ZrCl$_4$, O$_2$, 5% HCl; g) Ac$_2$O/Py; h) PCC/CH$_2$Cl$_2$

This modification of the Knoevenagel reaction has been used in the synthesis of a number of pheromones with an (E)-alkene fragment [124]: in particular, dodec-3E-en-1-yl acetate (60) — the main component of the sex pheromones of the beet-mining moth *Scrobipalpa ocellatella* and the potato moth *Scrobipalposis solanivora* [125].
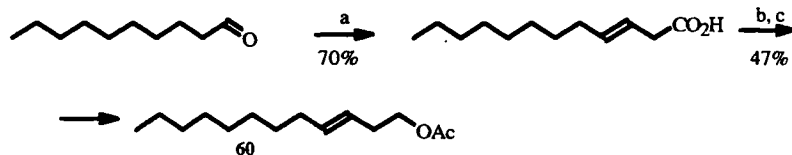
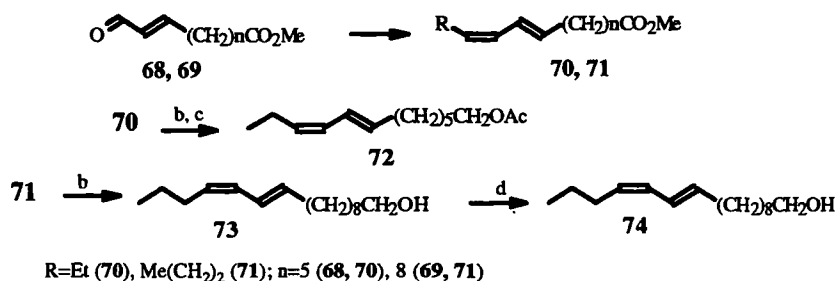a) $CH_2(CO_2H)_2/Pip$; b) $LiAlH_4$; c)Ac_2O/Py

Interesting synthetic possibilities are opened up by the discovery of the reaction of ketenylidenetriphenylphosphorane (61) with Grignard reagents [126], giving, after hydrolysis, acylmethylidenetriphenylphosphoranes (62) the interaction of which with aldehydes leads to E-α,β-unsaturated ketones (63). Carbonyl-containing analogs of pheromones (64), (65) are formed with ω-acetoxy derivatives of aldehydes [126]. Hydrolysis of the phosphorane (66) in an acid medium led to the ketoaldehyde (54), the interaction of which with methoxycarbonylmethylidenetriphenylphosphorane gave the methyl ester (67), while subsequent alkaline hydrolysis led to the queen substance of the honeybee (55) [126].
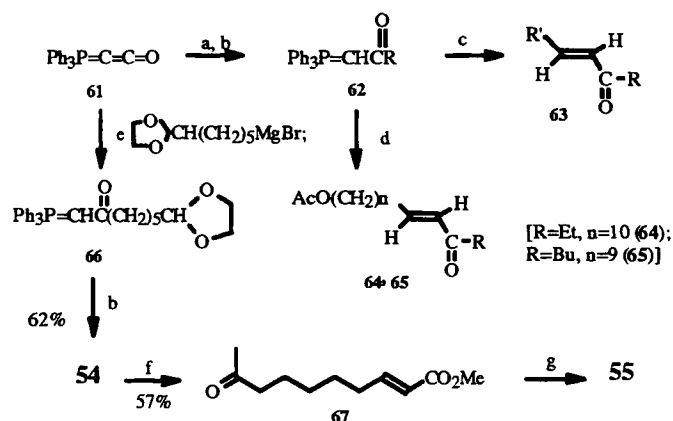
a) RMgBr/THF; b) H_3O^+; c) R′CHO; d) $AcO(CH_2)_nCHO$ (n=9, 10);
f) $Ph_3P=CHCO_2Me$; g) HO⁻

SYNTESIS OF DI- AND TRIENIC PHEROMONES WITH CONJUGATED DOUBLE BONDS

The Wittig reaction and its modifications are widely used in the synthesis of di- and trienic compounds with double bonds of the (Z)- or (E)- configuration or containing simultaneously double bonds of both geometries. By using a (Z)-selective Wittig reaction or by coupling alk-2E-enals with alkylidenetriphenylphosphoranes, pheromones with alka-E,Z-dienic structures are obtained. Thus, dodeca-7E,9Z-dienoates (70) and hexadeca-10E,12Z-dienoates (71) (with isomeric purities of 92.5%) have been synthesized by the interaction of the (E)-α,β-unsaturated aldehydes (68) and (69) with propylidene- and pentylidenetriphenylphosphoranes, respectively. Reduction of the dienoate (70) and acylation of the alcohol obtained gave dodeca-7E,9Z-dien-1-yl acetate (72)— the sex pheromone of the European grape moth *Lobesia botrana* — while reduction of the dienoate (71) and oxidation of the alcohol formed gave successively hexadeca-10E,12Z-dien-1-ol (73) and hexadeca-10E,12Z-dienal (74) — components of the sex pheromone of the silkworm moth *Bombyx mori* [127, 128].

$$O \diagdown\diagup\diagup (CH_2)nCO_2Me \longrightarrow R\diagdown\diagup\diagup\diagup (CH_2)nCO_2Me$$

68, 69   **70, 71**

70 $\xrightarrow{b, c}$ $\diagdown\diagup\diagup (CH_2)_5CH_2OAc$

72

71 $\xrightarrow{b}$ $\diagdown\diagup\diagup (CH_2)_8CH_2OH$ $\xrightarrow{d}$ $\diagdown\diagup\diagup (CH_2)_8CH_2OH$

73   **74**

R=Et (**70**), Me(CH$_2$)$_2$ (**71**); n=5 (**68, 70**), 8 (**69, 71**)

a) RCH=PPh$_3$; b) LiAlH$_4$; c) Ac$_2$O/Py; d) PCC/CH$_2$Cl$_2$

The Horner olefination of 7-*tert*-butoxyheptenal (**75**) followed by the low-temperature hydride reduction of the ester (**76**) formed the alcohol (**77**); this was converted into the phosphonium salt (**78**), which was used in a Wittig reaction with propanal, leading to a mixture (53:47) of the (7E,9Z)- (**79**) and (7E,9E)- (**80**) isomers of the *tert*-butyl ether of dodeca-7,9-dien-1-ol, which was converted into the pheromone (**72**) [129].


79 (7E, 9Z), **80** (7E, 9E)
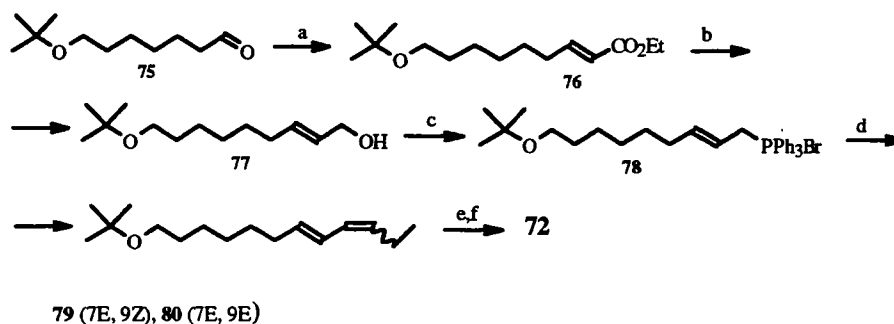
a) (EtO)$_2$P(O)CH$_2$CO$_2$Et; b) LiAlH$_4$, -78°C; c) [Ph$_3$PBr]$^+$Br$^-$/PhH; d) EtCHO; e) Ac$_2$O/FeCl$_3$;
f) column chromatography (CC)/SiO$_2$

A convenient synthon for obtaining the pheromone (**72**) and a number of other (di- and trienic) pheromones has proved to be 4,4-dimethoxybut-2E-enal (**81**) [130].

2E, 4Z/2E, 4E=85:15
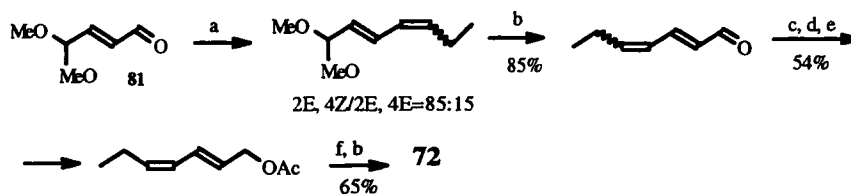
a) MeCH$_2$CH$_2$PPh$_3$Br/NaNH$_2$; b) H$_3$O$^+$/0°C; c) NaBH$_4$/Et$_2$O, 0°C; d) Ac$_2$O/Py; e) CC/SiO$_2$;
f) THPO(CH$_2$)$_8$MgBr/Li$_2$CuCl$_4$

The Wittig coupling of the ω-halogenated 2E-unsaturated aldehydes (**82**) gave predominantly the dodeca-7E9Z-dien-1-yl halides (**83**) (contamination with the 7E,9E- isomer did not exceed 12%), readily convertible into the acetate (**72**) [131].

