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SYNTHESIS OF *Lepidoptera* PHEROMONES USING ACETYLENES

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Syntheses of acetogenin pheromones using acetylene derivatives are reviewed.

Key words: acetogenin pheromones, synthesis, literature review.

The chemistry of pheromones has developed extensively during the last three decades. Success in the identification, synthesis, and application of pheromones as alternatives to traditional means of controlling insect populations has been documented in reviews and monographs during the 1980s and 1990s [1-9]. Achievements in the synthesis of pheromones from the *Lepidoptera* family of insects, among which are species that inflict much damage to forests and farms, have been reported. Such pheromones include compounds that are mono-, di-, and trienes with either the (*Z*)- or (*E*)-configuration. Several reviews [1, 4, 5, 9] include publications from before 1983. A review on the synthesis of these pheromones using the Wittig reaction and its modifications was recently published [10]. The present review examines work primarily from the last 10-15 years that concerns the synthesis of acetogenin pheromones using acetylenes derivatives (acetylenic synthesis).

SYNTHESIS OF MONOENE PHEROMONES

The method using acetylenes became one of the principal means of synthesizing insect pheromones owing to the availability of acetylene and its homologs and their ability to undergo metallation and addition reactions and stereoselective conversions to alkene derivatives with a given (*Z*)- or (*E*)-configuration.

Alkynes are usually selectively hydrogenated to (*Z*)-alkenes over Lindlar catalyst. Performing the reaction in the presence of quinoline gives the best results. The temperature affects the stereoselectivity of the hydrogenation. The content of the (*E*)-isomer usually reaches 1.5-5%. However, increasing the temperature above ambient gives 10% whereas hydrogenation at (-30)-(-10)°C yields the (*Z*)-alkene of 99.5% purity [9]. Alkynes are selectively converted to (*Z*)-alkenes via hydrogenation over $BaSO_4$, Ni-P2 catalyst, and Cu-containing catalyst and via reduction using borohydrides [9, 11-14].

A one-step method for stereospecific conversion of acetylenic aldehydes into (*Z*)-alken-1-ols using 9-borabicyclo[3.3.1]nonane (9-BBN) with subsequent acetolysis of the hydroboration product has been reported [15].

Reduction of acetylenes to the (*E*)-olefins is usually carried out using Na or Li in liquid ammonia. The reaction is highly stereospecific. A different method is used for long-chain alkynes owing to their low solubility in liquid ammonia. The method uses $LiAlH_4$ in THF [16]. Using 9*Z*- (**4**) and 9*E*-dodecen-1-ols (**5**) and the corresponding aldehydes (**6** and **7**) as examples, a general acetylenic synthesis of (*Z*)- and (*E*)-alkenic pheromones from the α,ω-diols can be written [9, 17, 18]. According to Scheme 1, octan-1,8-diol (**1**) is selectively converted to bromohydrin **2**, in which the hydroxyl is protected before reaction with the appropriate lithium alkynide. The acetylene derivative **3** is converted in three steps into the desired alcohols of the (*Z*)- (**4**) or (*E*)-configuration (**5**). Oxidation of these gives the corresponding aldehydes (**6** or **7**).

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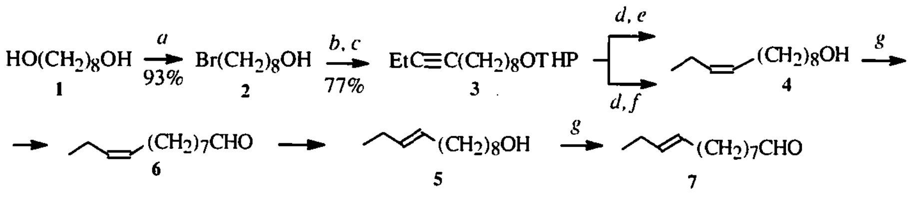
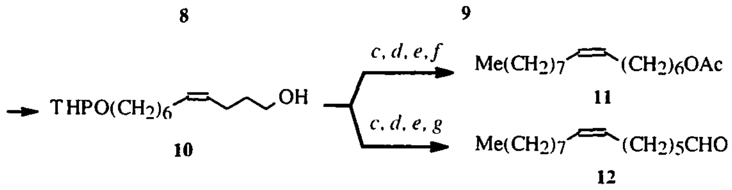


a. HBr; b. DHP/H^+; c. EtC ≡ CLi/NH_3/THP; d. AcCl/AcOH; e. H_2/Pd–$CaCO_3$–PbO; f. OH–; g. PCC/CH_2Cl_2

Scheme 1.

Stereoisomeric 11-hexadecenals [19, 20] and isomeric C_{10}- and C_{12}-alken-1-ols [21, 22], including 7Z-dodecen-1-ol 1-^{14}C-acetate [23], are synthesized analogously.

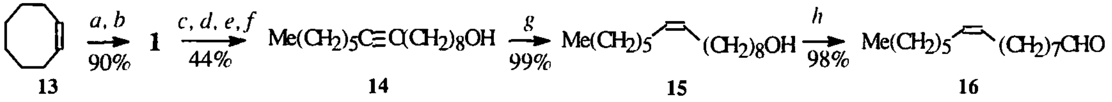
Bromohydrin **8** with a protected hydroxyl is reacted with the dianion generated from pent-4-yn-1-ol to produce selectively substituted α,ω-alkyndiol **9**, which is converted to the corresponding (*Z*)-alkendiol **10**. The last compound is a convenient synthon for 7Z-hexadecen-1-ylacetate (**11**) and 7Z-hexadecenal (**12**) (Scheme 2) [24].



a. HC ≡C$(CH_2)_3$OH/2LiNH_2-NH_3; b. H_2/Pd-$CaCO_3$; c. $MeSO_2Cl$/NEt_3;
d. Me$(CH_2)_4$MgBr/Li_2CuCl_4; e. TsOH/MeOH; f. Ac_2O/Py/DMAP; g. PCC/AcONa/CH_2Cl_2

Scheme 2.

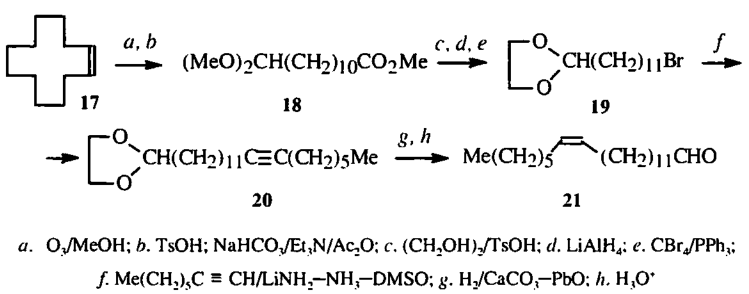
Diol **1**, which is required for the synthesis of 9Z-hexadecenal (**16**), a component of the sex pheromone of the cotton bollworm *Heliotis armigera* (Scheme 3) [25], is prepared by ozonolysis of cyclooctene (**13**). Conversion of the acetylenic alcohol **14** into Z-alkene **15** is effected via a Grignard reaction.



a. O_3; b. $NaBH_4$; c. HBr; d. DHP/H^+; e. Me$(CH_2)_5$C ≡ CLi; f. H_3O^+; g. ^{i}BuMgBr/CP_2TiCl_2; h. PCC/CH_2Cl_2

Scheme 3.

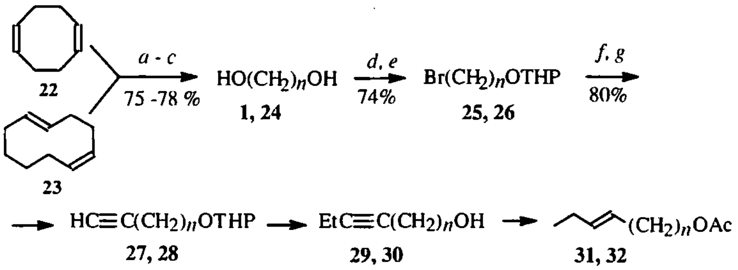
Functionally differentiated ozonolysis of cyclododecene (**17**) through intermediates **18**-**20** provides a convenient route to 13Z-octadecenal (**21**) (Scheme 4) [26].



a. O_3/MeOH; b. TsOH; $NaHCO_3$/Et_3N/Ac_2O; c. $(CH_2OH)_2$/TsOH; d. $LiAlH_4$; e. CBr_4/PPh_3;
f. Me$(CH_2)_5$C ≡ CH/LiNH_2–NH_3–DMSO; g. H_2/$CaCO_3$–PbO; h. H_3O^+

Scheme 4.

Partial ozonolysis of cyclooctadiene (**22**) and cyclodecadiene (**23**) at one of the double bonds with subsequent catalytic hydrogenation of the remaining double bonds and transformation of the resulting diols **1** and **24** through intermediates **25**, **27**, and **29** or **26**, **28**, and **30** according to Scheme 5 gives 9*E*-dodecen- (**31**) and 11*E*-tetradecen-1-ylacetates (**32**) (components of the sex pheromones of the wine moth *Sparganothis pilleriana* and the meadow moth *Loxostege sticticalis*, respectively) [27].



$n = 8$ (**1,25,27,29,31**), 10 (**24, 26, 28, 30,32**)

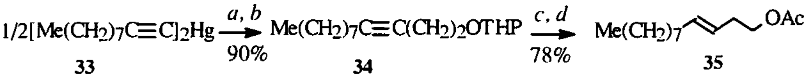
a. O_3/O_2, c-C_6H_{12}-MeOH, 5° C; *b*. H_2/Pd-C; *c*. $NaBH_4$; *d*. 48%HBr; *e*. DHP/TsOH;

f. HC ≡ CH/$LiNH_2$; *g*. Li-NH_3; EtBr/THF-DMSO

Scheme 5.

Acetylenides of alkali metals that are generated by reaction of Li or Na with alkynes are reacted with alkyl halides, as a rule, in liquid ammonia. However, polar aprotic solvents are added to increase the yield if higher alkynes are used [9]. Metallation of alkynes using butyllithium or alkylmagnesium halides is carried out in ethers [28-30].

Lithium acetylenides can be obtained through mercury bis(alkynides) [31]. This method was used to synthesize several (*Z*)- and (*E*)-alken-1-ylacetates, which are components of several insect species [32-39]. As an example, Scheme 6 shows the synthesis of 3*E*-dodecen-1-ylacetate (**35**), the principal component of the sex pheromone of the beet leaf-miner moth *Scrobipalpa ocellatella*, via transformations of mercury bis(decynide) (**33**) through the intermediate alkynol **34** [38].



a. Li/THF; *b*. CH_2CH_2/DMSO ; *c*. $LiAlH_4$/THF, *d*. Ac_2O/Py
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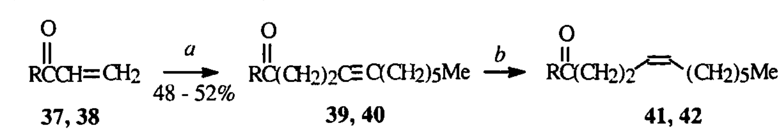
Scheme 6.

Addition of Cu—Zn reagents to 1-haloalkynes and acetylenic ethers produce acetylenic precursors of pheromones [40]. We should mention a communication [41] about the addition of diethyl(oct-1-yn-1-yl)aluminum (**36**) to 1-alkenones (**37**, **38**) to give 7-alkyn-11-ones (**39**, **40**), which are readily converted to 7Z-nonadecen-11-one (**41**) and 7Z-eicosen-11-one (**42**). These are components of the peach moth *Carposina niponensis* pheromone (Scheme 7).



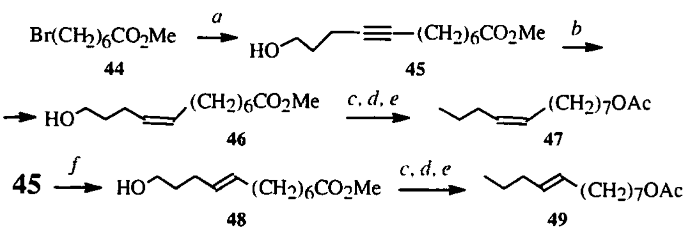
R = $Me(CH_2)_7$ (**37, 39, 41**), $Me(CH_2)_8$ (**38, 40, 42**)

a. $Et_2AlC \equiv C(CH_2)_5Me$ (**36**); *b*. H_2/Pd-$CaCO_3$-PbO

Scheme 7.

Reaction of lithium acetylenide or its homologs with ω-unsaturated bromides or aldehydes produces 1-alkenynes with a terminal or inner triple bond. Ozonolysis of the products occurs selectively at the double bond, providing a convenient route to acetylenic aldehydes and alcohols, key synthons of insect sex pheromones [26, 29, 42, 43].

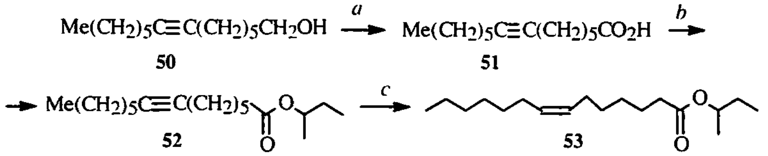
Components of the sex pheromone of the eastern peach moth *Grapholitha molesta* (*Z*)-**47** and (*E*)-**49** 8-dodecen-1-ylacetates can be synthesized by the literature methods [1, 5, 9] and from 4-pentyn-1-ol (**43**) and the methyl ester of 7-bromoheptanoic acid (**44**), the addition of which gave the ester of 11-hydroxy-8-undecynoic acid (**45**). The latter is converted into the corresponding (*Z*)-hydroxyester **46** and then into the desired (*Z*)-acetate **47** [44]. *Trans*-selective reduction of the triple bond in the acetylenic hydroxyester **45** and subsequent conversions of the (*E*)-hydroxyester **48**, identical to those of its *Z*-isomer, give the (*E*)-acetate **49** (Scheme 8).



a. HC ≡ C$(CH_2)_3$OH(**43**)/LiNH_2/NH_3; *b*. H_2/Ni-2P; *c*. MsCl/Py; *d*. LiAlH_4; *e*. Ac_2O/Py; *f*. Na/NH_3

Scheme 8.

