Tetrahedron Vol. 40, No. 14, pp. 2741 to 2750, 1984
Printed in the U.S.A.

0040-4020/84 $3.00 + .00

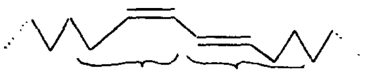
GENERAL METHODOLOGY FOR THE SYNTHESIS OF CONJUGATED DIENIC INSECT SEX PHEROMONES

M. GARDETTE, N. JABRI, A. ALEXAKIS* and J. F. NORMANT
Laboratoire de chimie des Organo-Elements, Tour 44-45, 4 Place Jussieu, 75230, Cedex 05, France

(Received in France 18 *July* 1983)

Abstract—A general methodology for the synthesis of various types of dienic insect sex pheromones (Z-E, E-Z, Z-Z) is based on the carbocupration of acetylene by functionalised or non-functionalised lithium dialkyl cuprates, followed by the coupling of the resulting Z dialkenyl cuprates with fimctionalised or non-functionalised E or Z alkenyl iodides under Pd" catalysis. The following compounds were efficiently synthesized with a high degree of stereoisomeric purity: **(E–Z)7,9-dodecadien,-1-yl** acetate 1 ***(Lobesia botrana)*, (E–Z)10,12-hexadecadien,-1-ol** 2 ***(Bombyx mori)*, (Z–E)9,11-tetradecadien,-1-yl** acetate 3 ***Spoabptera littoralis)*, (Z–E)5,7-dodecadien-1-ol** 4 ***(Malascoma disstria)*, (Z–Z)11,13-Hexadecadien-1-al** 5 ***(Amyelois transitella)*, (Z)9,11-dodecadien-1-yl** acetate 6 ***(Diparopsis castanea)*** and **(Z–Z)9,11-tridecadien-1-yl** acetate 22 (a known "pseudo-pheromone").

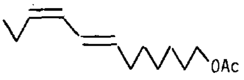
Insect sex pheromones are a class of biologically active compounds of growing interest and many new methodologies have been developed for their synthesis.’ The chemical structure of many of these pheromones contains a long carbon chain with a terminal functionality Y (–CH_2OH, –CH_2OAc, –CHO) and which often incorporates a conjugated diene system: $CH_3–(CH_2)_n–CH=CH–CH=CH–(CH_2)_m–Y$. This diene system may be of E-E type, of Z-Z type or, more frequently, of E-Z and Z-E type. In these two last cases the terminal functionality could be on the "Z part" of the molecule or on the "E part":



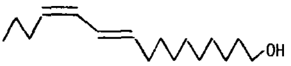
Many syntheses of these pheromones have been developed’ and may be roughly divided into four classes: (a) the Wittig type approach,[3] in which the Z double bond is created by reaction of an E alkenal with an alkyl triphenylphosphonium ylide; (b) the carbon chain extention[4] of an already prepared diene system bearing an allylic functionality; (c) the syn reduction of the triple bond of an E enyne[5] which can be prepared by various ways; (d) the direct coupling of two alkenyl moieties,[6] one of Z configuration and one of E configuration (this highly convergent approach is the most recently developed).

Among these various approaches, few afford a product of high stereoisomeric purity and even fewer may be considered to be of preparative value. The need for preparative syntheses stems from the fact that these pheromones are more and more used for large scale field tests. In this respect, a synthesis of preparative value should satisfy two major requirements. First, it should use low cost reagents and starting materials and second it should avoid the expensive chromatographic purification or low temperature (— 35") recrystallization which are needed when the synthesis does not afford a product of high enough chemical or isomeric purity. In this article we present a general methodology for the synthesis of dienic pheromones of Z-Z, E-Z, and Z-E configuration, which, we believe, meets the above requirements. This methodology is illustrated by the synthesis of the following typical pheromones (or by the synthesis of their known direct precursor):

" E-Z "

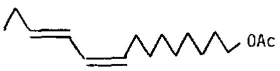


Lobesia botrana[7] 1

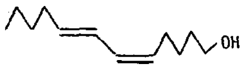


Bombyx mori[8] 2

" Z-E "

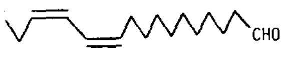


Spodoptera littoralis[9] 3



Malascoma disstria[10] 4

" Z-Z "



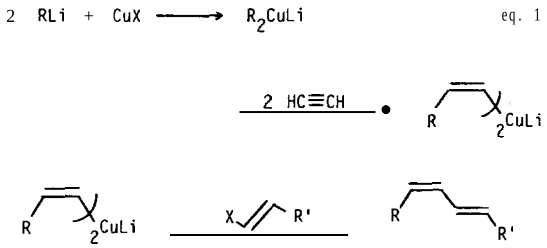
Amyelois transitella[11] 5

" -Z "