**82**   **83**

X=Br, Cl

a) EtCH=PPh$_3$; b) AcONa

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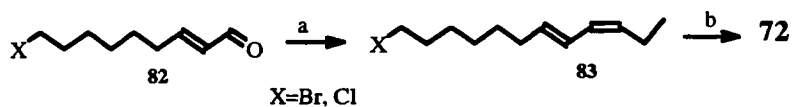
Alk-2E-enals are formed predominantly on the elimination of hydrogen halides from α-halogen derivatives of acetals of the corresponding aldehydes. 9-Hydroxynon-2E-enal (84), converted by the Wittig reaction into the pheromone (72), was obtained in this way [132]. A convenient route to the preparation of alk-2E-enals, including ω-hydroxy-substituted compounds, is the acetylene—allene isomerization of alk-2-yn-1-ols under the action of strong bases [133]. This method has also been used in the synthesis of the sex pheromone of the European grape moth *Lobesia botrana* (72).
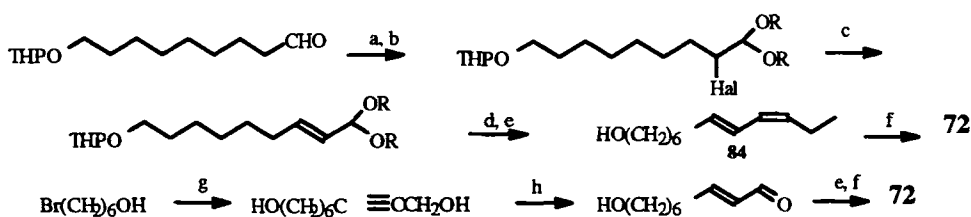
a) ROH$_2^+$; b) [HAl]; c) OH$^-$; d)H$_3$O$^+$; e) EtCH=PPh$_3$; f) Ac$_2$O/Py; g) LiOCH$_2$C≡CLi; h) BuLi

In the synthesis of the E/Z-dienyl acetates (72) and (91) a two-stage transformation of the ω-hydroxy derivatives of the alk-2-yn-1-ols (85) and (86) into the corresponding alk-2E-enals (89) and (90) by the E-selective reduction of the triple bond and subsequent oxidation of the corresponding E-allyl alcohols (87) and (88) was used [134, 135].
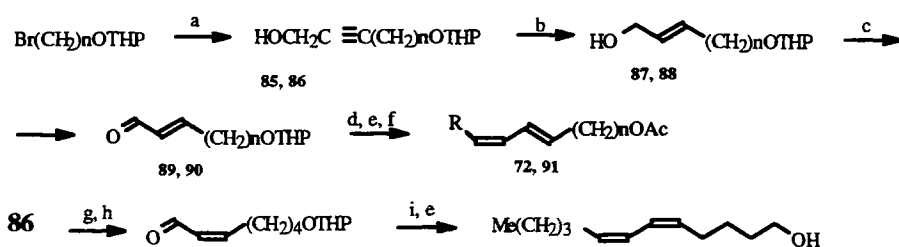

R=Et (72), Me(CH$_2$)$_3$ (91); n=4 (86, 88, 90, 91), 6(72, 85, 87, 89)

a) HC≡CCH$_2$OH/NH$_2$Li; b) LiAlH$_4$; c) PCC/CH$_2$Cl$_2$; d) RCH=PPh$_3$; e) H$_3$O$^+$; f) AcCl/Py;
g) H$_2$/Ni-2P; h) MnO$_2$; i) BuCH=PPh$_3$

Sex pheromones with the Z,E-configuration have been synthesized by using formylolefination followed by the Wittig reaction [136]. Thus, in reactions with the imide generated from (formylmethyl)triphenylarsonium bromide (95) in the presence of K$_2$CO$_3$, the aldehydes (92—94) gave the corresponding E-α,β-unsaturated aldehydes (90), (96), and (97) (yields 75—90%), the interaction which with alkylidenephosphoranes proceeded with high selectivity and led with good yields to the corresponding olefination products the subsequent transformation of which — shown in the scheme — gave tetradeca-3Z,5E-dien-1-yl acetate (98), dodeca-5Z,7E-dien-1-ol (99), dodeca-5Z,7E-dien-1-yl acetate (100), dodeca-5E,7Z-dien-1-ol (101), and dodeca-5E,7Z-dienal (102) — components of the sex pheromones of *Prionoxystus robiniae*, *Dendrolimus spectabilis*, *Dendrolimus punctatus*, and *Malacosoma californicum* [136].

The coupling of unsubstituted alk-E-enals with the ylide generated from an ω-acetoxyalkyltriphenylphosphonium salt by the action of sodium bis(trimethylsilyl)amide has yielded alka-Z,E-dienyl acetates or alka-Z,E-dienals. In this way, from hept-2E-enal and the phosphonium salt (103) was synthesized dodeca-5Z,7E-dienal (104) — the sex pheromone of the pine caterpillar moth *Dendrolimus pini* [137].
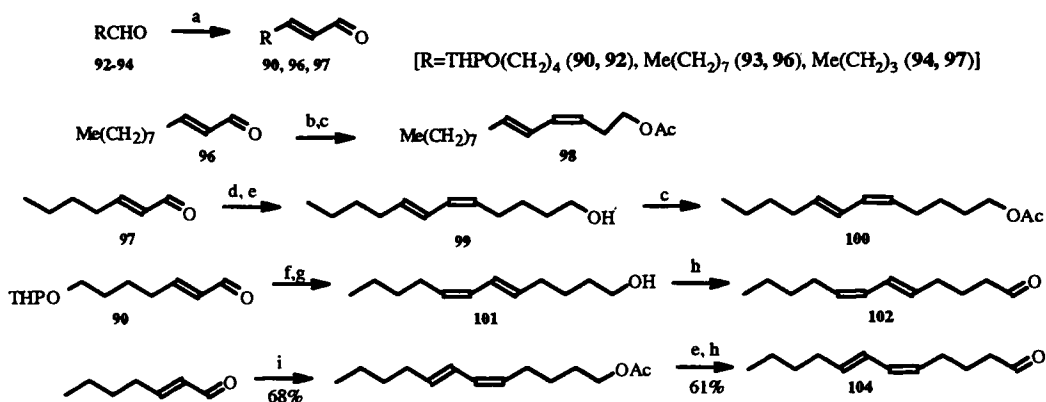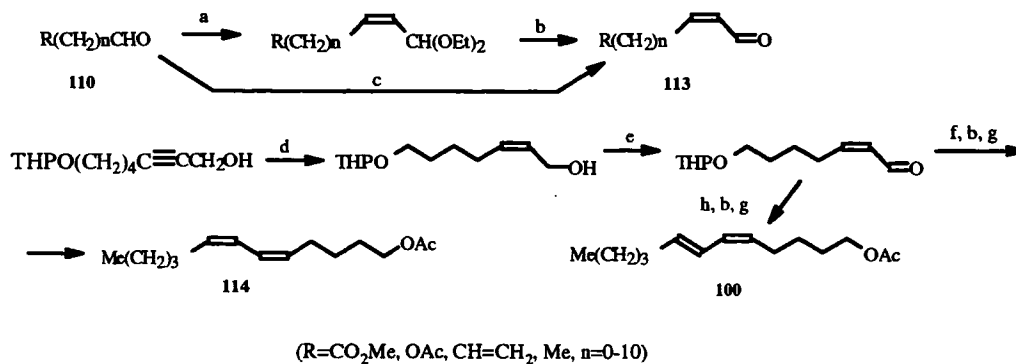
a) [Ph₃AsCH₂CHO]⁺Br⁻ (95)/K₂CO₃/Et₂O-THF-(traces of) H₂O; b) [Ph₃P(CH₂)₃OTHP]⁺Br⁻/BuLi/THF-HMPA;

c) Ac₂O/Py; d) AcO(CH₂)₄CH=PPh₃; e) EtOH/OH⁻; f) BuCH=PPh₃; g) MeOH₂⁺; h) PCC/CH₂Cl₂;

i) [Ph₃P(CH₂)₅OAc]⁺Br⁻ (103)/ (TMS)₂NNa

The interaction of hex-2E-enal with the imide generated from 10-hydroxydecenyltriphenylphosphonium bromide (105) gave the di-E,E-enic alcohol (106), the oxidation of which led to hexadeca-10E,12E-dienal (107) — the main component of the sex pheromone of the spiny bollworm *Earias insulana*, containing 20% of the 10E,12Z- isomer [138]. The reaction between 7-(tetrahydropyran-2-yloxy)hept-2E-enal (90), a *n*-pentyltriphenylphosphonium salt, and two moles of *n*-BuLi led to the predominant (95%) formation of the dienic compound (108) the hydrolysis of which and acylation of the resulting alcohol gave dodeca-5E,7E-dien-1-yl acetate (109) — a component of the sex pheromones of insects of the family Lasiocampidae [134, 139].
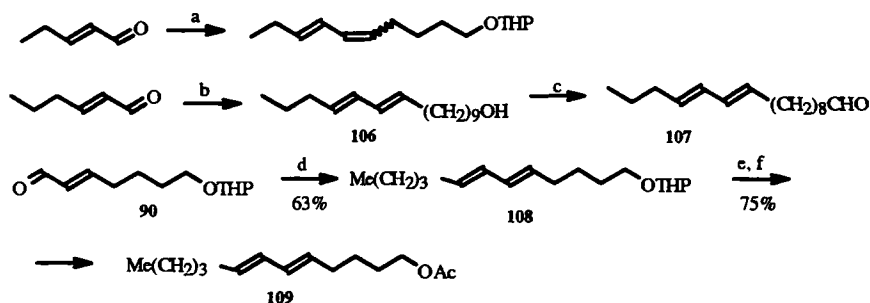
a) [Ph₃P(CH₂)₄OTHP]⁺Br⁻/BuLi; b) [Ph₃P(CH₂)₁₀OH]⁺Br⁻(105)/ 2BuLi/THF; c) PCC/CH₂Cl₂;

d) Me(CH₂)₄PPh₃Br/2BuLi; e) H₃O⁺; f) AcCl/Py

The alk-2Z-enals (113) were synthesized by the reaction of aldehydes (110) with (2,2-diethoxyethylidene) triphenylphosphorane (111) [53] and (ethoxyvinylidene)triphenylphosphorane (112) [137]. On being involved in a Z-selective Wittig reaction, the alk-2Z-enes gave Z,Z-dienic components of pheromones, while E-directed olefination led to di-Z,E-enic systems. The dodeca-5Z,7Z- and -5Z,7E-dienyl acetates (114) and (100), which are components of a number of sex pheromones, were synthesized in this way [140, 141].