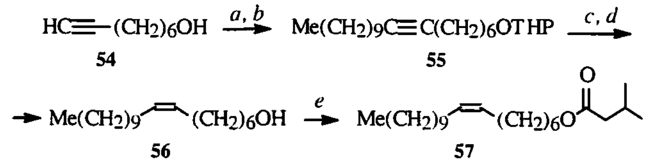
The *sec*-butyl esters of C_{10}- and C_{12}-unsaturated carboxylic acids and the isopropyl and *sec*-butyl esters of 7Z-tetradecenoic acid have been identified as components of the sex pheromone of the grape pest *Harrisin brillians* [45]. Ester **53** was the main component of the pheromone. It was prepared by oxidation of 7-tetradecyn-1-ol **50** with subsequent esterification of alkynoic acid **51** and selective hydrogenation of **52** (Scheme 9) [45, 46].



a. CrO_3; *b*. EtMeCHOH/BF_3•Et_2O; *c*. H_2/Pd-$BaSO_4$

Scheme 9.

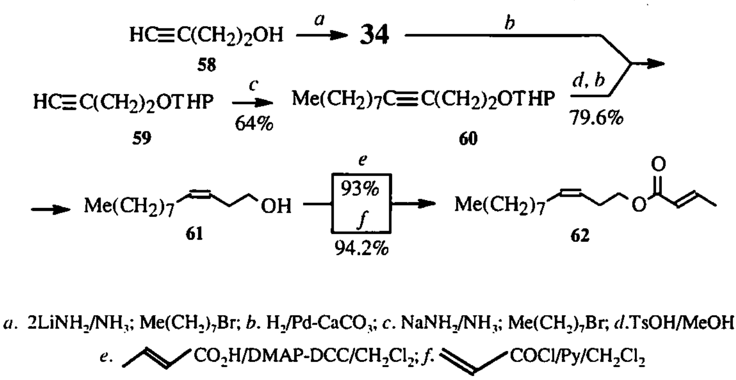
The extract of the pheromone glands of *Euproctis similis* contained 7Z-octadecen-1-yl (**57**), 6Z-octadecen-1-yl, and 9Z-octadecen-1-yl esters of *iso*-valerianoic acid in addition to the 6Z-octadecen-1-yl ester of valerianoic acid [47]. Ester **57** was synthesized from 7-octyn-1-ol (**54**) in five steps through intermediates **55** and **56** (Scheme 10).



a. DHP/H^+; *b*. ^{n}BuLi; Me$(CH_2)_9$Br; *c*. H_2/Pd-C; *d*. H_3O^+; *e*. $Me_2CHCH_2CO_2H/H^+$

Scheme 10.

The sex pheromone of the yam weevil *Cylas formicarius*, 3Z-dodecen-1-yl-2'*E*-butenoate (**62**), was identified among isomeric butenoates of 3-dodecen-1-ols [48]. It was synthesized by alkylation of 3-butyn-1-ol (**58**) [49] or its THP-derivative (**59**) [50] with octylbromide followed by conversion of **34** or **60**, respectively, into 3Z-octen-1-ol (**61**) and its esterified crotonic acid or its chloroanhydride (Scheme 11).



a. $2LiNH_2/NH_3$; $Me(CH_2)_7Br$; *b*. $H_2/Pd\text{-}CaCO_3$; *c*. $NaNH_2/NH_3$; $Me(CH_2)_7Br$; *d*.TsOH/MeOH;
e. $CO_2H/DMAP\text{-}DCC/CH_2Cl_2$; *f*. $COCl/Py/CH_2Cl_2$

Scheme 11.

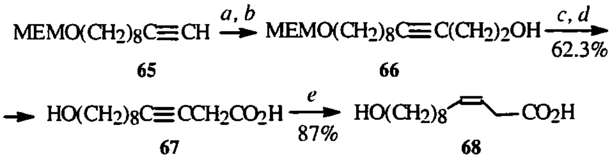
A different synthetic route to **62** used 1-decyne (**63**) as the starting acetylene. It was converted to the *bis*-homolog using bromoacetaldehyde diethylacetal in greater yield than if ethylene bromohydrin THP-ester was used. The final standard transformations of the resulting acetylene derivative **64** were carried out according to Scheme 12 [51].

$$\underset{\mathbf{63}}{Me(CH_2)_7C\equiv CH} \xrightarrow[40\%]{a} \underset{\mathbf{64}}{Me(CH_2)_7C\equiv CCH_2CH(OEt)_2} \xrightarrow[65\%]{b,\,c,\,d} \mathbf{62}$$

a. $BrCH_2CH(OEt)_2$; *b*. H_3O^+/Me_2CO; *c*. $NaBH_4$; *d*. $H_2/Ni\text{-}P2$

Scheme 12.

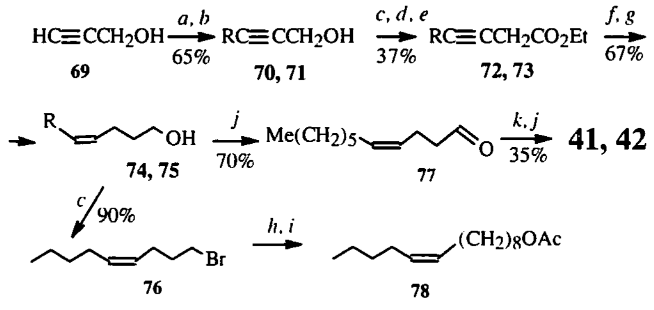
For the synthesis of 12-hydroxy-1Z-dodecenoic acid (**68**), a precursor of the macrolide component of the associative pheromone of the flat grain beetle *Cryptolestes pusillus* (for the synthesis of macrolide pheromones, see [52]), **65**, was converted to the *bis*-homolog by ethylene oxide. The resulting β-hydroxyalkyne **66** was then converted in two steps to alkynoic acid **67** and finally into the desired product **68** (Scheme 13) [53].



a. $EtMgBr/Et_2O$; *b*. $\underset{O}{CH_2CH_2}$; *c*.H_2CrO_4/Me_2CO; *d*. H_3O^+; *e*. $H_2/Ni\text{-}P2$

Scheme 13.

Propargyl alcohol (**69**) is a convenient starting material for synthesizing pheromones. Acetylenic synthons that are readily converted to the desired pheromones with the (*Z*)- [54-57] or (*E*)-configuration [58, 59] are obtained via C-aklylation of **69** by alkylbromides. For example, 9Z-tetradecen-1-ylacetate (**78**), a component of many *Lepidoptera* species (through intermediates **70**, **72**, **74**, and **76**) [47] and the (*Z*)-unsaturated aldehyde **77** (through intermediates **71**, **73**, **75**, and **77**) are prepared using this method. The latter is further converted in two steps into **41** and **42**, components of the peach moth pheromone (Scheme 14) [56].



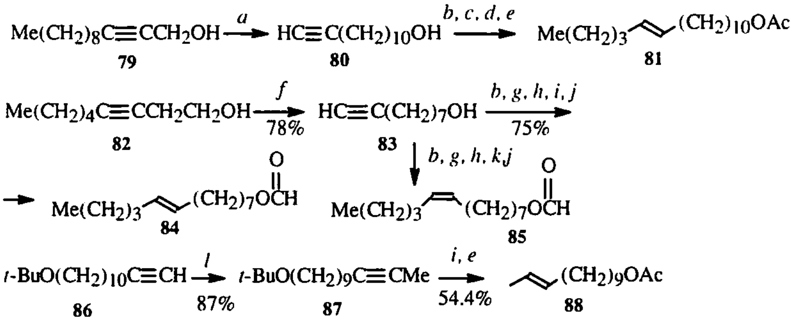
R = Me(CH$_2$)$_3$ (**70, 72, 74**); Me(CH$_2$)$_5$ (**71, 73, 75**)

a. Li/NH$_3$-Fe(NO$_3$)$_2$; *b*. RBr (R=Me(CH$_2$)$_3$, Me(CH$_2$)$_5$); *c*. PBr$_3$/Py; *d*. NaCH(CO$_2$Et)$_2$;
e. NaCl/DMF, 180° C; *f*. H$_2$/Pd-CaCO$_3$; *g*. LiAlH$_4$; *h*. BrMg(CH$_2$)$_5$OTHP; *i*. AcCl/AcOH;
j. PCC/AcONa/CH$_2$Cl$_2$; *k*. RMgBr (R=Me(CH$_2$)$_7$, Me(CH$_2$)$_8$)

Scheme 14.

The compounds 7Z-tetra- and 9Z-hexadecen-1-ylacetates, which were isolated from *Amalthes configurata nidrum* and *Manestra configurata* [60], were synthesized analogously. Homopropargyl alcohol was used to synthesize 2,5-dioxo-3*E*-alkenes, which control agressive behavior in bees [61].

Prototopic isomerization of internal acetylenes and alcohols into terminal ones using 3-aminopropylamides [62-66] or 2-aminoethylamides [67, 68] of alkali metals in a solution of 1,3-propylenediamine or the corresponding 1,2-ethylenediamine is used to prepare alkenes. This made it possible to synthesize pheromones [69, 70]. The synthesis of 11*E*-hexadecen-1-ylacetate (**81**), a sex pheromone of the eggplant grinder *Leucinodes ozbonalis* [71], and the corresponding 8*E*- (**84**) and 8*Z*-tetradecen-1-ylformates (**85**) was based on the "acetylenic lightning" reaction of propargyl (**79**) and homopropargyl (**82**) alcohols. These compounds in a 10:1 ratio exhibit pheromonal activity in the yellow peach moth *Dichocrocis punctiferalis* that is analogous to that induced by the natural pheromone, which is a mixture (10:1) of (*E*)- and (*Z*)-10-hexadecenals [72]. Prototopic isomerization of **79** and **82** gave terminal acetylenic alcohols **80** and **83**, respectively. These are routinely converted into the desired compounds **81**, **84**, and **85** (Scheme 15) [71, 72].

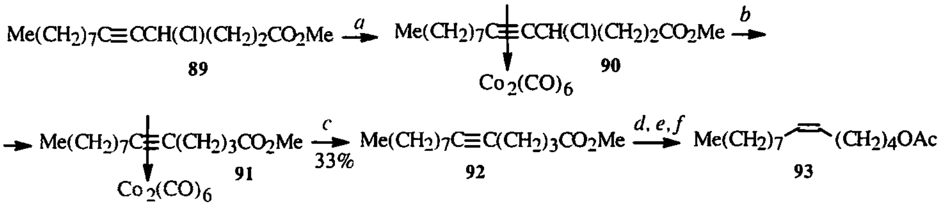


a. NaH/(CH$_2$NH$_2$)$_2$; *b*. DHP/H$^+$; *c*. BuLi/Me(CH$_2$)$_3$Br; *d*. Na/NH$_3$; *e*. AcCl/AcOH;
f. H$_2$N(CH$_2$)$_3$NHK/CH$_2$(CH$_2$NH$_2$)$_2$, 0° C, Ar; *g*. BuLi/Me(CH$_2$)$_4$Br; *h*. TsOH/MeOH-H$_2$O;
i. LiAlH$_4$/THF; *j*. HCO$_2$H; *k*. H$_2$/Pd-CaCO$_3$; *l*. KOH/(CH$_2$OH)$_2$, 160°C

Scheme 15.

The triple bond in terminal alkyne **86** is shifted to the adjacent position by heating in ethyleneglycol in the presence of KOH during the synthesis of 10*E*-dodecen-1-ylacetate (**88**), the sex pheromone of *Lithocolletis blancardella*. The resulting alkyne **87** is then converted in two steps into acetate **88** (Scheme 15) [73].

Reduction of methyl-4-chloro-5-tetradecynoate (**89**) by zinc in acetic acid was performed after blocking the triple bond as the dicobalthexacarbonyl complex (**90**) in order to avoid an acetylene—allene isomerization of the triple bond during the synthesis of 5Z-tetradecen-1-ylacetate (**93**), the sex pheromone of the borer *Agrotic exclamationis*. The complex in the product of reductive dechlorination is decomposed using ceric ammonium nitrate. Subsequent transformations of alkyne ester **92** gave in three steps the desired compound **93** (Scheme 16) [74].