Diparopsis castanea[12] 6

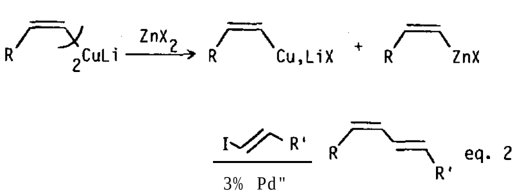
GENERAL METHODOLOGY

The syntheses shown below are of the convergent type, linking together in a “one-pot” operation two alkenyl moieties of which the Z alkenyl moiety is brought about by an organometallic species. This organometallic reagent is a Z dialkenyl cuprate easily obtained by the known carbocupration of acetylene:[13,14]

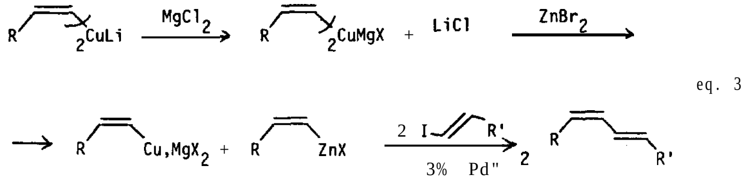

eq. 1

Many monoolefinic,[15] enynic[16] or non-conjugated dienic[17,18] pheromones have already been synthesized[19] by the reaction of these Z dialkenyl cuprates with an appropriate electrophile. These pheromones have been shown to be of greater than 99.9% Z purity and they are obtained in high yield by simple distillation of the crude product.

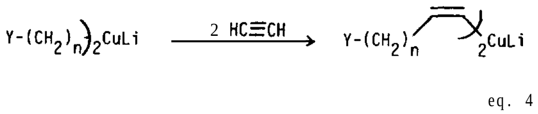
In our syntheses of the dienic pheromones we needed to couple the Z dialkenyl cuprates with an alkenyl moiety of E configuration (eqn 1). Toward this end, two preliminary studies have been undertaken on model systems. In the first one we optimized the conditions of the coupling of the Z dialkenyl cuprates with E iodo-alkenes. These cuprates are usually inert towards iodo-alkenes. However, we found that upon *in situ* transmetallation into the zinc reagent, they are able to couple with alkenyl[20] and aryl[21] iodides in the presence of catalytic amounts of Pd” complex.


eq. 2

In this reaction, only one alkenyl group of the cuprate is used. This loss is not a serious drawback when the alkenyl iodide is the valuable partner of the coupling reaction. On the contrary, when the cuprate is the valuable partner, this loss becomes an evident disadvantage. Thus, we were led to seek conditions where both alkenyl groups are transfered, and we found that this is possible, if the *lithium* cuprate is first transformed-into a *magnesium* cuprate:[22]

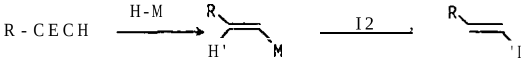

eq. 3

In the second preliminary study we optimized the carbocupration of acetylene with ω-functionalised cuprates in order to be able to introduce the functionality on the “Z part” of a dienic pheromone:


eq. 4

Among the various functionalities Y, we found that the most convenient and efficient one was the alcohol group, protected as an ethoxyethyl ether.” With this functionality, the experimental conditions of the carbocupration reaction are only slightly different from the standard ones.

Having secured the two key reactions (eqns 2-4) on which we based our synthetic strategy, we turned our attention to the preparation of the E alkenyl iodides which are the other partners of the coupling reaction (eqn 1). Among the various methods for the synthesis of these alkenyl iodides, the most efficient and straightforward are based on the hydrometallation of a terminal alkyne:[24]

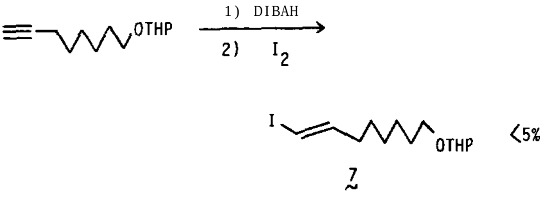


The products obtained by this way are usually pure enough (> 99%) to avoid any further purification and separation of isomers. Hydroboration,[25] hydrocupration,[26] hydrozirconation[27] and hydroalumination[28] are the most often used reactions, but as far as cost is concerned, the hydroalumination reagent DIBAH[29] (diisobutyl aluminum hydride) is by far the less expensive. The non-functionalised E alkenyl iodides prepared by this way are of high isomeric purity (99.3–99.8%) and they are also obtained in good yield (45–80%). The main drawback lies in the fact that functionalised alkynes (bearing an oxygenated functionality) do not react as well,[30] but this difficulty was easily circumvented as shown below.