R(CH₂)nCHO $\xrightarrow{a}$ R(CH₂)n⟍⟋CH(OEt)₂ $\xrightarrow{b}$ R(CH₂)n⟍⟋=O
110   **113**

$\xrightarrow{c}$

THPO(CH₂)₄C≡CCH₂OH $\xrightarrow{d}$ THPO⟍⟋⟍⟋⟍OH $\xrightarrow{e}$ THPO⟍⟋⟍⟍=O $\xrightarrow{f, b, g}$

↓ h, b, g

Me(CH₂)₃⟍⟋=⟍⟍OAc   Me(CH₂)₃⟍=⟍⟍⟍OAc
114   **100**

(R=CO₂Me, OAc, CH=CH₂, Me, n=0-10)

a) Ph₃P=CHCH(OEt)₂ (111); b) H₃O⁺; c) Ph₃P=C=CHOEt (112); d) H₂/Ni-P2; e) PCC/CH₂Cl₂;
f) Me(CH₂)₃CH=PPh₃; g) Ac₂O/Py; h) Me(CH₂)₄PPh₃Br/2BuLi

The interaction of 5-tetrahydropyranyloxyhex-2E-enal (**115**) with the phosphonium salt (**116**) in the presence of potassium *tert*-butanolate, followed by hydrolysis and acetylation, constituted the synthesis of hexadeca-4E,6Z,10Z-trien-1-yl acetate (**117**) — a trienic component of the sex pheromone of *Conopomorpha cramerella* [142].
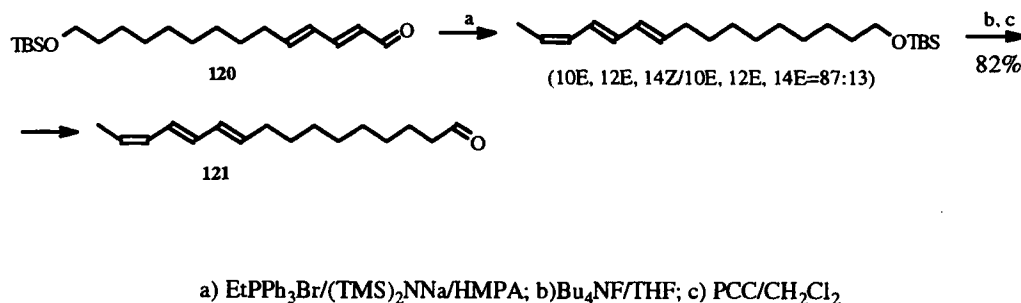
Dodeca-3Z,6Z,8E-trien-1-ol (**119**) — the trail pheromone of the termite *Reticulitermes virginicus* — has been obtained by the olefination of hex-2E-enal with the phosphorane (**118**), generated from but-3-yn-1-yl bromide followed by hydroxyethylation of the terminal acetylene and hydrogenation of the resulting β-hydroxyacetylene [143].

THPO⟍⟋⟍=O $\xrightarrow{a, b, c}$ ⟍⟋⟍⟋=⟍⟋⟍=⟍⟍OAc
115   **117**

⟍⟋⟍=O $\xrightarrow{d, e, f}$ ⟍⟋⟍=⟍=⟍⟍OH
                               119

a) Me(CH₂)₃ /\ (CH₂)₃PPh₃Br (**116**)/t-BuOK; b) Py · TsOH; c) Ac₂O/Py;
d) HC≡CCH₂CH=PPh₃ (**118**); e) Li NH₂/CH₂CH₂O; f) H₂/Pd-CaCO₃
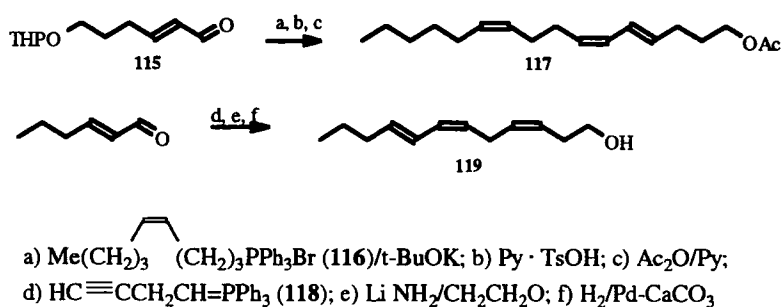
Hexadeca-10E,12E,14Z-hexadecatrienal (**121**), the sex pheromone of the tobacco horn worm *Manduca sexta* L., has been synthesized by the olefination of the ω-hydroxy derivative of the 2,4-dienic aldehyde (**120**) with the ylide generated from ethyltriphenylphosphonium bromide under the action of sodium silazide, followed by removal of the protection from the hydroxy group and its oxidation [144].


TBSO⟍⟍⟍⟍⟍=⟍=O $\xrightarrow{a}$ ⟍=⟍=⟍⟍⟍⟍⟍OTBS $\xrightarrow{b, c}$
120   (10E, 12E, 14Z/10E, 12E, 14E=87:13)   82%

$\longrightarrow$ ⟍=⟍=⟍⟍⟍⟍⟍=O
121

a) EtPPh₃Br/(TMS)₂NNa/HMPA; b)Bu₄NF/THF; c) PCC/CH₂Cl₂

270

With the aim of synthesizing hexadeca-10Z,12E,14E-trienyl acetate (122) and its geometric isomers, which are among the probable sex pheromones of the mulberry pyralid, hex-2E,4E-enal was coupled with 10-hydroxydecylidenetriphenylphosphorane. This gave a mixture of (10Z,12E,14E)-, (10E,12E,14E)-, (10Z,12E,14Z)-, and (10E,12E,14Z)- isomeric alcohols in a ratio of 67:21:9:3, after the acetylation of which the desired acetate (122) was isolated by HPLC [145].
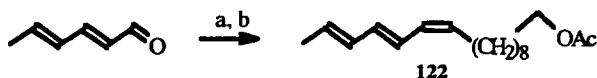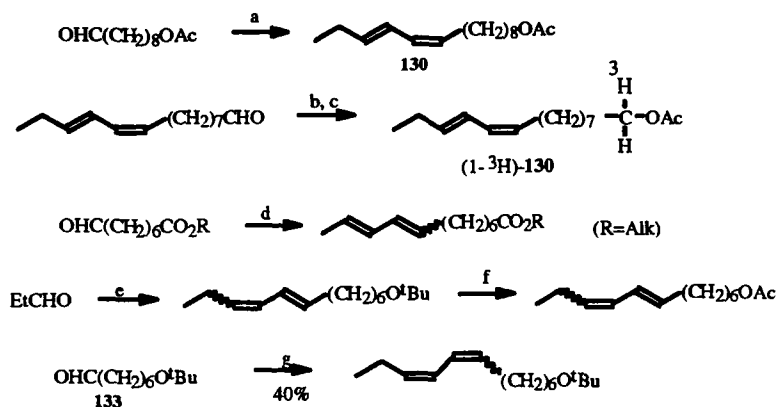

a) HO(CH$_2$)$_{10}$PPh$_3$Br/(TMS)$_2$NLi/THF; b) Ac$_2$O/Py

By the reaction of 2-fluoroundec-2Z-enal (123) with the phosphorane generated from the phosphonium salt (124), a mixture of the isomeric 5-fluorotetradecadi-3Z,5Z- and -3E,5Z-en-1-ols was obtained, and this was separated chromatographically on Florisil. The 3Z,5Z-dienic alcohol (125) was converted into the corresponding acetate (126), which is the fluorinated analog of the pheromone of the carpenterworm *Prionoxystus robiniae* [146]. The interaction of 3-bromododec-2-enal (127) with carbomethoxymethylidenetriphenylphosphorane or trimethyl phosphonoacetate gave a mixture of 2E- and 2Z-isomers, which were separated by HPLC. Reduction of the bromine derivative with the E-configuration by divalent chromium ions led to the allenic compound (128) — the racemic analog of the sex pheromone of the dried-bean beetle *Acanthoscelides obtectus* [147].
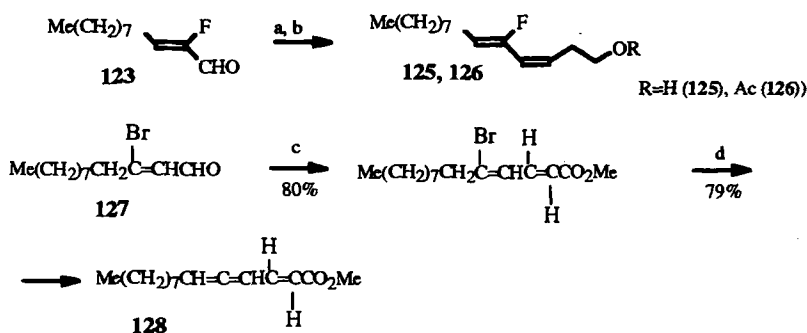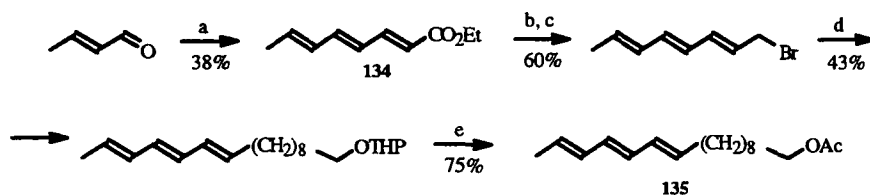

a) [EEO(CH$_2$)$_3$PPh$_3$]$^+$Cl$^-$ (124)/BuLi; b) H$_3$O$^+$; c) Ph$_3$P=CHCO$_2$Me; d) CrCl$_2$/AcOH/THF-HMPA