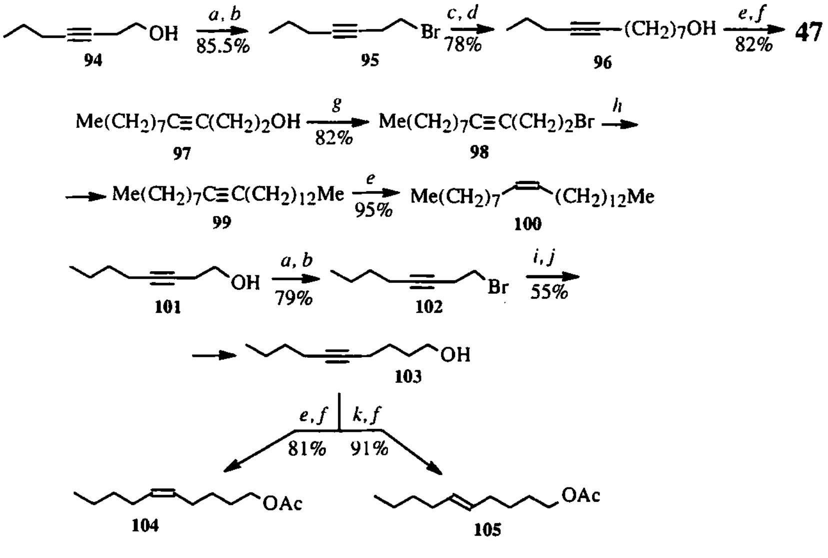
a. Co$_2$(CO)$_8$; *b*. Zn/AcOH; *c*. Ce(NH$_4$)$_2$(NO$_3$)$_6$; *d*. LiAlH$_4$; *e*. H$_2$/Pd-BaSO$_4$; *f*. AcCl/Et$_3$N

Scheme 16.

The synthesis of monounsaturated sex pheromones of *Lepidoptera* using alk-3-yn-1-ols has been studied several times. According to a detailed study [75], in contrast with previous results (for example, [76]), the reaction of alkynylmagnesium bromides with ethylene oxide gives several products including alk-3-yn-1-ols and alk-3-yn-2-ols. The desired product was obtained using lithium alkynides generated from dialkynylmercury [75] or directly from alk-1-ynes and *n*-butyllithium or lithium amide in THF [75, 77]. Alk-3-yn-1-ols can also be synthesized via the reactions of lithium alkynides with ethylene chlorohydrin *tert*-butyl ether [75] and with 2-chloroethylvinylether [78].

Several pheromones based on alk-3-yn-1-ols were synthesized by converting them to the corresponding 1-bromoalk-3-ynes and subsequent addition to ω-hydroxy derivatives of Grignard reagents [75, 79, 80].

The triple bond is converted to a (*Z*)-olefin via hydroboration (Scheme 17) in the syntheses of 8Z-dodecen-1-ylacetate (**47**), a component of the pheromone of the eastern moth (from alkyne **94** through intermediates **95** and **96**) [79] and 9Z-tricosene (**100**), a pheromone of *Musca domestica* (from alkyne **97** via compounds **98** and **99**) [80].



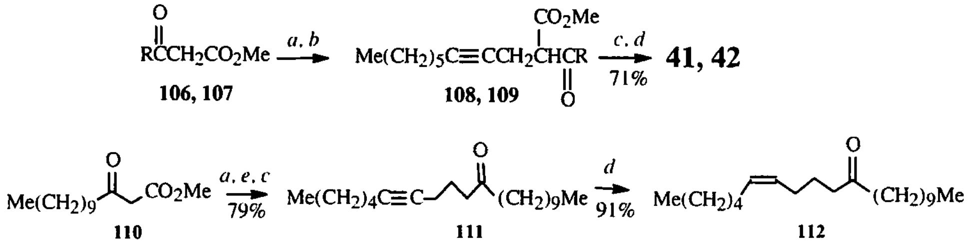
a. TsCl/Py; *b*. LiBr; *c*. EEO(CH$_2$)$_5$MgBr/CuI/bpy; *d*. H$_3$O$^+$; *e*. 9-BBN; AcOH; *f*. Ac$_2$O/Py; *g*. Br$_2$ · PPh$_3$; *h*. Me(CH$_2$)$_{10}$MgBr/CuI/bpy; *i*. Li; *j*. $\underset{\begin{smallmatrix}\backslash\ /\\ O\end{smallmatrix}}{H_2C - CH_2}$; *k*. Na/NH$_3$

Scheme 17.

Conversion of oct-3-yn-1-ol (**101**) to the bromide (**102**) and reaction of the lithium derivative of the latter with ethylene oxide provided a simple route to *Z*-(**104**) and *E*-(**105**) 5-decen-1-ylacetates, components of pheromones of the borer *Agrotis segetum* and the striped fruit moth *Anarsia lineatella* (Scheme 17).[81].

β-Hydroxyalkyne **97** and its homolog were used to synthesize alkenones **41** and **42** [82].

Addition of propargyl bromides to esters of β-ketocarboxylic acids proceeds smoothly using sodium hydride to generate carbanions of the latter. This provides a convenient path to alkenone pheromones. Thus, 1-bromo-2-nonyne was added to acetylenic ketoesters **108** and **109** starting with esters of 3-oxoundecanoic (**106**) and 3-oxododecanoic (**107**) acids. Decarboxylation and subsequent *cis*-hydrogenation of the triple bond gives (*Z*)-alkenones **41** and **42**, components of the peach moth pheromone (Scheme 18) [83].



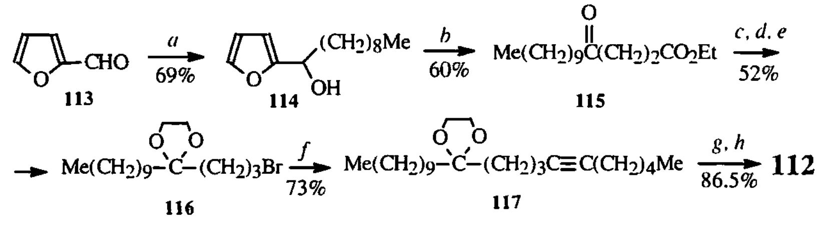
R = $Me(CH_2)_7$ (**41, 106, 108**), $Me(CH_2)_8$ (**42, 107, 109**)

a. NaH; *b*. $Me(CH_2)_5C \equiv CCH_2Br$; *c*. DMSO; *d*. $H_2/Pd\text{-}BaSO_4$; *e*. $Me(CH_2)_4C \equiv C(CH_2)_2Br$

Scheme 18.

Analogously the ester of 3-oxotridecanoic acid (**110**) and 1-bromonon-3-yne give the intermediate alkynone **111** and then 6Z-heneicosen-11-one (**112**), a component of the pheromone of moth *Orgiya pseudotsugata* (Scheme 18) [83].

The synthesis of **112** from furfurol (**113**), which is easily converted into 1-furfuryldecan-1-ol (**114**), has been described. Acid cleavage of the latter gave γ-ketoester **115**, which was transformed in three steps into bromide **116**. Addition of lithium heptynide to bromide **116** led smoothly to the acetylene derivative **117**, which was converted by standard means into desired compound **112** (Scheme 19) [84].

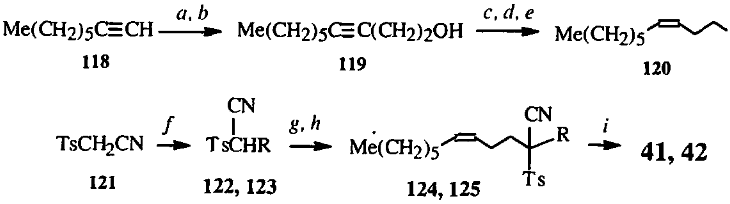


a. $Me(CH_2)_8MgBr/Et_2O$; *b*. EtOH/HCl; *c*. $(CH_2OH)_2$/TsOH; *d*. $LiAlH_4/Et_2O$; *e*. Br_2 $PPh_3/Et_3N/CH_2Cl_2$; *f*. $LiC \equiv C(CH_2)_4Me$/HMPA; *g*. H_3O^+; *h*. H_2/Ni-2P

Scheme 19.

The tritium-labelled (at the double bond) analog of **112** has been prepared [85].

Double alkylation of the nitrile of tosylacetic acid (**121**) with subsequent acid hydrolysis is a convenient route to ketones [77]. If at first an *n*-octyl- or *n*-nonyliodide is used in this reaction followed by 1-iodo-3Z-decene (**120**), then the stepwise production of 2-tosylnitriles **122** and **123** followed by **124** and **125** give unsaturated ketones **41** and **42** (Scheme 20). Iodide **120** is prepared from 3-octyn-1-ol (**118**) through the intermediate β-acetylenic alcohol **119** [77].



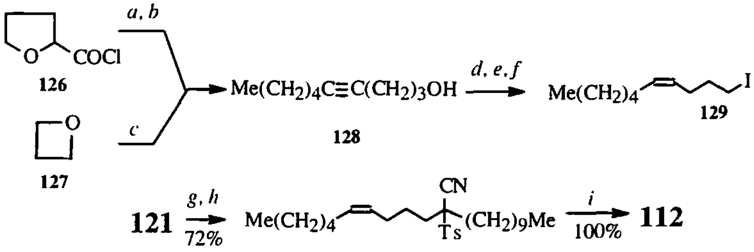
R = Me(CH$_2$)$_7$ (**122**, **124**); Me(CH$_2$)$_8$ (**123**, **125**)

O
/ \
a. ^{n}BuLi/THF; *b*. $H_2C - CH_2$ /BF$_3$ • Et$_2$O; *c*. H$_2$/Pd-CaCO$_3$; *d*. MsCl/Et$_3$N; *e*. NaI;

f. RI (R=Me(CH$_2$)$_7$, Me(CH$_2$)$_8$)/ NaOH/Bu$_4$NBr; *g*. NaH/DMSO; *h*. **120**; *i*. H$_3$O$^+$

Scheme 20.

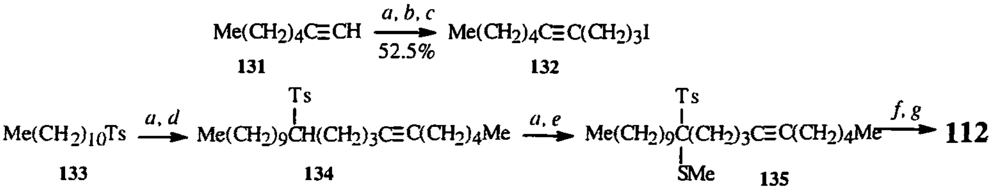
Analogously nitrile **121**, iododecane, and 1-iodo-4Z-decene (**129**) give enone **112** [86]. The precursor to iodide **129**, alk-4-ynic alcohol **128**, is prepared by cleaving tetrahydrofurfurylchloride (**126**) with subsequent treatment with pentylbromide [86] or reaction of hept-1-ynylmagnesium chloride with oxetane **127** (Scheme 21) [87].



a. Li/NH$_3$; *b*. Me(CH$_2$)$_4$Br; *c*. Me(CH$_2$)$_4$C ≡ CMgCl; *d*. H$_2$/Pd-CaCO$_3$; *e*. MsCl/Et$_3$N; *f*. NaI; *g*. Me(CH$_2$)$_9$I/ NaOH; *h*. **129**/NaOH; *i*. H$_3$O$^+$

Scheme 21.

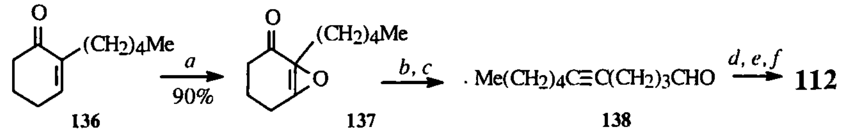
Alkylation of sulfone **133** with 1-iodo-4-decyne (**132**), which is prepared from 1-heptyne (**131**), is yet another route to **112** (Scheme 22) [88]. The intermediates in this scheme are tosyl derivatives **134** and **135**.



a. ^{n}BuLi; *b*. Br(CH$_2$)$_3$Cl; *c*. NaI; *d*. **132**; *e*. (MeS)$_2$; *f*. H$_2$O/SiO$_2$/CuCl$_2$; *g*. H$_2$/Pd-BaSO$_4$

Scheme 22.

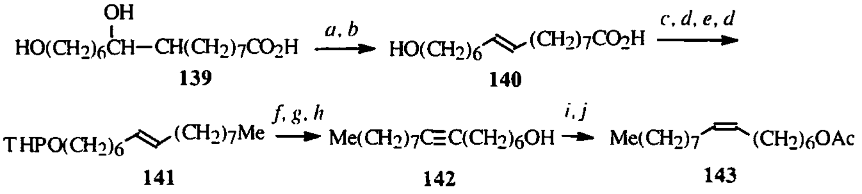
A convenient route to acetylenic aldehydes, synthons for pheromones, is Eschenmoser's fragmentation of alkyl derivatives of α,β-epoxycyclohexanones [9, 89, 90]. Starting with epoxide **137** which is prepared from 2-pentyl-2-cyclohexen-1-on (**136**), aldehyde **138** is synthesized via this route and is easily converted to **112** (Scheme 23) [89].



a. H_2O_2/KOH/MeOH; *b*. $TsNHNH_2$; *c*. HCl; *d*. $Me(CH_2)_9MgBr$; *e*. CrO_3 Py; *f*. H_2/Pd-$BaSO_4$

Scheme 23.

Elimination from vicinal diols or vicinal and geminal dibromides is one of many routes to acetylenes [5, 91]. Elimination of vicinal hydroxyls in aleuritic acid (**139**) and functionalization into 16-hydroxy-9*E*-hexadecenoic acid (**140**) gave the (2-tetrahydropyranyl)ester of 7*E*-hexadecen-1-ol (**141**), which is transformed through acetylenic alcohol **142** into the *Z*-isomer of acetate **143**, a sex attractant of the pink cotton box worm *Pectinophora gossypiella* (hexalure) (Scheme 24) [92].