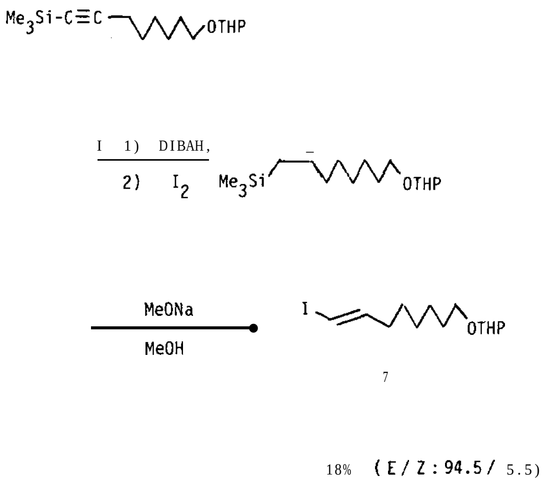
Synthesis of E-Z *pheromones*

Among the pheromones which possess a conjugated diene system of E-Z type the most representative are the pheromone of *Lobesia botrana* (Denis and Schiff), the European grape vine moth 1 and the pheromone of *Bombyx mori,* the silkworm moth 2. Due to the importance of the damage caused by the grape vine moth, compound 1 has been synthesized many times[31] using almost all the known methodologies. The diene system of this pheromone is of E-Z type with the functionality lying on the “E part” of the molecule. This means, that, for a convergent approach, the alcohol or acetate functionality will be carried by the E alkenyl iodide moiety (see eqn 1).

Thus, for the synthesis of the pheromone of ***Lobesia botrana* 1 *we*** needed to prepare I-iodo, (E) **1-octen,8-o1** or its acetate. The standard **hydro**alumination of **7-octyn,** l-o **l,** protected as THP ether, afforded, as expected, less than **5%** of the desired iodide **7**:



However, Zweifel ***et al.*** reported recently that terminal alkynes protected by a trimethylsilyl group may be hydroaluminated even in the presence of an oxygenated functionality.[32] After reduction and **io**dination, the trimethylsilyl group may **be** removed without isomerisation of the stereochemistry of the newly created double bond. Unfortunately, in our hands, this procedure afforded only a 18% yield of iodo-alkene 7 with only 94.5% isomeric purity:



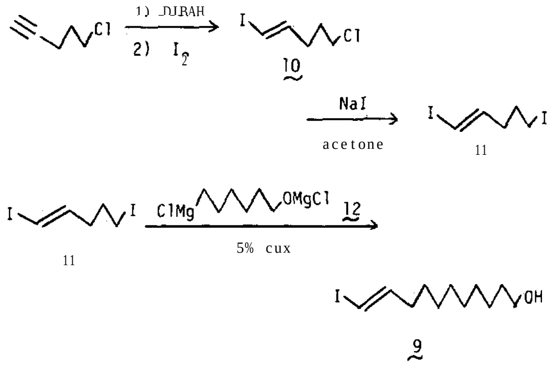
Nevertheless, we carried out the synthesis of the pheromone 1 with this material in order to explore the feasability of our key coupling reaction. Thus, the iodo-alkene 7 was directly transformed into the corresponding acetate 8 by treatment with **AcOH/AcCl** (10: **1**).[33] This direct acetylation procedure preserves the geometrical integrity of the double bond. The acetate 8 was then added admixed with 3% **Pd(PPh$_3$)$_4$** to a THF solution of Z dibutenyl **cuprate** which had previously been transmetallated into the zinc species by addition of one equivalent of zinc bromide:

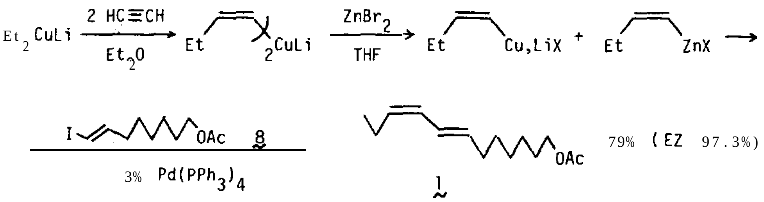
This reaction **afforded** in a one-pot procedure the pheromone **1** in a *78%* distilled yield and with a 97.3% E-Z purity. The increase in stereoisomeric purity of the diene **1 as** compared to the starting iodide 8 was not unexpected since we observed in the preliminary study that E iodo-alkenes were much more reactive than their Z **counterparts.**[20,22b] Noteworthy is also the fact that the acetate functionality was completely unaffected by the organometallic reagent used. Thus, we demonstrated that our key coupling reaction was highly efficient for pheromone synthesis. It is clear that if the iodo-alkene was of higher **stereo**isomeric purity, the pheromone would have been obtained in an even higher steroisomeric purity. The main drawback of our synthesis of the pheromone of ***Lobesia botrana*** 1 does not lie in the key coupling reaction, but in the preparation of the functionalised E iodo-alkene. This drawback was circumvented for the synthesis of the other typical E-Z dienic pheromone bomyko12.