Another approach to the construction of conjugated dienic pheromones consists in the use of α,β-unsaturated phosphoranes. Thus, the interaction of pent-2-enylidenetriphenylphosphorane, generated from the phosphonium salt (129) and sodium hydride in DMSO, with 9-acetoxynonanal has given tetradeca-9Z,11E-dienyl acetate (130), the main component of the sex pheromone of *Spodoptera littoralis* [148]. The tritylated pheromone (1-^{3}H)-(130) has been synthesized by reducing tetradeca-9Z,11E-dienal with NaBT$_4$, followed by acetylation [149]. According to other reports, the olefination of 8-oxooctanoic ester with the ylide generated from the phosphonium salt (131) with the aid of sodium hexamethyldisilazide took place nonstereospecifically with the formation of a mixture of E/Z- isomers at the Δ^8-double bond in a ratio of 66:34 (at room temperature) and 47:53 (at -78°C). Moreover, at room temperature, isomerization of the double bond in the ylide took place, with the formation of about 52% of 10Z- isomers [127]. The 2E-unsaturated ω-tert-butoxy-substituted ylide generated from the phosphonium salt (132) under conditions of interphase catalysis by the action of aqueous alkali reacted with propionaldehyde nonstereospecifically to form a mixture of the 7E,9Z- and 7E,9E- isomers in a ratio of 53:47 [150]. The reaction of pent-2Z-enylidenetriphenylphosphorane with the ω-hydroxy-substituted aldehyde (133) formed a mixture of geometric isomers of the tert-butyl ether of dodeca-7,9-dien-1-ol the main components of which were the 7Z,9Z- and the 7E,9Z-isomers (49.5 and 40.5%, respectively) [151].
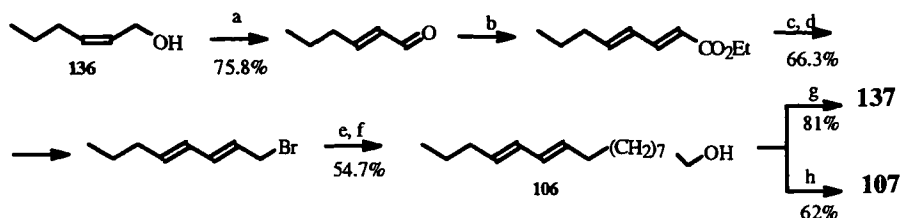
271

OHC(CH$_2$)$_8$OAc $\xrightarrow{a}$ ⟍⟋⟍⟋⟍(CH$_2$)$_8$OAc
130

⟍⟋⟍⟋(CH$_2$)$_7$CHO $\xrightarrow{b, c}$ ⟍⟋⟍⟋⟍(CH$_2$)$_7$ $-\overset{\overset{3}{\overset{H}{|}}}{\underset{\underset{H}{|}}{C}}-$OAc

(1-^{3}H)-**130**

OHC(CH$_2$)$_6$CO$_2$R $\xrightarrow{d}$ ⟍⟋⟍⟋⟍(CH$_2$)$_6$CO$_2$R (R=Alk)

EtCHO $\xrightarrow{e}$ ⟍⟋⟍⟋⟍(CH$_2$)$_6$O^{t}Bu $\xrightarrow{f}$ ⟍⟋⟍⟋⟍(CH$_2$)$_6$OAc

OHC(CH$_2$)$_6$O^{t}Bu $\xrightarrow[40\%]{g}$ ⟍⟋⟍⟋⟍(CH$_2$)$_6$O^{t}Bu
133

a) [EtCH=CHCH$_2$PPh$_3$]$^+$Br$^-$ (**129**)/NaH/DMSO; b) NaB^{3}H$_4$; c) Ac$_2$O/Py;

d) [MeCH=CHCH$_2$PPh$_3$]$^+$Br$^-$ (**131**)/(TMS)$_2$NNa;

e) [^{t}BuO(CH$_2$)$_6$CH=CHCH$_2$PPh$_3$]$^+$Br$^-$ (**132**)/ 0.5N NaOH/CH$_2$Cl$_2$-H$_2$O;

f) Ac$_2$O/FeCl$_3$; g) EtCH=CHCH=PPh$_3$

It has been possible to perform a stereoselective olefination of crotonaldehyde by means of a modified Wittig-Horner reaction [152] and to obtain, via the intermediate E,E,E-trienic ester (**134**), hexadeca-10E,12E,14E-trien-1-yl acetate (**135**) — the sex pheromone of the mulberry pyralid *Glyphodes pyloalis* [153].
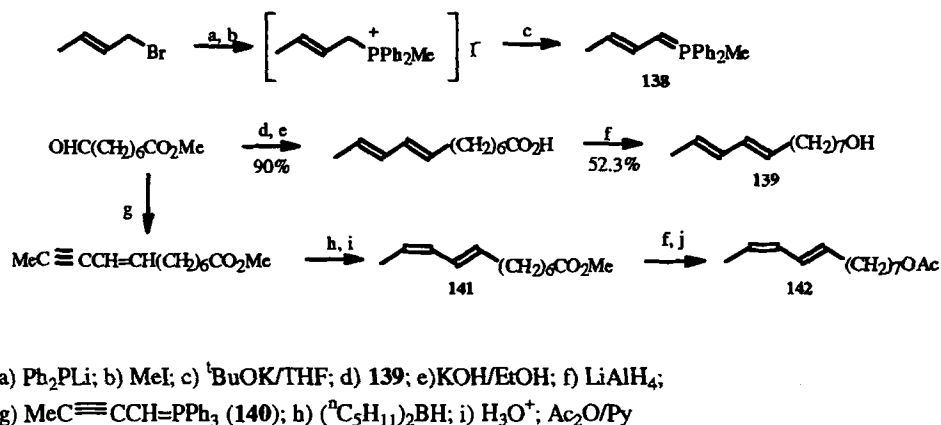
⟍⟋⟍⟋O $\xrightarrow[38\%]{a}$ ⟍⟋⟍⟋⟍CO$_2$Et $\xrightarrow[60\%]{b, c}$ ⟍⟋⟍⟋⟍Br $\xrightarrow[43\%]{d}$ **134**

$\xrightarrow{}$ ⟍⟋⟍⟋⟍(CH$_2$)$_8$⟍OTHP $\xrightarrow[75\%]{e}$ ⟍⟋⟍⟋⟍(CH$_2$)$_8$⟍OAc
135

a) (EtO)$_2$P(O)CH$_2$CH=CHCO$_2$Et/NaH, THF, 0°C; b) LiAlH$_4$; c) PBr$_3$/Py, Et$_2$O, 20°C;

d) THPO(CH$_2$)$_8$MgBr/Li$_2$CuCl$_4$; e) AcCl/AcOH, 40°C, 16h

Hexadeca-10E,12E-dien-1-ol (**106**) and the acetate (**137**) and aldehyde (**107**) corresponding to it, which are components of the sex pheromone of the sphingid moth *Smerinthus jamaiscensis*, have been synthesized from hex-2E-enal, obtained by the oxidation of hex-2Z-en-1-ol (**136**) with pyridine chlorochromate [154].

⟍⟋⟍OH $\xrightarrow[75.8\%]{a}$ ⟍⟋⟍O $\xrightarrow{b}$ ⟍⟋⟍CO$_2$Et $\xrightarrow[66.3\%]{c, d}$
136

$\xrightarrow{}$ ⟍⟋⟍⟋Br $\xrightarrow[54.7\%]{e, f}$ ⟍⟋⟍⟋(CH$_2$)$_7$⟍OH
106

$\xrightarrow[81\%]{g}$ **137**

$\xrightarrow[62\%]{h}$ **107**

a) PCC/CH$_2$Cl$_2$; CC (Al$_2$O$_3$); b) (MeO)$_2$P(O)CH$_2$CO$_2$Et/NaH, THF, 25°C;

c) LiAlH$_4$/Et$_2$O, 0-5°C; d) PBr$_3$Py/Et$_2$O; e) BrMg(CH$_2$)$_8$OTHP/Li$_2$CuCl$_4$, THF, -10°C;

f) TsOH/MeOH, 25°C; g) Ac$_2$O/Py; h) PCC/CH$_2$Cl$_2$

It has also been found that if alk-2E-enylidenetriphenylphosphoranes are replaced by alk-2E-enylidenediphenyl-alkylphosphoranes the olefination of aldehydes in the absence of lithium salts takes place stereospecifically with high yields of the alka-E,E-dienic compounds [155]. Thus, the pheromone (139) has been synthesized with the aid of but-2E-enylidenediphenylmethylphosphorane (138) [155, 156]. The olefination of the aldehyde by the stabilized ylide (140) took place as an E-selective Wittig reaction, and, after reduction of the triple bond by hydroboration, the ester (141) with the 8E,10Z-configuration (containing less than 10% of other isomers) was formed, and this was converted into dodeca-8E,10Z-dien-1-yl acetate (142) [127].