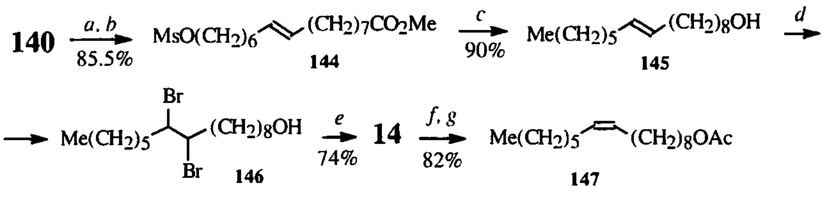


a. $HC(OEt)_3$; *b*. t°; *c*. DHP/H^+; *d*. $LiAlH_4$; *e*. MsCl/Et_3N; *f*. H_3O^+; *g*. Br_2; *h*. $NaNH_2$; *i*. H_2/Ni-P2; *j*. Ac_2O/Py

Scheme 24.

Treatment of dibromides with sodium amide in hexametapol followed by reaction with α,ω-chlorohydrins gave alkyn-1-ols, the reduction of which with lithium aluminum hydride ($LiAlH_4$) and then acylation produced (*E*)-alken-1-ylacetates [93]. Using diols as cocatalysts of the basic dehydrohalogenation of 1,2-dihalides under phase-transfer catalytic conditions substantially increased the selectivity of 1-alkynes formation [94].

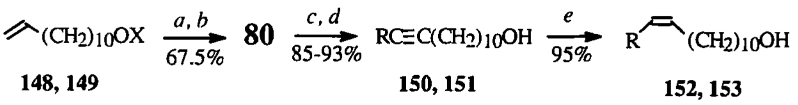
If hydroxycarboxylic acid **140** is converted to mesyloxyester **144**, then treatment with $LiAlH_4$ gives 9*E*-hexadecen-1-ol (**145**), the transformation of which into 9Z-hexadecen-1-ylacetate (**147**), a sex pheromone of *Naranga aenescens*, is achieved via dibromide **146** and alkyn-1-ol **14** (Scheme 25) [95].



a. $MeOH_2^+$; *b*. MsCl/Et_3N; *c*. $LiAlH_4$; *d*. Br_2; *e*. $NaNH_2$; *f*. H_2/Ni-P2; *g*. Ac_2O/Py

Scheme 25.

Successive bromination and dehydrobromination of 11-dodecen-1-ol (**148**) or its acetate (**149**) gives dodec-11-yn-1-ol (**80**). Treatment of **80** with an excess of butyllithium or sodium amide and then an alkylhalide gives alk-11-yn-1-ols **150** and **151**, *cis*-hydrogenation of which leads to pheromones or their precursors **152** and **153** (Scheme 26) [96].

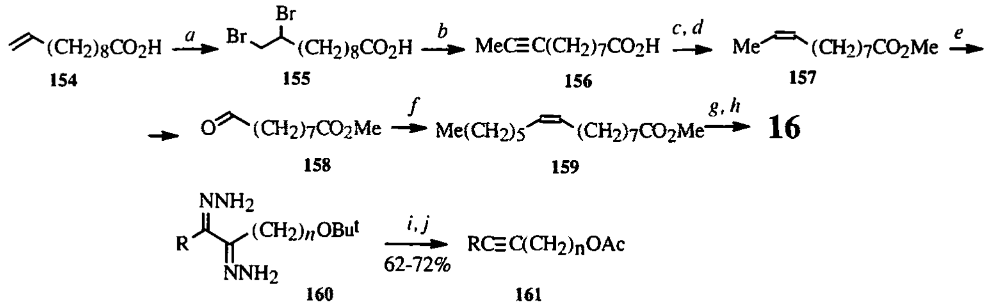


X = H (**148**), Ac (**149**); R = Et (**150, 152**), $Me(CH_2)_3$ (**151, 153**)

a. Br_2; *b*. KOH; *c*. BuLi/THF; *d*. RHal(Hal = Br, I)/HMPA; *e*. H_2/Pd-$BaSO_4$

Scheme 26.

Attempted debromination of the dibromide (**155**) of 10-undecenoic acid (**154**) by heating in superbasic medium resulted in a shift of the triple bond to the neighboring position. 9-Undecynoic acid (**156**) was converted to the methyl ester of 9Z-undecenoic acid (**157**) and converted by ozonolysis to aldehydeester **158** and then the olefin. Subsequent transformations of the resulting **159** gave hexadecenal **16** (Scheme 27) [97].

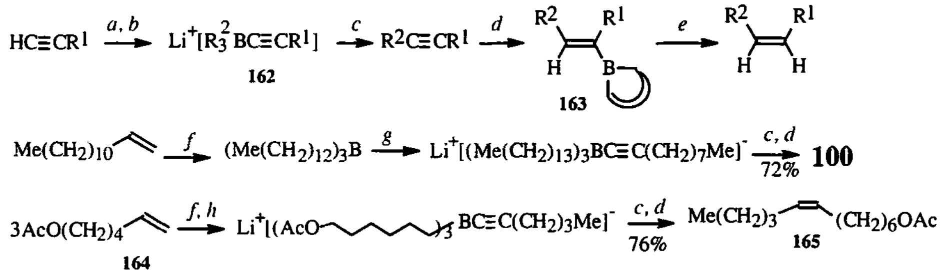


a. Br_2/CCl_4; *b*. KOH/$HO(CH_2CH_2O)_nH$, 150° C; *c*. $MeOH_2^+$; *d*. H_2/Pd-$CaCO_3$; *e*. O_3/MeOH; *f*. $Me(CH_2)_6PPh_3Br/NaNH_2$/THF;
g. $LiAlH_4/Et_2O$; *h*. PCC/CH_2Cl_2; *i*. O_2/CuCl-Py; *j*. AcCl/AcOH

Scheme 27.

Acetylenic precursors of pheromones **161** can be prepared by elimination from dihydrazones **160** of α-diketones, which occurs by oxidation with oxygen in pyridine in the presence of cuprous chloride (Scheme 27) [98].

A general method for synthesizing acetylenes and pheromone derivatives of them involves organoboranes [99-109]. Reaction of trialkylboranes and lithium acetylenides gives trialkylborates **162**, which react readily with iodine to give quantitative yields of the alkynes. Hydroboration of alkynes using 9-BBN and subsequent protonolysis of alkenyldialkylboranes **163** leads exclusively to the Z-olefinic insect pheromones (Scheme 28) [101, 103, 104]. The fly pheromone Z-tricosene (**100**) is prepared via this route from tridecene and dec-1-yne. A pheromone of the cabbage moth, 7Z-dodecen-1-ylacetate (**165**) is prepared from 5-hexen-1-ylacetate (**164**) and hex-1-yne (Scheme 28). The reaction of BH_3·THF and acetate **164** occurs only at the double bond without affecting the acetate group. The presence of the acetate group does not affect other reactions [104]. Another series of *Lepidoptera* pheromones is synthesized analogously.

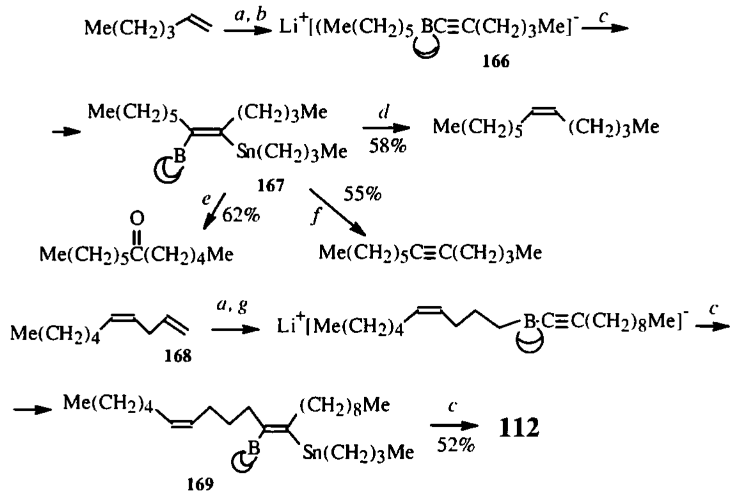


R^1, R^2 = Alk

a. ⁿBuLi; *b*. R_3^2B; *c*. I_2, -78° C; *d*. 9-BBN; *e*. [H⁺]; *f*. BH_3 • THF; *g*. LiC ≡ $C(CH_2)_7Me$; *h*. LiC ≡ $C(CH_2)_3Me$

Scheme 28.

The hydroboration of alkenes is highly selective for the terminal double bond if 9-BBN is used. Only the *n*-alkyl group in the corresponding organoborate complex **166** migrates to give adduct **167**. Protonolysis of the latter gives the (*Z*)-alkene. Oxidation gives the ketone. Iodination gives the alkyne (Scheme 29) [101].



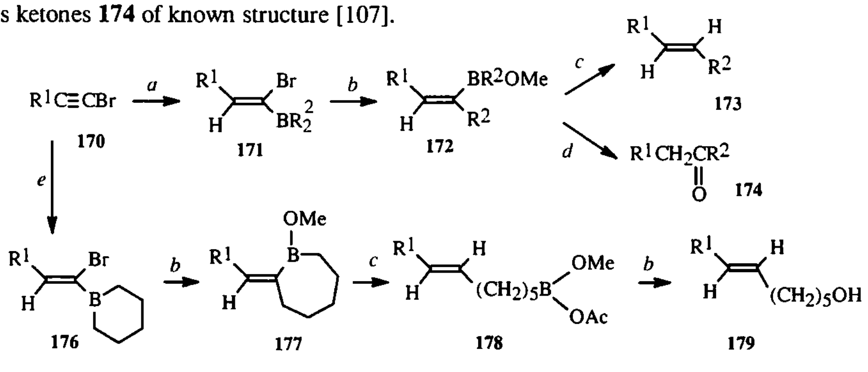
a. 9-BBN; *b*. $Me(CH_2)_3C \equiv CLi$; *c*. $[Me(CH_2)_3]_3SnCl$; *d*. AcOH; *e*. $H_2O_2/NaOH$; *f*. I_2; *g*. $Me(CH_2)_8C \equiv CLi$

Scheme 29.

A whole series of *Lepidoptera* pheromones is synthesized by this method. For example, if 1,4Z-decadiene (**168**) is used as the alkene and undec-1-yne as the alkyne, then the final product after oxidation of **169** is 6Z-enone **112** (Scheme 29) [101].

This same pheromone (**112**) is synthesized using $BHBr_2 \cdot SMe_2$ as the hydroboration reagent [110]. Other pheromones are prepared analogously [111, 112].

Hydroboration of 1-bromoalk-1-ynes **170** and subsequent treatment of B-(*cis*-1-bromo-1-alkenyl)dialkylboranes **171** with base initiates intramolecular substitution of bromine by one of the alkyl groups on the boron. The resulting B-(*trans*-1-alkyl-1-alkenyl)alkylborinate esters **172** give after protonolysis *trans*-alkenes **173** in high yields (Scheme 30) [107, 113]. Oxidation of esters **172** produces ketones **174** of known structure [107].



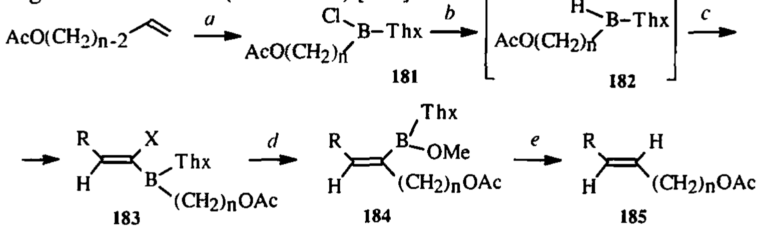
$R^1, R^2 = Alk$

a. R_2^2BH; *b*. MeONa; *c*. AcOH; *d*. $H_2O_2/NaOH$; *e*. $HB(CH_2)_4CH_2$ (**175**)

Scheme 30.

Hydroboration of 1-haloalk-1-ynes **170** using boracyclane **175** gives the corresponding B-(*cis*-1-halo-1-alkenyl)borinanes **176**, treatment of which with sodium methoxide in methanol yields borenanes **177**. Protonolysis of **177** by acetic acid gives boronate esters **178**, oxidation of which by basic H_2O_2 produces in high yields 6*E*-alken-1-ols, components of insect sex pheromones (Scheme 30) [114].

Hydroboration of ω-unsaturated acetates using thexylchloroborane—dimethylsulfide (**180**) is used to synthesize *E*-disubstituted alkenes [102]. The reaction occurs selectively at the terminal double bond to produce thexylalkylchloroborane **181**, treatment of which with potassium tris(isopropoxy)borohydride gives thexylalkylborane **182**, which acts as a hydroboration agent for the corresponding 1-haloalkyne. The reaction produces B-(*cis*-1-halo-1-alkenyl)thexylalkylborane **183**, treatment of which with sodium methoxide in methanol gives B-(*trans*-1-alkyl-1-alkenyl)thexylborinate **184**. Protonolysis of **184** produces the acetate of the corresponding *E*-alken-1-ol **185** (Scheme 31) [115].

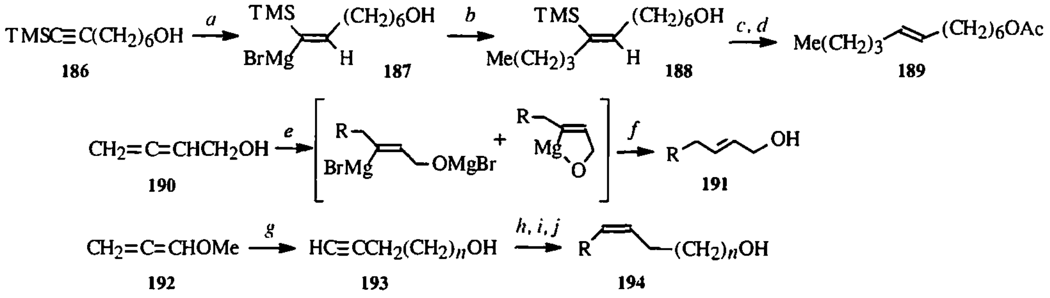


R = Alk; X = Br, I; n=5, 6, 10; Thx = CMe_2CHMe_2

a. ThxBHCl • SMe_2 (**180**); *b*. KBH(O^iPr)$_3$; *c*. RC ≡ CX; *d*. MeONa/MeOH; *e*. AcOH

Scheme 31.

The Gringard reaction of 1-alkynylsilanes occurs stereospecifically. Subsequent treatment of the resulting alkenylmagnesium bromides with alkyliodides in the presence of CuI gives the corresponding addition products, desilylation of which yields (*E*)-alkenes. Starting with 8-trimethylsilyl-7-octyn-1-ol (**186**), this method using butyliodide to alkylate intermediate **187** produced **188**, desilylation of which followed by acetylation led to 7*E*-dodecen-1-ylacetate (**189**), the sex pheromone of the false cabbage moth *Argyroploce leucotrete* (Scheme 32) [116].



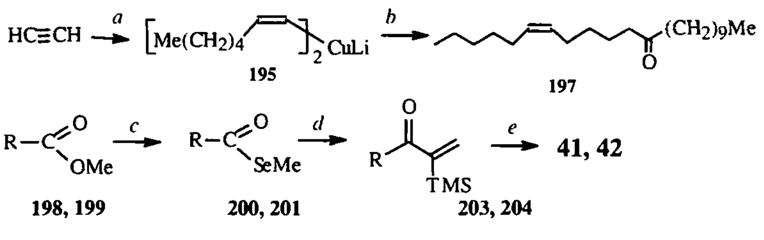
a. Bu^iMgBr/Cp_2TiCl_2; *b*. $Me(CH_2)_3I/CuI$; *c*. I_2; *d*. Ac_2O/Py; *e*. RMgBr/CuI; *f*. H_2O;
g. $BrMg(CH_2)_nOMgBr/CuI$; *h*. EtMgBr; *i*. ROTs; *j*. H_2/Ni-P2

Scheme 32.

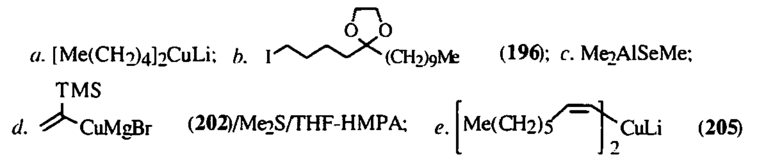
(*E*)-Olefinic alcohols and their acetates are also synthesized by treating terminal acetylenic alcohols and their O-derivatives with an excess of lithium in liquid ammonia followed by reaction with alkylbromides [117].

(*E*)-Alken-1-ols **191** are produced by the reaction of Gringard reagents with allenic alcohol **190** [118]. Using methoxyallene (**192**) as the starting material yields terminal alkynes **193**, which can then be converted to the (*Z*)-alken-1-ols **194** (Scheme 32) [119].

Syntheses of pheromones with the (*Z*)-configuration that are based on stereospecific addition of cuprate reagents to acetylene are very effective. They produce lithium bis(Z-alkenyl)cuprates as intermediates that react readily with electrophiles such as alkylhalides [120-127]. Thus, (*Z*)-alkenylcuprate **195** reacts with iodide **196** to give 6*Z*-docosen-12-one (**197**), the sex pheromone of the Douglas Fir Tussock Moth (Scheme 33) [122].



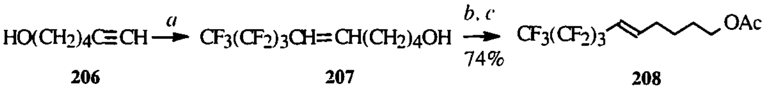
R=Me(CH$_2$)$_7$ (**41**, **198**, **200**, **203**), Me(CH$_2$)$_8$(**42**, **199**, **201**, **204**)



Scheme 33.

(Z)-Unsaturated ketones **41** and **42** are synthesized by the reaction of lithium di-(1Z-octenyl)cuprate (**205**) with 2-(trimethylsilyl)-1-undecen-3-one (**203**) or its homolog (**204**) (Scheme 33) [123, 124]. The α,β-unsaturated ketones **203** and **204** are prepared by the reaction of (1-trimethylsilyl)vinylcuprate **202** with methyl esters of selenocarboxylic acids **200** and **201** [124]. Esters **198** and **199** are the starting materials.

. Radical-initiated addition of perfluorobutyliodide to hex-5-yn-1-ol (**206**) produces 7,7,8,8,9,9,10,10,10-nonafluoro-5Z-decen-1-ol (**207**) as a mixture of geometric isomers that is converted to the (E)-isomeric acetate **208**, an analog of the pheromone of the turnip moth *Agrotis segetum* (Scheme 34) [128].



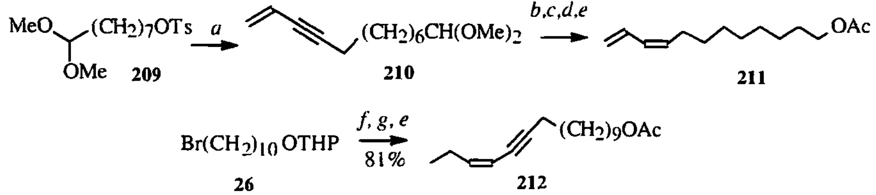
a. $CF_3(CF_2)_3I$/AIBN; *b*. BuLi/MeOH; *c*. Ac_2O/Py-DMAP

Scheme 34.

Analogs of pheromones that contain fluorine and are labelled with tritium or deuterium are interesting for studying the metabolism and biosynthetic pathways of pheromones in insects [129, 130].

SYNTHESIS OF DI- AND TRIENE PHEROMONES WITH CONJUGATED DOUBLE BONDS

The stereoselective synthesis of pheromones with conjugated dienes takes advantage of the ability to transform selectively acetylenes into olefins of either (Z)- or (E)-configuration [1, 9]. 1,3-Enynes [131, 132] and 1,3-diynes [133, 134] are convenient synthons for these pheromones. Addition of lithium 1,3-butenynide to tosylate **209** gave enyne acetal **210**, which was converted to 9Z,11-dodecadien-1-ylacetate (**211**), a component of the sex pheromone of the red cotton moth *Diparopsis castanea* (Scheme 35) [135].

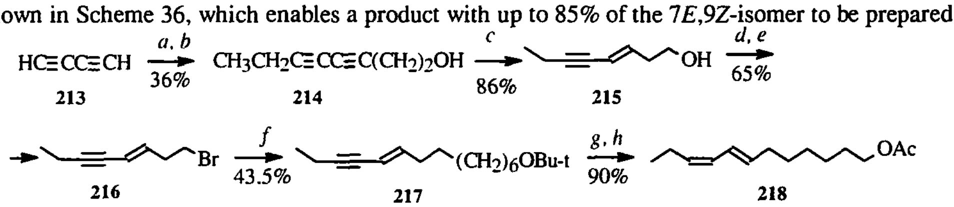


a. CH_2=CHC ≡ CLi/liq.NH_3; *b*. H_3O^+; *c*. 9-BBN; *d*. H_2O_2/NaOH; *e*. Ac_2O/Py; *f*. (Z)-EtCH=CHC ≡ CLi; *g*. TsOH/MeOH

Scheme 35.

Analogously addition of lithium 3Z-hexen-1-yne to bromohydrin **26** produced 13Z-hexadecen-11-ynylacetate **212**, the main component of the sex pheromone of silkworm *Thaumetopoea pityocampa* [136].

Syntheses of 7*E*,9Z-dodecadien-1-ylacetate (**218**), the sex pheromone of the European leaf roller moth *Lobesia botrana* [137-139], and 7Z,9Z-dodecadien-1-ylacetate (**222**), a component of the sex pheromones of *Epinotia* (forest pests) and *Eucosma womonana* (sunflower pest) leaf roller moths, were developed using buta-1,3-diyne (**213**) [140]. The most rational synthesis of **218** is that shown in Scheme 36, which enables a product with up to 85% of the 7*E*,9Z-isomer to be prepared.



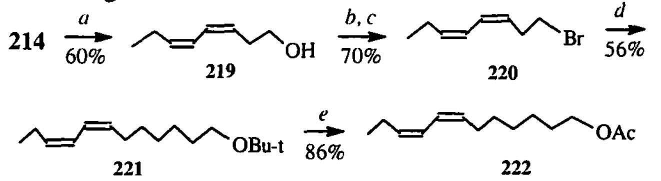
a. Li/NH$_3$; EtI/DMSO; *b.* H_2C - CH_2/DMSO; *c.* $LiAlH_4/Et_2O$; *d.* $TsCl/Et_2O/KOH$; *e.* LiBr/DMF;

f. t-BuO$(CH_2)_5$Cl/Mg/THF + $LiCuCl_4$/THF; *g.* H_2/Pd-$CaCO_3$-PbO (Quin); *h.* $Ac_2O/FeCl_3$

Scheme 36.

Successive alkylation of **213** with ethyliodide and hydroxyalkylation with ethylene oxide produced diyne alcohol **214**, which was converted to enyne bromide **216** through alcohol **215**. Addition of **216** to the *tert*-butyl ester of 4-chlorobutan-1-ol using the Grignard—Schlosser cross-coupling yielded the enyne precursor **217**, which is easily converted in two steps to the desired product **218** [139].

Diyne alcohol **214** is stereoselectively (≥96%) converted to (*Z*,*Z*)-diene **219** using a zinc—copper couple in aqueous isopropanol during the synthesis of pheromone **222**. Addition of bromide **220**, obtained from **219**, was performed analogously to that described in Scheme 36 for **216** to give **221**, which was converted into the desired acetate **222** with 87% of the principal isomer (Scheme 37) [140].

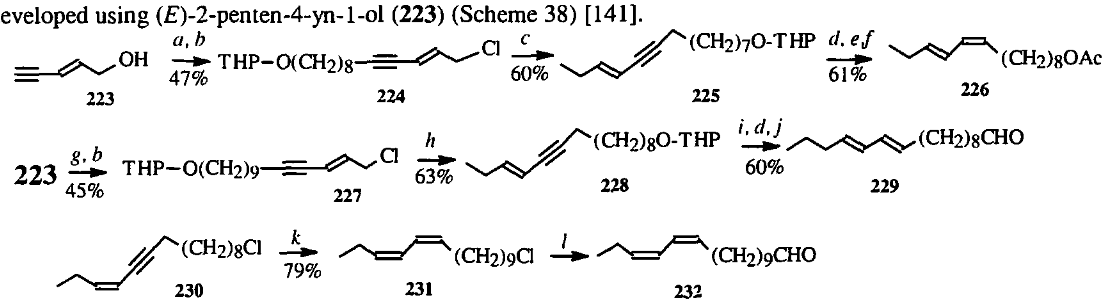


a. Zn(Cu)/i-PrOH-H_2O, 130-140° C; *b.* $TsCl/Et_2O$/KOH(sld); *c.* LiBr/DMF;

d. Cl$(CH_2)_4$OBu-t/Mg/THF; Li_2CuCl_4; *e.* Ac_2O-$FeCl_3/Et_2O$

Scheme 37.

Syntheses of 9Z,11*E*-tetradecadien-1-ylacetate (**226**) and 10*E*,12*E*-hexadecadienal (**229**), sex pheromones of cotton pests, were developed using (*E*)-2-penten-4-yn-1-ol (**223**) (Scheme 38) [141].

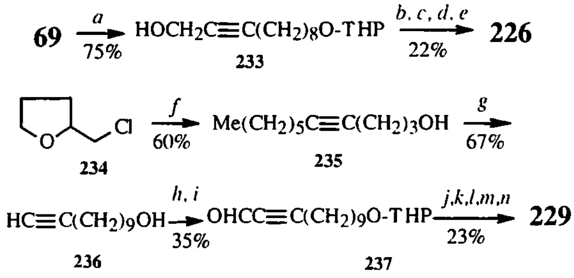


a. $LiNH_2$/liqNH_3; Br$(CH_2)_8$O-THP; *b.* CCl_4-PPh_3; *c.* MeMgI/CuI/Et_2O; *d.* TsOH/MeOH; *e.* H_2/Ni-P2; *f.* Ac_2O/Py; *g.* $LiNH_2/NH_3$; Br$(CH_2)_9$O-THP;
h. EtMgI/CuI/Et_2O; *i.* Na/liqNH_3; *j.* PCC/CH_2Cl_2; *k.* (cyclo-$C_6H_{11})_2$BH;AcOH;H_2O_2/NaOH; *l.* Mg/THF;HC$(OEt)_3$;AcOH

Scheme 38.

Key intermediates for this were enyne chlorides **224** and **227**. Addition of these to methyl- and the corresponding ethylmagnesium bromide gave enyne precursors **225** and **228**, which readily produce the desired compounds **226** and **229**. Hydroboration of (*Z*)-enyne chloride **230** gave (*Z,Z*)-diene **231**, homologization of which through the magnesium derivative produced 11*Z*,13*Z*-hexadecadienal (**232**), a pheromone of the citrus worm (Scheme 38) [142].