a) Ph$_2$PLi; b) MeI; c) ^{t}BuOK/THF; d) 139; e)KOH/EtOH; f) LiAlH$_4$;

g) MeC≡CCH=PPh$_3$ (140); h) (^{n}C$_5$H$_{11}$)$_2$BH; i) H$_3$O$^+$; Ac$_2$O/Py

The Wittig olefination of ethyl 10-oxodecanoate with the phosphorane generated from the trimethylsilyl derivative of propargyltriphenylphosphonium bromide (143), followed by the transformation of the ester obtained (144) into the enynes (145) and (146), led, after cis-selective hydrogenation of the triple bond in (146), to bombykol (73). Analogously, dodeca-5Z,7E-dien-1-ol — a component of the sex pheromone of the forest tent caterpillar Malacosoma disstria — was obtained from (143) and valeraldehyde [157].


a) BuLi/Et$_2$O-THF, -78°C; b) OHC(CH$_2$)$_8$CO$_2$Et; c) NH$_4$F/DMF, 20°C, 8h;

d) LiAlH$_4$/Et$_2$O, 20°C; e) PrBr/HMPA; f) Zn/CuCl$_2$/H$_2$O
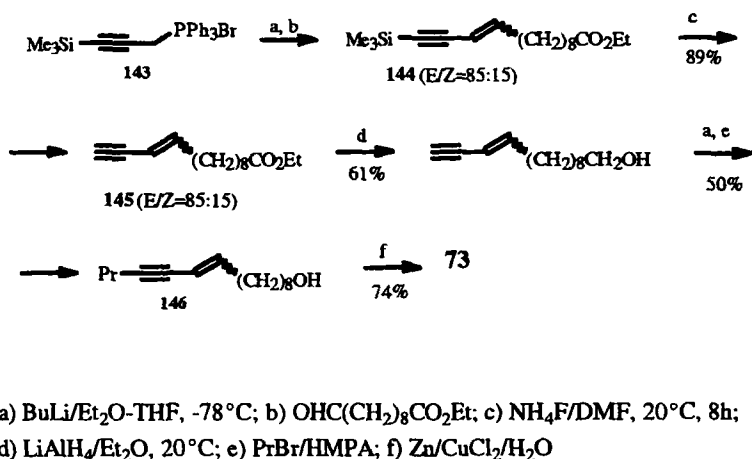
The olefination of the aldehyde (148) with the aid of an allyltitanium derivative generated from 1-tert-butylthio)-3-(trimethylsilylprop-1-ene (147) led to the diene (149), which was used in stereoselective coupling with a Grignard reagent catalyzed by nickel(II)-1,3-bis(diphenylphosphino)propane dichloride [158]. After oxidation of the alcohol (150) and olefination of the resulting aldehyde the 2E,6Z,8E-trienic ester (151) was obtained, and the isomerization of its Δ^2-double bond under the action of potassium bis(trimethylsilyl)azide led to the Z-Δ^3- isomeric ester (152), which was converted into dodeca-3Z,6Z,8E-trien-1-ol (153) — the trail pheromone of subterranean termites [158—160].
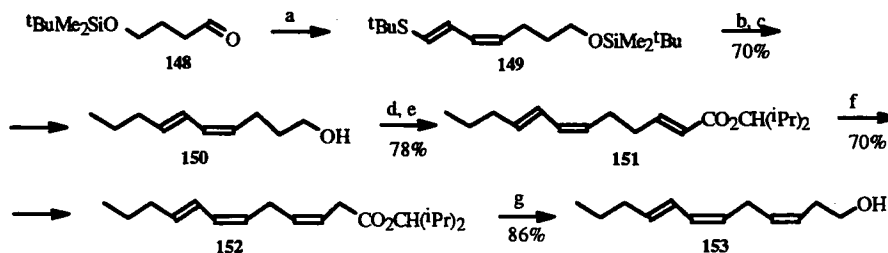
a) $^tBuSCH=CHCH_2TMS$ (147)/$^tBuLi/Ti(O^iPr)_4$; b) $PrMgI/Ni(dppp)Cl_2$; c) Bu_4NF/THF;

d) $NCS\cdot Me_2S$; e) $(EtO)_2P(O)CH_2CO_2CH^iPr_2$; f) $(TMS)_2NK$; g) $LiAlH_4$

By the Woodward—Horner—Emmons reaction, the phosphonate (154) and octanal produced a mixture of methyl E,Z- and E,E-dodecadienoates (155) which were isomerized under the action of a base into a mixture of methyl dodeca-3E,5Z- and -3E,5E-dienoates (156) with the E,Z- isomer predominating, the reduction of which, followed by acetylation of the resulting alcohol, led to a mixture of the corresponding acetates. This mixture of stereoisomeric acetates was subjected to HPLC, with the isolation of dodeca-3E,5Z-dien-1-yl acetate (157) — the sex pheromone of *Phtheochroa cranaodes* [161].
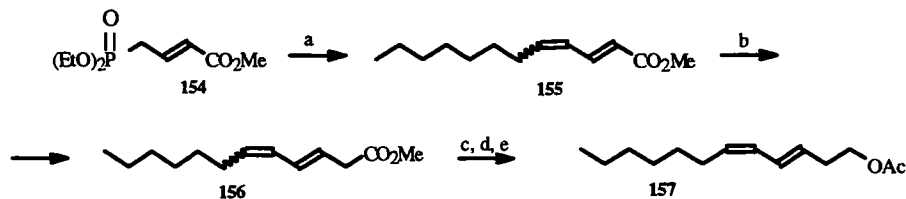

a) $Me(CH_2)_6CHO/LDA$, $-78\,°C$; b) $LDA/MeN\overset{\displaystyle C(O)}{\underset{\displaystyle (CH_2)_2}{\diagdown\diagup}}ME$; c) DIBAH; d) Ac_2O/Py; e) HPLC

## SYNTESIS OF DI- AND TRIENIC PHEROMONES WITH HOMOCONJUGATED DOUBLE BONDS

The synthesis of pheromone components with double bonds separated by one methylene group (homoconjugated) makes use of either β,γ-unsaturated aldehydes or β,γ-unsaturated phosphoranes [53, 162].

Tetradeca-9Z,12E-dien-1-yl acetate (161) — the pheromone of the flour moths *Plodia interpunctella* and *Anagasta kuhniella* — has been synthesized by the use of an (E)-stereoselective Julia reaction and a (Z)-stereoselective Wittig reaction, starting from the methylcyclopropylcarbinol (158) via the intermediate homoallyl bromide (159) and the dienoate (160) [163—166].
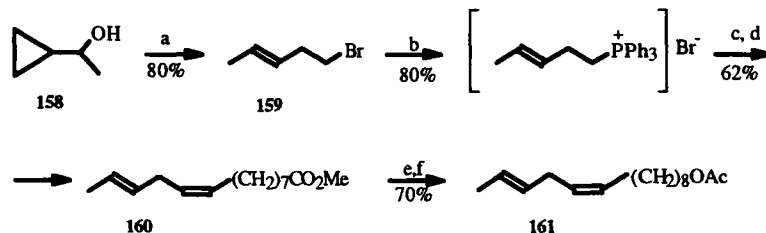
a) 48% HBr; PPh_3; c) (TMS)_2NNa; d) OHC(CH_2)_7CO_2Me; LiAlH_4; f) Ac_2O/Py

The olefination of hexanal with the phosphonate (163) obtained by a Pummerer rearrangement of the methylsulfinylmethanephosphonate (162) in the presence of hex-5-en-1-yl acetate yielded the intermediate (164) the desulfonylation of which, with subsequent stages of hydrolysis and acetylation, led to trideca-4E,7Z-dien-1-yl acetate (165) — a component of the sex pheromone of the potato tuberworm moth *Phthorimaea operculella* [167].