Pheromone **226** was also synthesized from propargyl alcohol **69**, which was converted into the selectively protected C_{11}-acetylenic diol **233**. After selective oxidation by pyridinium chlorochromate, formation of the olefin from the aldehyde, and two simple reactions, **233** was converted to the desired product (Scheme 39) [143].



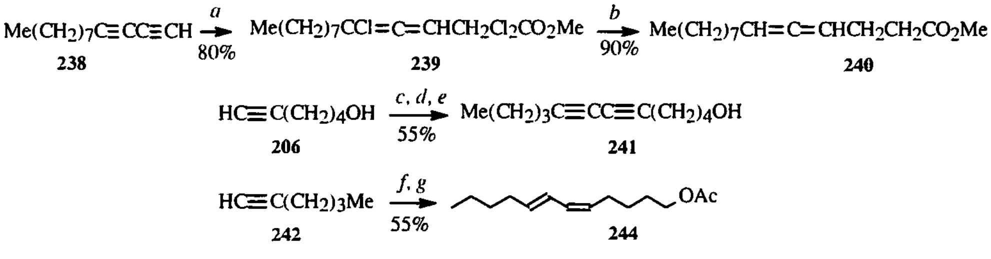
a. $LiNH_2/Br(CH_2)_8O$-THP; *b*. PCC/CH_2Cl_2; *c*. $Me(CH_2)_2PPh_3Br$/BuLi/LiBr/THF; *d*. H_2/Pd-$CaCO_3$; *e*. AcCl/AcOH; *f*. $LiNH_2/Me(CH_2)_5Br$; *g*. $NaNH_2/CH_2(CH_2NH_2)_2$; *h*. DHP/TsOH; *i*. EtMgBr/THF; DMF; *j*. $Me(CH_2)_3PPh_3Br$/BuLi/THF; *k*. $NH_4Cl/liqNH_3$; *l*. Amberlite(H); *m*. I_2/C_6H_{14}; *n*. PCC/CH_2Cl_2

Scheme 39.

The starting material in an alternative synthesis of **229** was 2-chloromethyltetrahydrofuran (**234**), which is easily converted to C_{11}-acetylenic alcohol **235**. Prototropic isomerization of **235** gave terminal acetylene **236**, which was homologized using Iotsich reagent to produce aldehyde **237**, which was converted using standard methods to the desired pheromone (Scheme 39) [144].

1,3-Alkadiynes, which are of interest as synthons for pheromones with conjugated double bonds, can be prepared by addition of copper acetylenides to (bromoethynyl)trimethylsilane followed by desilylation [145], by hydrocupration of terminal alkynes [146], and by prototropic isomerization of diacetylenes [147]. Conjugated internal diynes were prepared by catalytic addition of 1-alkynes to 1-bromoalkynes in the presence of CuCl [148]. Homoaddition of terminal acetylenes can be accomplished in the same way [149].

The condensation of terminal diacetylene **238** and methyltrichloroacetate in the presence of Cu_2O produced trichloroallene **239**, reductive dehalogenation of which using a zinc—copper couple gave the methyl ester of 4,5-tetradecadienoic acid (**240**), a synthon of the pheromone of the parasitic bean weevil *Acanthos celides obtectus* (Scheme 40) [150].



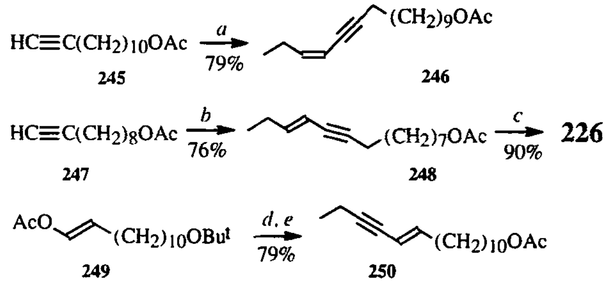
a. CCl_3CO_2Me/Cu_2O/MeOH; *b*. Zn/Cu; *c*. DHP/H^+; *d*. $Me(CH_2)_3C{\equiv}CBr/CuCl/EtNH_2$ /MeOH; *e*. TsOH;

f. $THPO(CH_2)_4$CH=CHI (**243**)/DIBAH/$(Ph_3P)_2PdCl_2$; *g*. AcCl/AcOH

Scheme 40.

Addition of hexynol **206** to 1-bromo-1-hexyne gave 5,7-dodecadiyn-1-ol (**241**), a precursor of (*Z,Z*)- and (*E,E*)-5,7-dodecadien-1-ols, components of the sex pheromone of the pine silkworm (Scheme 40) [151]. Addition of hex-1-yne (**242**) to vinyliodide **243** gave 5*Z*,7*E*-dodecadien-1-ylacetate (**244**), the sex pheromone of the hairy Chinese pine caterpillar (Scheme 40) [152].

Addition of ω-hydroxyacetylenes to vinylhalides catalyzed by tetrakis(triphenylphosphine)palladium [$(PPh_3)_4Pd$] provides a smooth and convenient stereospecific route to conjugated enyne and the corresponding diene alcohols, acetates, aldehydes, and esters, components of insect pheromones [153-162]. Thus, addition of dodec-11-yn-1-ylacetate (**245**) to (*Z*)-1-bromo-1-butene gives 13*Z*-hexadecen-11-yn-1-ylacetate (**246**), the sex pheromone of the pine silkworm *Thaumetopoea pityocampa* (Scheme 41) [163]. Dec-9-yn-1-ylacetate (**247**) and (*E*)-1-chloro-1-butene give analogously enyne acetate **248**, which is converted into 9*Z*,11*E*-tetradecadien-1-ylacetate (**226**), the sex pheromone of the Egyptian cutworm *Spodoptera littoralis* (Scheme 41) [164]. Addition of but-1-yne to C_{12}-allylic acetate **249** gave the (*E*)-isomer of enyne acetate **250**, a component of the female pheromone of the oak moth *Thaumetopoea processionea* (Scheme 41) [165].

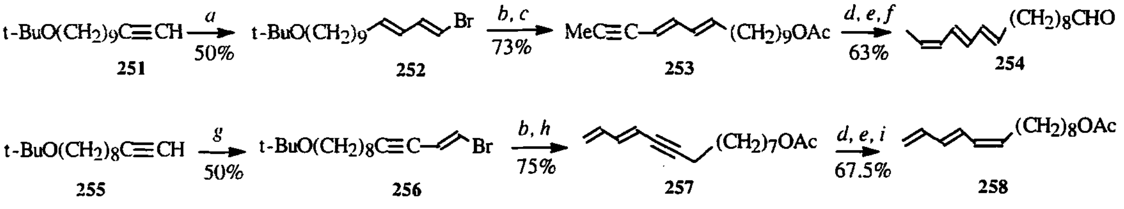


a. Br /Pd(PPh$_3$)$_4$ ^{n}PrNH$_2$/CuI; *b*. Br/Pd(PPh$_3$)$_4$^{n}PrNH$_2$/CuI; *c*. (SIAM)$_2$BH; AcOH; H$_2$O$_2$ /NaOH;

d.HC≡CEt/BuLi/ZnBr$_2$/Pd(PPh$_3$)$_4$/THF; *e*. H$_2$SO$_4$

Scheme 41.

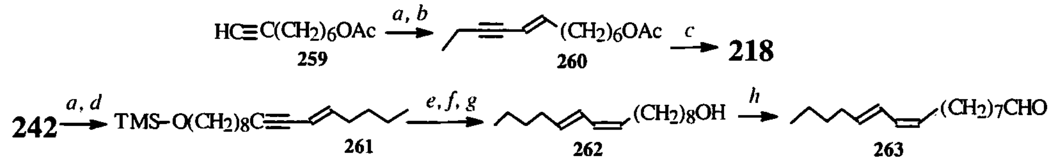
Addition of terminal alkynes **251** and **255** to 1,2-dibromoethylene produced diene **252** and enyne **256** vinyl bromides, respectively. These were then converted to acetates **253** and **257**, respectively, via the propynyl and vinyl zinc derivatives, respectively. The acetates are readily transformed to 10*E*,12*E*,14*Z*-hexadecatrienal (**254**) and 9*Z*,11*E*,13-tetradecatrien-1-ylacetate (**258**), respectively, components of the sex pheromones of *Manduca sexta* [166] and *Stenoma cecropia* (Scheme 42) [167].



a. DIBAH; BrCH=CHBr/Pd(PPh$_3$)$_4$/Et$_2$O; *b*. Ac$_2$O/FeCl$_3$/Et$_2$O; *c*. MeC ≡ CZnBr/Pd(PPh$_3$)$_4$; *d*. KOH; *e*. Zn/KCN/PrOH; *f*. (COCl)$_2$-DMSO/Et$_3$N;
g. BuLi/ZnBr$_2$/BrCH=CHBr/Pd(PPh$_3$)$_4$; *h*. CH$_2$=CHZnBr; *i*. Ac$_2$O/Py

Scheme 42.

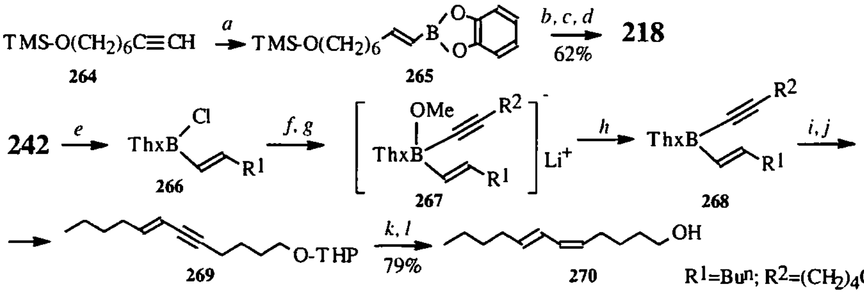
Hydroboration of terminal acetylenes or their 1-bromo- or 1-stannyl- derivatives and subsequent addition of the resulting vinylboranes to lithium or tin alkynides provides a general synthesis of conjugated enynes [168]. Enynes **260** and **261**, which are obtained using this method from alkynes **259** and **242**, are used to synthesize 7*E*,9*Z*-dodecadien-1-ylacetate (**218**) [9] and 9*Z*,11*E*-hexadecadienal (**263**), the sex pheromone of the sugarcane pyralid moth *Diatraea saccharalis* (Scheme 43) [169].



a. $(cyclo\text{-}C_6H_{11})_2BH$; *b.* $EtC \equiv CLi$; *c.* $Zn/{}^nPrOH$; *d.* $HC \equiv C(CH_2)_8OTMS/{}^nBuLi$; *e.* ${}^nBu_3SnCl$; *f.* AcOH; *g.* $H_2O_2/NaOH$; *h.* $(CN)_2C{=}C(CN)_2$

Scheme 43.

Organoboron intermediates that are produced by hydroboration of 1-alkynes such as disiamylborane or catecholborane [170] react smoothly with vinylhalides in the presence of $(PPh_3)_4Pd$ and base to give conjugated *E*,*E*- or *E*,*Z*-alkadienes [170, 171]. The pheromone of the leaf roller **218** is synthesized using this method from alkyne **264** through boron compound **265** (Scheme 44) [171].



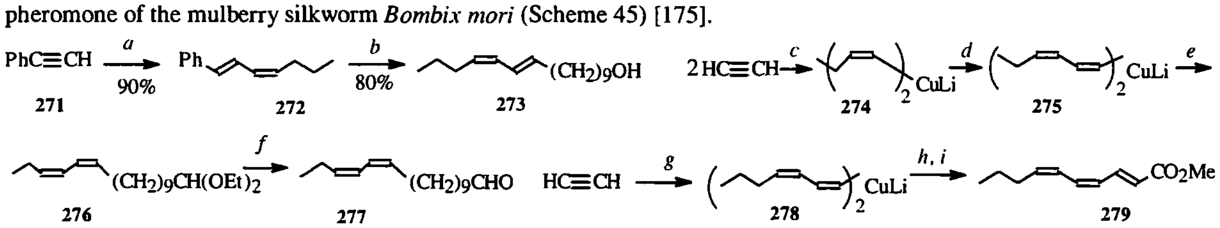
$R^1{=}Bu^n$; $R^2{=}(CH_2)_4O\text{-}THP$

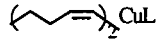
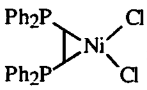
a. CtO_2BH; *b.* aq.NaOH; *c.*  $I/Pd(PPh_3)_4$; *d.* Ac_2O/Py; *e.* $ThxCl\ Me_2S/CH_2Cl_2$; *f.* MeOH; *g.* $R^2C \equiv CLi/THF$; *h.* $BF_3\ OEt_2$; *i.* MeOK/MeOH; *j.* I_2; *k.* $(SIAM)_2BH$; AcOH; $H_2O_2/NaOH$; *l.* TsOH/MeOH

Scheme 44.

The hydroborating complex of thexylchloroborane and dimethylsulfide is used to prepare from alkyne **242** via intermediates **266** and **267** thexylalkenylalkynylborane **268**, treatment of which with iodine in the presence of potassium methoxide gives in good yield and excellent stereochemical purity (≥95%) *E*-1,3-enyne **269**, which is then converted to 5*Z*,7*E*-dodecadien-1-ol (**270**), the sex pheromone of *Malacosoma disstria* (Scheme 44) [172].

The stereoselective alkylation of electrophiles by alkenylcuprates, which has been called the Normant reaction [173, 174], provides a convenient route to pheromones with (*E*,*Z*)- and (*Z*,*E*)-conjugated dienes. Thus, reaction of phenylacetylene (**271**) and bis(1-penten-1-yl)cuprate produces 1-phenyl-1*E*,3*Z*-heptadiene (**272**), the phenyl group of which is then stereoselectively replaced by a Grignard reagent in the presence of a nickel complex to give 10*E*,12*Z*-hexadecadien-1-ol (**273**), a pheromone of the mulberry silkworm *Bombix mori* (Scheme 45) [175].



a.  ; *b.* $HO(CH_2)_9MgBr/$  ; *c.* Et_2CuLi; *d.* $CH{\equiv}CH$; *e.* $I(CH_2)_9CH(OEt)_2$; *f.* $(CO_2H)_2/H_2O\text{-}THF$;

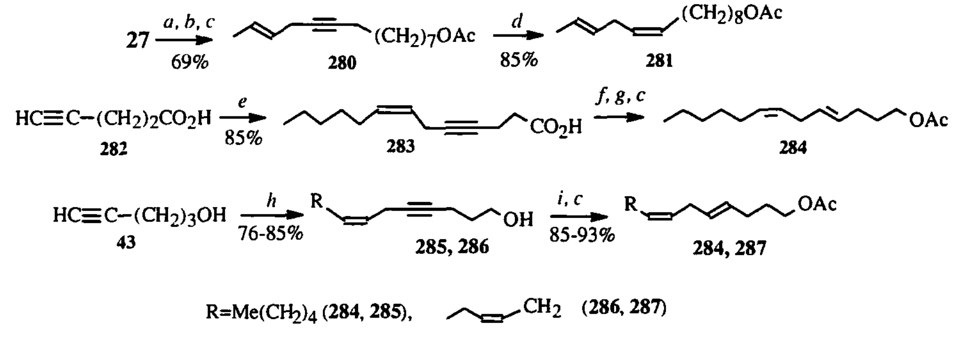
g. $Pr^nLi/CuBr{\cdot}Me_2S/C_6H_{14}\text{-}Et_2O$, -40°C; $CH{\equiv}CH$; *h.* $CH{\equiv}CCO_2Me$, -78°C; *i.* SiO_2

Scheme 45.

The synthetic power of the Normant reaction increased significantly after it was found that Z-alkenylcuprates, which are readily prepared by treatment of organocuprates with acetylene at -50 °C, are converted in good yield to Z,Z-dienylcuprates by treatment with acetylene at a higher temperature. The reaction of the latter with electrophiles led to highly stereoselective production of conjugated Z,Z-dienes [176]. For example, alkylation of lithium bis-(1Z,3Z-hexadien-1-yl)cuprate (**275**), that was prepared from acetylene and lithium bis-(1Z-buten-1-yl)cuprate, by the diethylacetal of 10-iododecanal gives acetal **276**. Hydrolysis of **276** produced (in 33% total yield) 11Z,13Z-hexadecadienal (**277**), a pheromone of the orange worm *Amyelois transitella* (Scheme 45) [177]. Analogously the methyl ester of 2*E*,4Z,6Z-decatrienoic acid (**279**), a sex pheromone isolated from male specimens of *Thyanta pallidovirens*, was synthesized in one step from the dienylcuprate intermediate **278** (Scheme 45) [178]. The total yield of **279** after chromatographic separation from methyl-2*E*,4Z-decadienoate was 13%.

SYNTHESIS OF DI-, TRI-, AND TETRAENE PHEROMONES WITH HOMOCONJUGATED DOUBLE BONDS

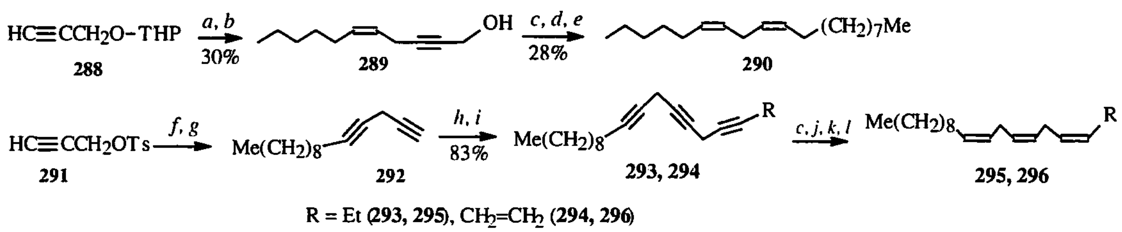
Pheromone components with double bonds separated by methylene groups can be prepared by addition of metal acetylenides to allylhalides [5, 9, 179, 180]. For example, 9Z,12*E*-tetradecadien-1-ylacetate (**281**), the sex pheromone of the grinding pyralid moth *Plodia interpunctella* and the grain pyralid moth *Ephestia elutella* and a component of those of several other insect species, is synthesized by this method [181, 182]. Enyne acetate **280** is prepared from terminal acetylene **27** and crotylbromide and is readily converted to the desired pheromone (Scheme 46). An analogous method using a cuprous catalyst gives enyne acid **283** from the magnesium derivative of alkynic acid **282** and 2Z-octen-1-ylbromide. Then **283** is converted as usual to 4*E*,7Z-tridecadien-1-ylacetate (**284**), the sex pheromone of the miner moth *Lithocolletis corylifoliella* (Scheme 46) [183].



Scheme 46.

A single attempt was made to synthesize acetate **284** and 4*E*,7Z,10Z-tridecatrien-1-ylacetate (**287**), the principal components of the sex pheromone of female potato moths *Phtorimaea operculella*, using the corresponding allyl bromides to produce the enyne (**285**) and dienyne (**286**) alcohols, respectively, which are readily converted to the desired products **284** and **287** (Scheme 46) [184].

The use of propargyl alcohol as a bifunctional alkyne has great promise for the synthesis of homoconjugated di- and triene pheromones. Addition of Iotsich reagent as its THP-ether (**288**) to 2Z-octen-1-ylbromide gives (Z)-enynol **289**, which is then converted to 6Z,9Z-nonadecadiene (**290**), a component of the sex pheromone of *Bupalus piniarus* (Scheme 47) [185].

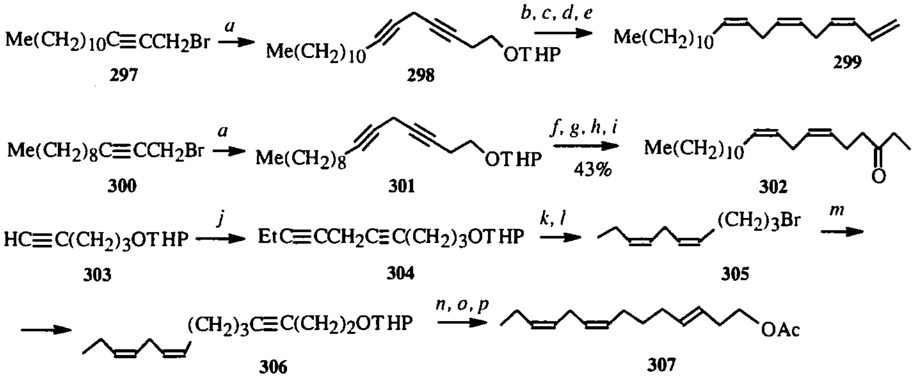


a. EtMgBr/CuCl/THF;$Me(CH_2)_4$ Br ; *b*. TsOH/MeOH; *c*. H_2/Pd-$CaCO_3$-PbO/C_6H_{14}; *d*. PBr_3•Py/Et_2O;
e. $Me(CH_2)_7MgBr/Li_2CuCl_4$/THF; *f*. $Me(CH_2)_8C≡CMgBr/CuBr·Me_2S$; *g*. $CH≡CCH_2OTs$;
h. $RC≡CCH_2OTs$ (R = Et, $CH=CH_2$)/$CuBr·Me_2S$; *i*. H_3O^+; *j*. $MsCl/Et_3N$; *k*. LiBr; *l*. KOH/MeOH

Scheme 47.

The tosyl derivative of propargyl alcohol (**291**) is used to synthesize 1,3Z,6Z,9Z-nonadecatetraene (**296**), a pheromone of *Operophtera brumata* [186-190], and 3Z,6Z,9Z-nonadecatriene (**295**), a component of *Boarmia selenaria* (Scheme 47) and certain other insect species (*Peribatodes rhomboidaria, Alsophila pometaria*) [186, 189-194] and also compounds **284** and **287** were mentioned above [195, 196], through intermediates **292-294**.

The compounds 1,3Z,6Z,9Z-undecatetraene (**299**), a component of the pheromone of the butterfly *Utetheisa ornatrix* [197], and 6Z,9Z-nonadecadien-3-one (**302**), identified in secretions of *Perilatodes rhomboidaria* [193], were synthesized by adding alkyne **59** to alkynylbromides **297** and **300** to prepare diynes **298** and **301** (Scheme 48).

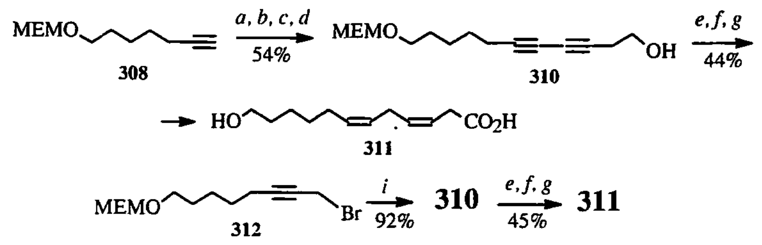


a. $THPO(CH_2)_2C ≡ CH$ (**59**)/EtMgBr/CuCl; *b*. TsOH/MeOH; *c*. H_2/Ni-Ra/EDA; *d*. PDC; *e*. $Ph_3P=CHCH=CH_2$;
f. H_2/Pd-$CaCO_3$-PbO; *g*. Br_2 PPh_3; *h*. KCN; *i*. EtMgBr/THF; *j*. EtMgBr; $EtC ≡ CCH_2OTs$/CuBr • Me_2S;
k. $(cyclo\text{-}C_6H_{11})_2BH$; AcOH; *l*. Br_2 • PPh_3; *m*. $THPO(CH_2)_2C ≡ CLi$; *n*. Dowex 50WX8/MeOH;
o. $LiAlH_4/(CH_2CH_2OMe)_2$; *p*. Ac_2O/Py

Scheme 48.

The THP-ether of pent-4-yn-1-ol (**303**) was used to prepare diyne **304** in the synthesis of 3*E*,8Z,11Z-tetradecatrien-1-ylacetate (**307**), a component of the sex pheromones of *Lepidoptera* insects [198]. Then diyne **304** was converted to *Z,Z*-dienylbromide **305** and further into dienyne **306** using the lithium derivative of alkyne **59**. Compound **306** was further converted to the desired acetate **307**, the total yield of which was 7% (Scheme 48) [198].

The addition of the magnesium derivative of alkyne **308** to tosylate **309** that is catalyzed by CuBr gave 1,4-diyne **310**, which was then converted to 12-hydroxy-3Z,6Z-dodecadienoic acid **311**, an acyclic precursor of the 3Z,6Z-dodecadienolide, a component of the aggregation pheromones of *Cryptolestes* and *Oryzaephilus* wheat beetles (Scheme 49) [199].



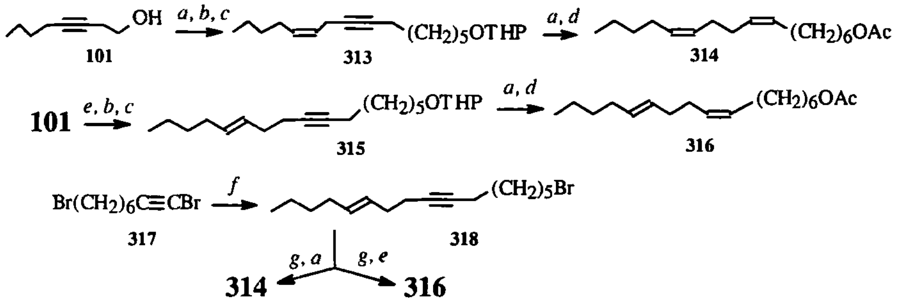
a. EtMgBr/THF; *b*. CuBr; *c*. TsOCH$_2$C ≡ C(CH$_2$)$_2$OSiMe$_2$Bu^t (**309**); *d*. TsOH/MeOH;
e. CrO$_3$/H$_2$SO$_4$/Me$_2$CO; *f*. HCl/aq.THF; *g*. H$_2$/Ni-P2; *i*. CH ≡ C(CH$_2$)$_2$OH (**58**)/EtMgBr/CuCl

Scheme 49.

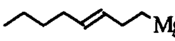
Bromide **312** and alkyne **58** are used in an alternate synthesis of hydroxyacid **311**. The resulting diynol **310** is then converted in three steps to the desired product (Scheme 49) [54].

SYNTHESIS OF DIENE PHEROMONES WITH ISOLATED DOUBLE BONDS

3-Alkynols, products of β-hydroxyethylation of terminal acetylenes, are convenient synthons for dienes with double bonds separated by two methylene groups [5, 9]. Starting with alkynol **101** and passing through the intermediate enynes **313** and **315** gives 7*Z*,11*Z*- (**314**) and 7*Z*,11*E*-hexadecadien-1-ylacetates (**316**), respectively, components of gossyplur, the sex pheromone of a cotton pest, the pink box worm *Pectinophora gossypiella* (Scheme 50) [5, 9, 76]. Enyne **315** is also synthesized by addition of the THP-ether of oct-7-yl-1-ol to 3*E*-octen-1-ylbromide [200]. Gossiplur is synthesized by addition of dibromide **317** to 3*E*-hexen-1-ylmagnesium bromide followed by conversion in two steps of enyne bromide **318** into components **314** and **316** (Scheme 50) [201].