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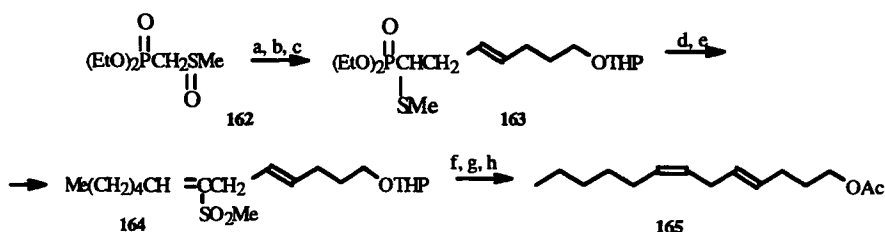
a) TFA/TFAA/CH$_2$=CH(CH$_2$)$_4$OAc; b) K$_2$CO$_3$/MeOH-H$_2$O; c) DHP; d) MCPBA;
e) Me(CH$_2$)$_4$CHO; f) NaHSO$_3$; g) TsOH · Py; h) Ac$_2$O/Py

A homoallyl iodide with the Z- configuration (166), obtained by the partial ozonolysis of 1-methoxycyclohexa-1,4-diene was converted into a triphenylphosphonium salt, from which the corresponding phosphorane was generated, and the latter was coupled with 6-hydroxyhexanal, giving in the final account the Z,Z-dienic α,ω-diol (167), which was then converted into the ω-fluorinated analog (168) of a Z,Z-dienic alcohol [168].
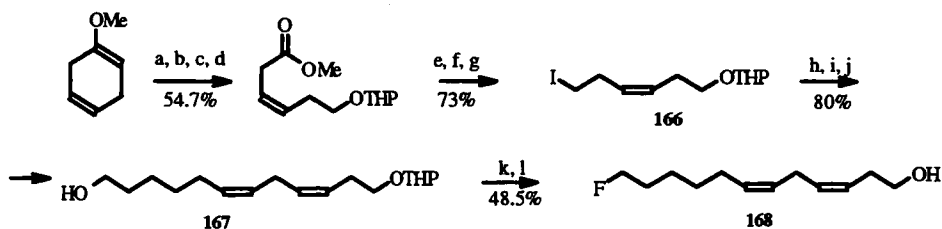
a) O$_3$/MeOH; b) Me$_2$S; c) NaBH$_4$/EtOH; d) DHP/TsOH; e) LiAlH$_4$; f) TsCl/Py;
g) NaJ/Me$_2$CO; h) PPh$_3$; i) BuLi; j) HO(CH$_2$)$_5$CHO; k) Et$_2$NSF$_3$; l)TsOH/MeOH

The olefination of aldehydes under the action of the silylated alkyltriphenylphosphonium salt (169) and a desilylating agent — cesium fluoride — took place with a high stereodirectivity, leading to alk-4-en-1-ynes and, after the Z- or E-selective reduction of the triple bond, to, respectively, alka-1Z,4Z- or -1E,4E-dienic components of pheromones [169]. The dienyl acetate (161) and nonadeca-6Z,9Z-diene (170) — components of the sex pheromones of many species of Noctuidae and of the pine looper *Bupalus piniarius* were obtained in this way [169]. This reaction has also been used in the synthesis of methylene-separated alka-1Z,4Z,7Z-trienes, such as, for example, nonadeca-3Z,6Z,9Z-triene (171) — a component of the sex pheromone of the avocado pest *Boarmia selenaria* (giant looper) [169]. The diene (170) has been synthesized by couping hexanal with the ylide generated by the action of sodium hexamethyldisilazide on the phosphonium iodide (172) obtained in five stages from undecyne [170].

In the first stage of the synthesis of the triene (171) use was made of the phosphonate modification of the the Wittig reaction. The hexadeca-2E,6Z-dienoate (173) so obtained was isomerized to the 3Z,6Z-hexadienoate (174) and this was converted into the corresponding dienal, the olefination of which with n-propylidenetriphenylphosphorane completed the synthesis [171].

The olefination of 4-(ethylenedioxy)hexanal (176), obtained from furfural, with the ylide prepared from the phosphonium salt (175), synthesized in four stages from undec-1-yne, led to the dienic acetal (177) the acid hydrolysis of which gave nonadeca-6Z,9Z-dien-3-one (178) — a component of the sex pheromone of the grape moth (willow beauty) *Peribatodes (Boarmia) rhomboidaria* [172].
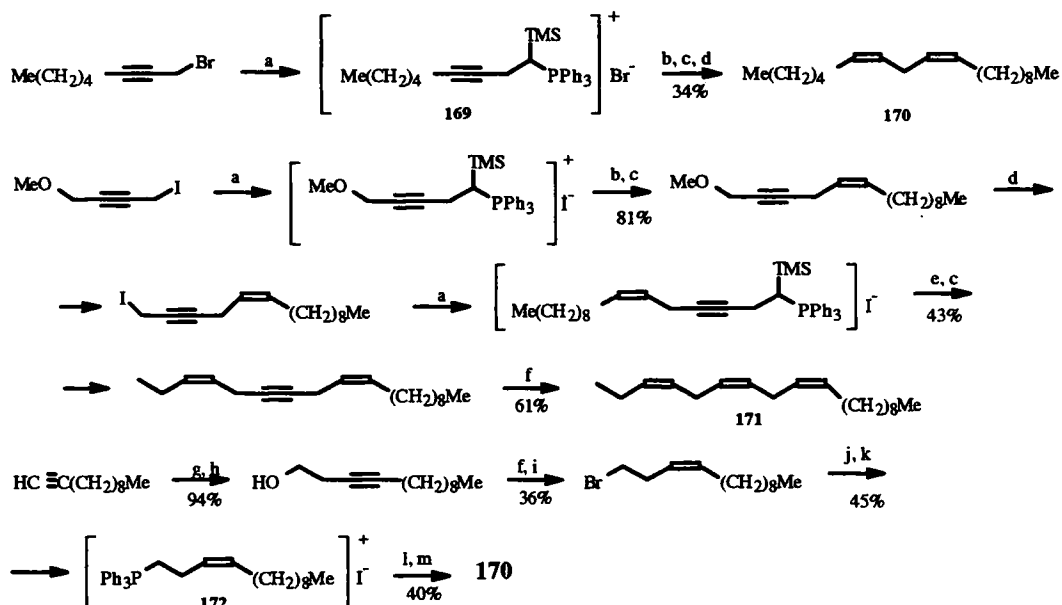
a) Ph₃P=CHTMS; b) Me(CH₂)₈CHO; c) CsF; d) TMSI; e) EtCHO; f) H₂/Ni-P2; g) EtMgBr; h) CH₂CH₂O;
i) CBr₄ · PPh₃; j) NaI/Me₂CO; k) PPh₃; l) (TMS)₂NNa; m) Me(CH₂)₄CHO
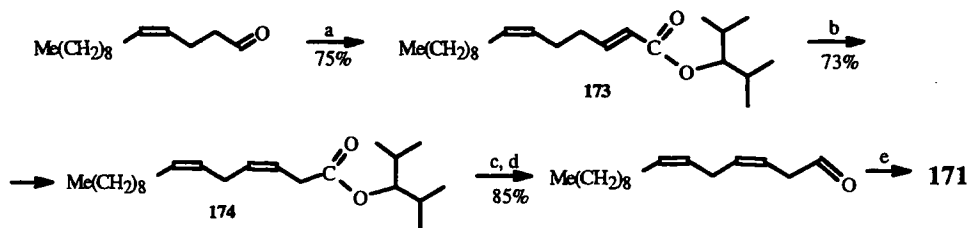
a) $(EtO)_2P(O)CH_2COOCHPr_2^i/NaH$, THF; b) $(TMS)_2NK$; c) $LiAlH_4/Et_2O$; d) CrO_3/Py, CH_2Cl_2;
e) $[PrPPh_3]^+Br^-/(TMS)_2NNa$, THF
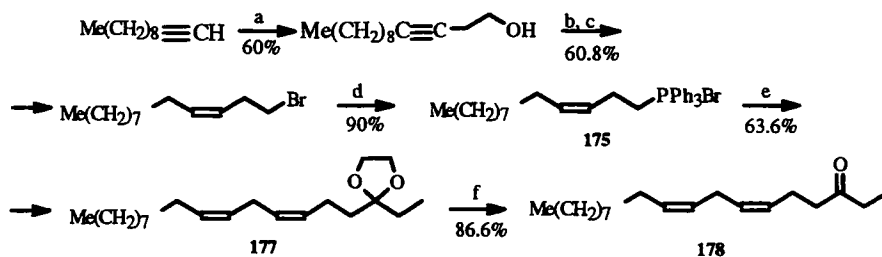
a) LiNH₂/HMPA, CH₂-CH₂-O; b) H₂/Ni-P2/(CH₂NH₂)₂EtOH; c) PPh₃·Br₂·Py/CH₂Cl₂; d) PPh₃;
e) (TMS)₂NNa/MeCH₂CCH₂CH₂CHO (176)/THF; f) 5% HCl/Me₂CO

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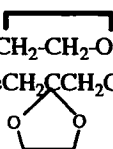
SYNTHESIS OF DI- AND TRIENIC PHEROMONES WITH ISOLATED DOUBLE BONDS

In the synthesis of alka-1,5- and -1,6-dienic pheromones, either Δ^4 and Δ^5-unsaturated aldehydes are olefinated or appropriately unsaturated phosphoranes are used for the olefination of saturated aldehydes [53]. For the synthesis of 4Z- and 5Z-unsaturated aldehydes (182) use has been made of the olefination of aldehydes by the appropriate ylides (179) generated from phosphonium salts with the aid of sodium disilazide.

$$Ph_3P = CH(CH_2)mCO_2R \xrightarrow{a} Me(CH_2)n \diagdown (CH_2)mCO_2R \xrightarrow{b}$$

179   **180**

$$\longrightarrow Me(CH_2)n \diagdown (CH_2)mCH_2OH \xrightarrow{c} Me(CH_2)n \diagdown (CH_2)mCHO$$

181   **182**

$$EtC \equiv C(CH_2)_3OH \xrightarrow[80\%]{d} \diagdown\diagup\diagdown OH \xrightarrow[58\%]{c} \diagdown\diagup\diagdown O$$

(n=0-5; m=2, 3)
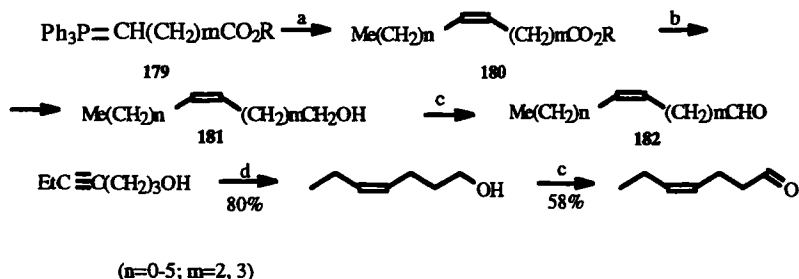
a) Me(CH₂)ₙCHO; b) LiAlH₄; c) PCC/AcONa/CH₂Cl₂; d) H₂/Pd-CaCO₃-PbO

The alk-4Z- and -5Z-enoates obtained (180) (containing ~2.5% of the E- isomers) were converted into the desired aldehdyes (182) via the alcohols (181) [53]. Hept-4Z-enal has been obtained by the hydrogenation of hept-4-yn-1-ol over a Lindlar catalyst and subsequent oxidation of the resulting hept-4Z-en-1-ol by pyridinium chlorochromate [173].