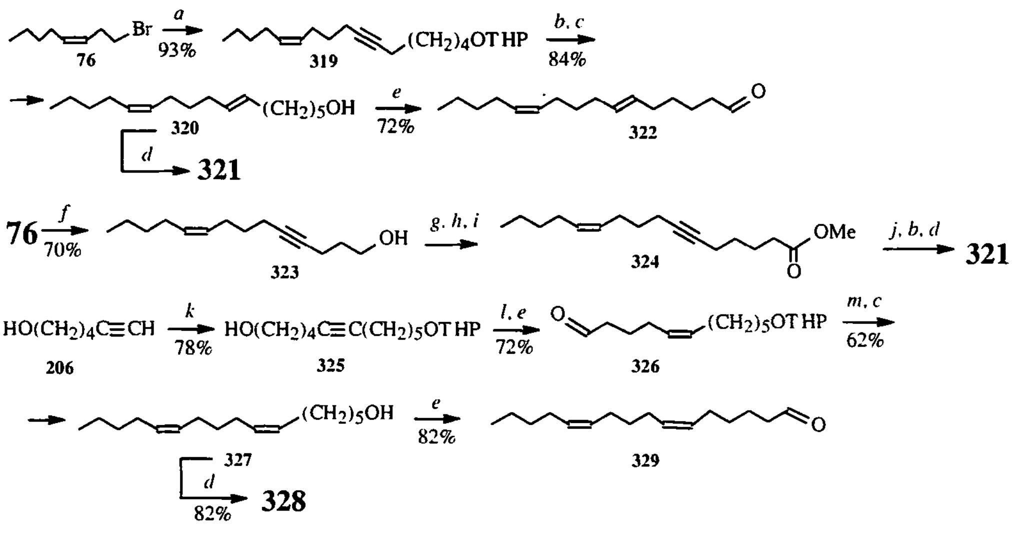


a. H$_2$/Pd-CaCO$_3$-PbO; *b*. PBr$_3$·Py; *c*. HC≡C(CH$_2$)$_6$OTHP/LiNH$_2$; *d*. AcCl/AcOH; *e*. Na/Liq/NH$_3$

f.  MgBr/CuCl; *g*. AcONa/AcOH

Scheme 50.

Addition of bromide **76** to the THP-ether of hept-6-yn-1-ol followed by (*E*)-selective reduction of enyne **319** gives 6*E*,11*Z*-hexadecadien-1-ol (**320**), which is then converted to its acetate (**321**) and aldehyde (**322**), components of the sex pheromone of *Antheraca polyphemus* (Scheme 51) [202].

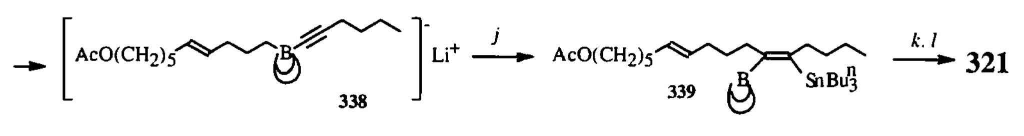


a. HC ≡ C$(CH_2)_5$OTHP/Bu^{n}Li/HMPA; *b*. Na/liq.NH_3; *c*. TsOH/MeOH; *d*. Ac_2O/Py; *e*. PCC; *f*. HC ≡ C$(CH_2)_3$OH/NH_2Li/liq.NH_3; *g*. Br_2 • PPh_3;
h. NaCH$(CO_2Me)_2$; *i*. LiCl/H_2O; *j*. $LiAlH_4$; *k*. NH_2Li/liq.NH_3; Br$(CH_2)_5$OTHP; *l*. H_2/Ni-P2; *m*. Bu^{n}CH=PPh_3

Scheme 51.

Alkylation of the dianion of pent-4-yn-1-ol by bromide **76** produced enyne alcohol **323**, which was converted successively to ester **324** and the desired acetate **321** (Scheme 51) [203]. Reaction of the dianion of alkynol **206** with the THP-ester of 5-bromopentan-1-ol gave the selectively protected alkyndiol **325**, which was then transformed into (*Z*)-aldehyde **326** or the corresponding (*E*)-isomer. Introducing an olefin into aldehyde **326** via the Wittig reaction and subsequent standard reactions gave 6*Z*,11*Z*-hexadecadien-1-ol (**327**), its acetate (**328**), and the aldehyde (**329**) (Scheme 51). Analogously (6*E*,11*Z*)-isomers **320**, **321**, and **322** were synthesized from the (*E*)-isomeric aldehyde. Compounds **321**, **322**, **328**, and **329** are components of the sex pheromones of Saturnidae insects [204]. Using tritium to convert the C_{16} enynol or the diynol into the corresponding (*Z*,*Z*)-dienol produced (after acetylation) the tritium-containing pheromone analogs of **328** [205].

Diene acetate **321** was also synthesized by reacting bromide **330** with lithium but-1-ynide followed by conversions of dienyne **331**. The key step was selective hydroboration of the terminal C atom of the vinyl group (Scheme 52) [206].



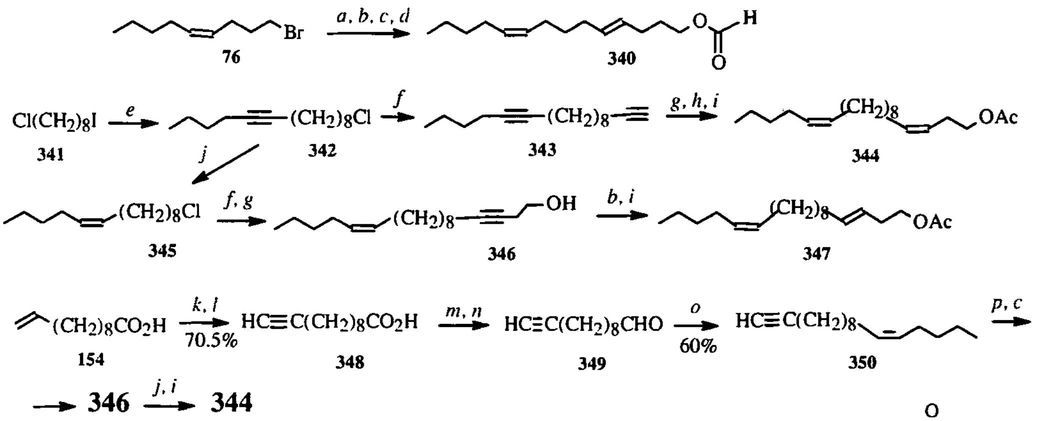
a. ^{n}BuC ≡ CLi; *b*. H_2/Pd-$CaCO_3$-PbO; *c*. 9-BBN; AcOH; H_2O_2/NaOH; *d*. Ac_2O/Py; *e*. ^{n}BuLi; [THPO$(CH_2)_5]_3$B; *f*. I_2; *g*. (cyclo-$C_6H_{11})_2$BH;
h. MeONa/MeOH; *i*. CuBr Me_2S; CH_2=$CHCH_2$Br; *j*. ^{n}Bu_3SnCl; *k*. AcOH; *l*. H_2O_2/NaOH

Scheme 52.

Alkenyne precursors of pheromones can be prepared by treating borate complexes with iodine. This method was used to synthesize C_{16}-enyne **319** from borate complex **333**, which was obtained from C_1l-enyne **332** (Scheme 52) [207].

The selective migration of a primary alkyl group from the B atom to the neighboring acetylene C atom in lithium 1-alkynyltrialkylborate complexes, which are prepared from B-alkyl-9-borabicyclo[3.3.1]nonane and lithium alk-1-ynides, that is initiated by trialkyltinchloride represents a general route to various dienes, enynes, enones, ynones, and diynes. This reaction has been successfully used in the stereoselective synthesis of several insect sex pheromones. Thus, hydroboration starting with alkynylacetate **334** and followed by reaction of organoboron compound **335** with allylbromide gives dienylacetate **336**, which is converted into another organoboron compound **337**. Further reaction of **337** with lithium hexynide gave borate complex **338**. Reaction of **338** with tributyltinchloride gave the intermediate **339** and then the desired pheromone **321** (Scheme 52) [101].

Addition of 1-bromonon-4-yne and *E*/*Z*-isomeric 1-bromo-4-nonenes to the lithium derivative of the THP-ether of pent-4-yn-1-ol and subsequent (*Z*)- or (*E*)-selective transformation of the resulting diyne or the corresponding (*E*)- and (*Z*)-isomeric enynes into the dienes gives all four geometric isomers of 4,9-tetradecadien-1-ylformate, which stimulate movement of *Philosamia cynthia* butterfly wings [208]. If (*Z*)-nonenbromide **76** is used, the most active 4*E*,9*Z*-tetradecadien-1-ylformate (**340**) is obtained (Scheme 53).



a. $THPO(CH_2)_3C \equiv CLi$; *b*. Na/liq.NH_3; *c*. H_3O^+; *d*. HCO_2H; *e*. $^nBuC \equiv CNa$; *f*. $HC \equiv CLi$ EDA/DMSO; *g*. ^nBuLi; $\overset{O}{H_2C - CH_2}$; *h*. 9-BBN; *i*. Ac_2O/Py; *j*. H_2/Pd-$CaCO_3$-PbO; *k*. Br_2; *l*. KOH; *m*. $LiAlH_4$; *n*. PCC; *o*. $[Me(CH_2)_4PPh_3]^+Br^-$/ ^tBuOK; *p*. ^nBuLi; $THPO(CH_2)_2Br$

Scheme 53.

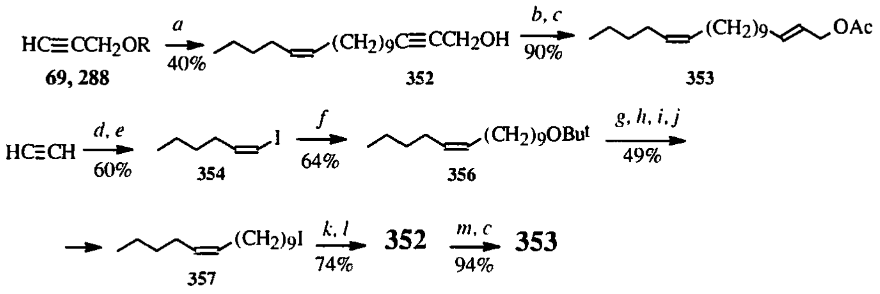
Selective substitution of the I atom of 1,8-chloroiodooctane (**341**) by sodium hexynide gives C_{14}-chloroalkyne **342**, which is converted to C_{16}-diyne **343** and then the desired 3Z,13Z-octadecadien-1-ylacetate (**344**) (Scheme 53). If chloroacetylene **342** is converted to (*Z*)-alkene **345**, then addition in two steps of lithium acetylide and ethylene oxide gives 13*Z*-octadecen-3-yn-1-ol (**346**), which is easily converted to 3*E*,13*Z*-octadecadien-1-ylacetate (**347**). Both acetates **347** and **344** are components of pheromones of many *Synathedon* butterfly species [209-211].

(*Z*,*Z*)-Dienylacetate **344** was also synthesized starting from acid **154**, which was converted in two steps to undecynoic acid (**348**), then to the corresponding aldehyde **349**, and finally through enynes **350** and **346** to the desired compound (Scheme 53) [212, 213].

Dienylacetate **344** was also identified as a sex pheromone of the poplar moth *Sphecia siningensis* and was synthesized in two steps from propargyl and homopropargyl alcohols to produce enyne precursor **346** of the target compound [214].

Several syntheses of 2*E*,13*Z*-octadecadien-1-ylacetate (**353**), known to be the sex pheromone of the grape-root borer *Vitacea polistiforma* [215] and *Synanthedon tipuliformis* and *Zenzera pyrina* [216, 217], have been reported. In one of these syntheses, like for the synthesis of **344** above, the starting material was undecenoic acid **154** [218].

In two other syntheses of **353**, the key step was the addition of propargyl alcohol **69** [216] or its THP-ether [217] to 10*Z*-pentadecen-1-ylbromide (**351**), which gives enyne precursor **352** of the desired compound (Scheme 54).



R = H (69), THP (288)

a. NH_2Na/liq.NH_3; **351**; *b*. $LiAlH_4$; *c*. Ac_2O/Py; *d*. $Me(CH_2)_3Br$/Li/CuI; *e*. I_2; *f*. *Cl*$(CH_2)_9OBu^t$ (**355**)/Li/$ZnBr_2$/ $Pd(PPh_3)_4$/THF; *g*. $Ac_2O/FeCl_3/Et_2O$; Na_2HPO_4; *h*. KOH/MeOH; *i*. TsCl/Py; *j*. NaI/Me_2CO; *k*. **288**/Bu^nLi/C_6H_{14}-THF-HMPA; *l*. TsOH; *m*. Al-Red

Scheme 54.

10Z-Pentadecen-1-yliodide (**357**) has been added to ether **288** [219]. It was prepared via stereospecific addition of a vinylcuprate reagent to acetylene with subsequent addition of the resulting 1Z-hexen-1-yliodide (**354**) to chloride **355** to give product **356**, which was converted by standard methods to the required iodide **357** (Scheme 54).

Thus, the ease of constructing the required C backbone using reactive metal acetylides, the possibility of converting stereoselectively alkynes into (*Z*)- or (*E*)-alkenes, and the stereospecific addition to terminal acetylenes of alkyl- and alkenylcuprates and borates suggests that the acetylenic synthesis is one of the most versatile and general routes to acetogenic pheromones.

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