The stereoselective cleavage of 2-alkyl-3-chlorotetrahydropyrans (183) has been used to obtain the alk-4E- and -5E-enyl derivatives (183) [53].
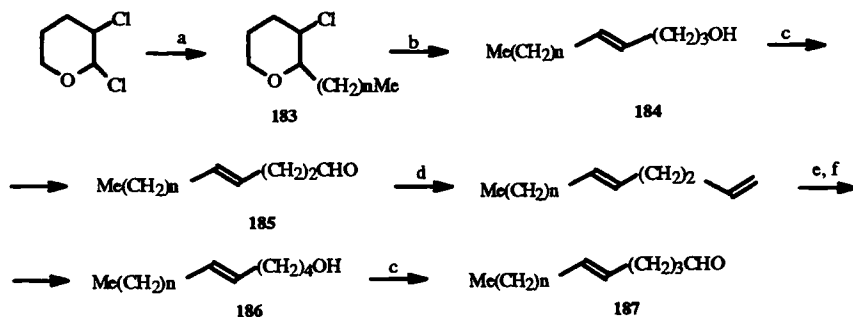
$$\text{(structures 183, 184)} \xrightarrow{a} \cdots \xrightarrow{b} Me(CH_2)n \diagdown (CH_2)_3OH \xrightarrow{c}$$

183   **184**

$$\longrightarrow Me(CH_2)n \diagdown (CH_2)_2CHO \xrightarrow{d} Me(CH_2)n \diagdown (CH_2)_2 \diagup\diagdown \xrightarrow{e, f}$$

185

$$\longrightarrow Me(CH_2)n \diagdown (CH_2)_4OH \xrightarrow{c} Me(CH_2)n \diagdown (CH_2)_3CHO$$

186   **187**

a) Me(CH₂)ₙMgBr; b) Na; c) PCC/CH₂Cl₂; d) Ph₃P=CH₂; e) 9-BBN; f) H₂O₂/OH⁻

Via the corresponding bromides and triphenylphosphonium salts, the alcohols (181), (184), and (186) have been converted into alk-Z- and -E-enylidenetriphenylphosphoranes, which, together with the aldehydes (182), (185), and (187), have been used in the synthesis of the sex pheromones of Lepidoptera [127, 174].

The coupling of the aldehyde (188) with the ylide generated by treating pentyltriphenylphosphonium bromide with butyllithium has given (after the replacement of the THP protection by an acetyl group) an equimolar mixture of hexadeca-7Z,11Z- and -7Z,11E-dien-1-yl acetates (189 and (190) (gossyplure), which exhibits attractant properties for the pink bollworm *Pectinophora gossypiella* [174]. Gossyplure has also been synthesized from the aldehydoester (191) [175].
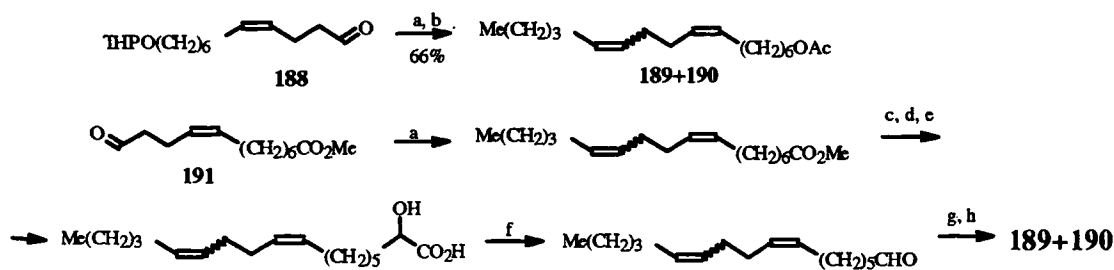
a) $[Me(CH_2)_4PPh_3]^+Br^-/^nBuLi$; b) AcOH/AcCl; c) KOH/aq MeOH; d) LDA/HMPA/THF; e) O_2; f) $NaIO_4$; g) $NaBH_4$;

h) Ac_2O/Py

The stereoselective occurrence of the coupling of Z- and E-unsaturated phosphoranes generated from the phosphonium salts (192) and (193) with 7-(tetrahydropyran-2-yloxy)heptanal [176] or 7-acetoxyheptanal [177] has formed the basis of the synthesis of the individual Z,Z- and Z,E- isomers (189) and (190) of gosssyplure.
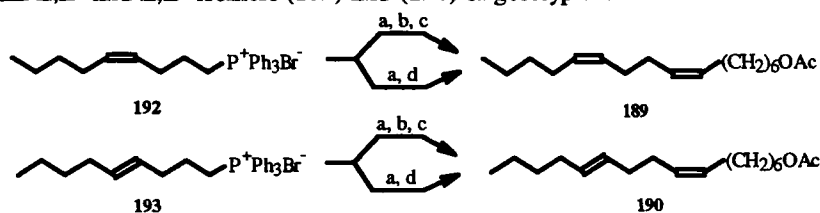
a) $(TMS)_2NNa/THF$, -60°C, 2h; -40°C, 4h; b) $THPO(CH_2)_6CHO$; c) AcCl/AcOH;

d) $AcO(CH_2)_6CHO$

Undec-4Z-enal, obtained from 2-methylpyridine, has been olefinated with the phosphorane generated from octadecyltriphenylphosphonium bromide with the aid of sodium hexamethyldisilazide, which led to nonacosa-7Z,11Z-diene (194) — the contact pheromone of Drosophila melanogaster [178, 179]. Another synthesis of pheromone (194) has used the unsaturated ylide generated from undec-4Z-enyltriphenylphosphonium iodide [180].
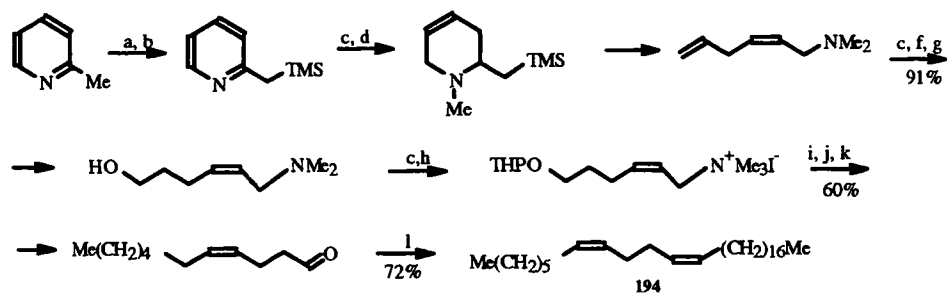
a) LDA; b) TMSCl; c) MeI/MeOH; d) $NaBH_4$; e) CsF/THF; f) BBN; g) $H_2O_2/NaOH$; h) DHP/H^+;

i) $Me(CH_2)_4MgCl/Li_2CuCl_4$; j) H_3O^+; k) PCC/CH_2Cl_2; l) $[PPh_3(CH_2)_{17}Me]^+Br^-/(TMS)_2NNa$

The action on the phosphonium salt (195) of sodium bis(trimethylsilyl)azide and then of 3-acetoxypropionaldehyde yielded octadeca-3Z,13Z-dien-1-yl acetate (196) — the sex pheromone of the lesser peachtree borer Synanthedon pictipes [181, 182]. The coupling of aldehyde (197) with pentylidenetriphenylphosphorane permitted the synthesis of hexadeca-6E,11Z-dien-1-yl acetate (198) and hexadeca-6E,11Z-dienal (199), which are components of the sex pheromone of the lappet moth Antherea polyphemus [183, 184]. The interaction of the Z,Z-dienic aldehyde (200) with the phosphorane (201) generated by the action of two molar equivalents of a base on 3-bromopropan-1-ol led to an equimolar mixture of the 3Z,7Z,11Z- and 3E,7Z,11Z-isomers of hexadecatrien-1-ol [138]. Analogously, the Z,Z-dienal (202) and the ω-hydroxyalkylidenephosphorane (203) have

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given a mixture (1:1) of the 5Z,9Z,13Z- and 5E,9Z,13Z- isomers of hexadecatrienyl acetate (204) — minor components of the sex pheromone of the processionary moth *Thaumetopoea pityocampa* [185]. The reaction of dec-6Z-enal (205) with 4-hydroxybutyltriphenylphosphonium bromide and a threefold excess of n-butyllithium led to tetradeca-4E,10Z-dien-1-ol, the acetylation of which gave the corresponding acetate (206) — a sex attractant of the apple leaf miner *Lithocolletis ringoniella* [186].
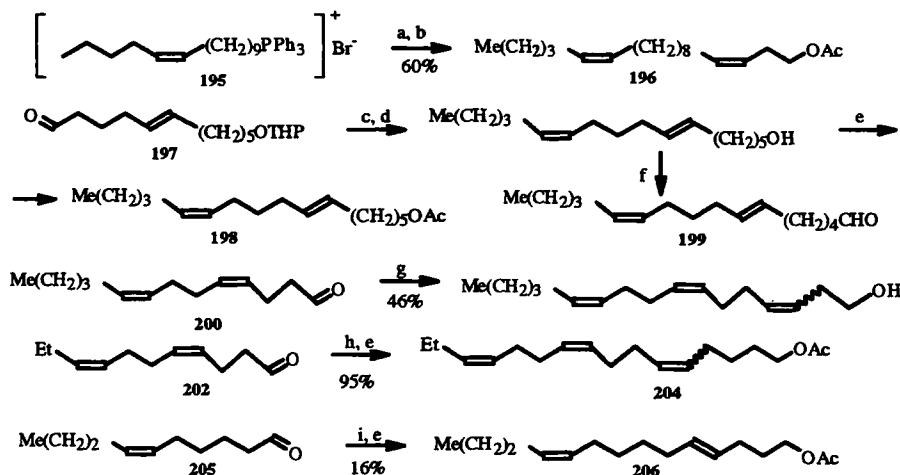
a) (TMS)$_2$NNa; b) AcO(CH$_2$)$_2$CHO; c) Ph$_3$P=CH(CH$_2$)$_3$Me; d) H$_3$O$^+$; e) Ac$_2$O/Py;
f) PCC/CH$_2$Cl$_2$; g) Ph$_3$P=CH(CH$_2$)$_2$O$^-$ (201) h) Ph$_3$P=CH(CH$_2$)$_4$OLi (203);
i) [HO(CH$_2$)$_4$PPh$_3$]$^+$Br$^-$/BuLi

The cyclic ylide (208), obtained from 1,1-diphenylphosphanium bromide (207), has been used in the synthesis of gossyplure. The action on compound (207) of potassium tert-butanolate in the presence of 7-(tetrahydropyran-2-yloxy)heptanal formed with a high yield the alkenylphosphine oxide (209), treatment of which with n-butyllithium and valeraldehyde gave the diastereomeric alcoholates (210) and (211), which were converted by heating in HMPA followed by acetylation into a mixture (1:1) of hexadeca-7Z,11Z- and -7Z,11E-dien-1-yl acetates (189) and (190) [187].
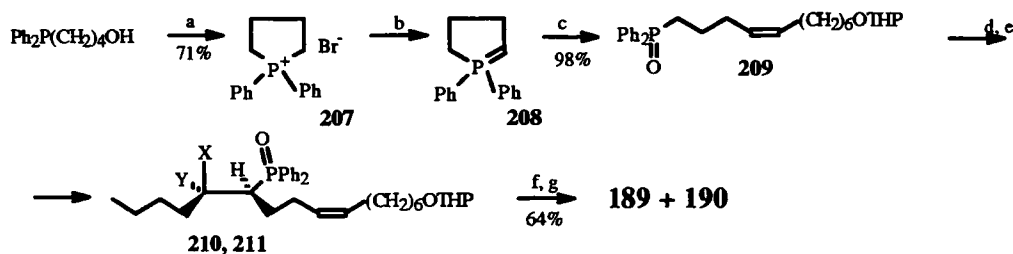
210 (X=OLi, Y=H),211 (X=H, Y=OLi)

a) HBr; b) ^{t}BuOK; c) THPO(CH$_2$)$_6$CHO; d) BuLi; e) Me(CH$_2$)$_3$CHO; f) HMPA/t°; g) AcOH/AcCl

Interaction of the Grignard reagent (212) with the phosphorane (61) yielded the phosphorane (213), which was used for the olefination of nonanal. Selective reduction of the resulting enone (214) gave heneicosa-1,6Z-dien-11-one (215) — a minor component of the sex pheromone of the peach fruit moth [188].
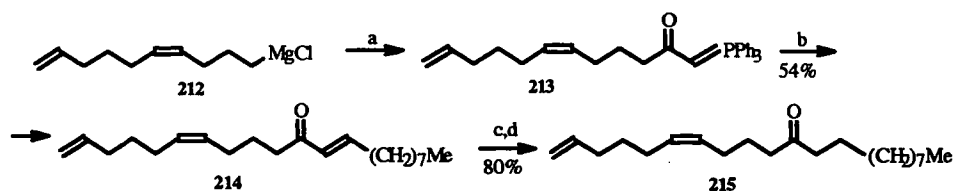
a) Ph$_3$P=C=C=O (61); b) Me(CH$_2$)$_7$CHO; c) NaAlH$_2$(OCH$_2$CH$_2$OMe)$_2$; d) H$_3$O$^+$

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The (Z,E)-dienoate (**217**) was synthesized by the Wittig—Horner reaction using hexadec-11Z-enal (**216**) as the carbonyl substrate, and its hydride reduction followed by acetylation of the resulting alcohol led to octadeca-2E,13Z-dien-1-yl acetate (**218**) — a component of the sex pheromone of the currant clearwing moth *Synanthedon tipuliformis*, while another component of this pheromone — octadeca-3E,13Z-dien-1-yl acetate (**219**) has been obtained by a modified Knoevenagel reaction of the aldehyde (**217**) with malonic acid [189].
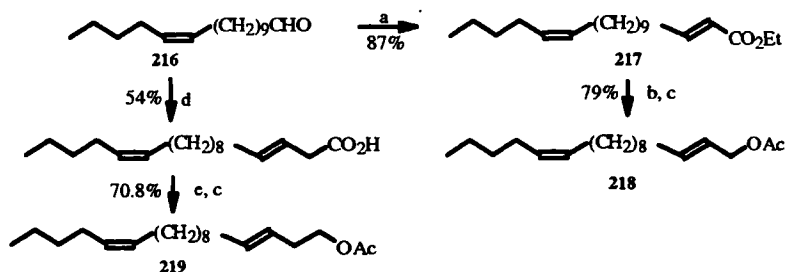
a) Ph₃P=CHCO₂Et; b) DIBAH; c) AcCl/Py; d) CH₂(CO₂H)₂/Pip·AcOH; e) LiAlH₄/Et₂O

The pheromone (**219**) has also been synthesized with the use of Julia's sulfone modification [191, 192] in the stage of the (Z)-olefination of the aldehyde (**220**), while the formation of the transoid double bond took place as the result of a cyclopropylcarbinyl rearrangement of compound (**221**) [193].
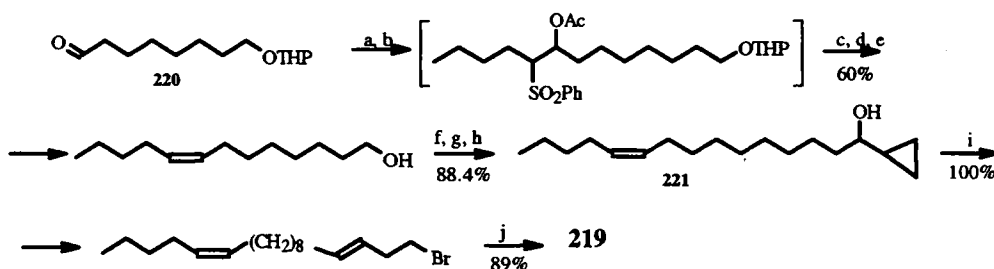
a) Me(CH₂)₄SO₂Ph/BuLi, c-C₆H₁₂-THF, -10°C; b) Ac₂O/DMAP; c) NaOH/MeOH; d) Na₂S₂O₄/NaHCO₃, EtOH-H₂O;
e) TsOH·Py/MeOH; f) BuLi/Ph₃CH/c-C₆H₁₂, Et₂O, HMPA, -30°C; TsCl, 25°C; NaBr/DMF, 50°C; g) NC₆H₁₁/LDA/THF-
c-C₆H₁₂; h) LiAlH₄/Et₂O; i) TMSBr/ZnBr₂/CH₂Cl₂; j) AcOK/18-Crown-6/MeCN

The sex pheromone of *Synanthedon tenuis*, having the structure of octadeca-3Z,13Z-dien-1-yl acetate (**223**), has been synthesized by the olefination of the acetylenic aldehyde (**222**) [190].
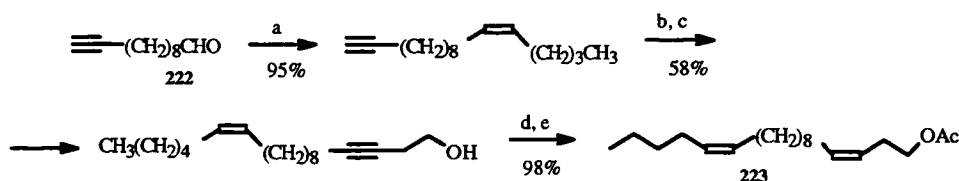
a) CH₃(CH₂)₃CH=PPh₃; b) NaNH₂/THF; THPOCH₂CH₂Br; c) H₃O⁺; d) H₂/Pd·CaCO₃; e) Ac₂O/Py

Thus, in the regio- and stereoselective construction of double bonds during the synthesis of pheromones with an acetogenin structure wide use is made of the conversion of carbonyl compounds into alkenes by interaction with phosphorus ylides — the Wittig reaction [41] — and also a number of its modifications — the phosphonate [34], silicone [37], boron [40], and sulfone [191] modifications.

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