Bombykol 2 is the pheromone of ***Bombyx mori,*** the silkworm moth. This compound owes its notoriety to the fact that it was the **first** isolated pheromone.* Since then, bombykol 2 has been synthesized by all known methods as representative of E-Z dienic **pheromones.**[34] Here again the functionality lies in the "E part" of the molecule, and therefore it will be carried by the E iodo-alkene moiety, which in the case of bombyko12 would be the 1-iodo-l(E)-undecen-1 **1-ol** 9.

9

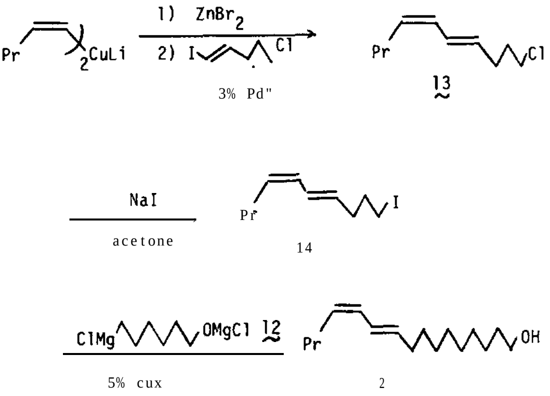
Since the hydroalumination of alkynes bearing an oxygenated functionality was not **succesful,** we chose another functionality which tolerates a strong Lewis acid, such as DIBAH. A halogen functionality, for example, is unaffected during hydroahunination and is easily transformed into an alcoholic one with the same or a higher number of carbon atoms. Thus, alkenyl iodide 9 could be prepared according to the following scheme:





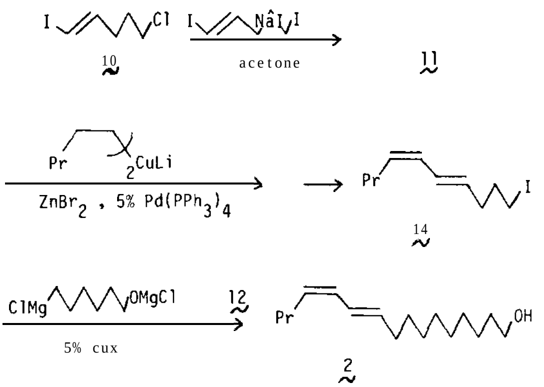
Hydroalumination of **1-chloro,4-pentyne,** followed by iodination, proceeded without any trouble, affording in **70–85%** isolated yield the alkenyl iodide **10**[35] (E purity **>99.5%).** An attempted carbon chain extention on compound 10 to obtain directly 9 was **unsuccesful** since functionalised Grignard reagent **12,**[36] in the presence of catalytic amounts of **Cu^I salt,** reacted mainly at the **sp^2** carbon-iodine bond instead of the **sp^3** carbon-chlorine bond. The chloro-iodide 10 could be easily transformed into the di-iodide 11 by halogen exchange with sodium iodide in acetone" (or methanol) with complete retention of the stereochemistry of the double bond. Compound **11,** in turn, reacted with the Grignard reagent **12,**[36] under copper(1) catalysis, to give mainly, but not exclusively (70% selectivity) the expected iodo-alcohol 9. Thus, this route, which needed chromatographic purification, was abandonned since it was not in agreement with one of the above requirements.

Another approach, also based on the use of alkenyl iodide 10, is depicted below:



The iodide 10 reacts easily with Z dipentenyl **cuprate,** in the presence of zinc bromide and 3% **$Pd(PPh_3)_4$,** to give chloro-diene 13 in 89% yield. As expected in this case, the organemetallic reagent completely discriminates between the alkenyl iodide and alkyl chloride functionalities in favor of the **former.**[22b] At this stage, **the** chloro-diene 13 showed a high stereoisomeric purity (> 99.5%) as checked by ^{13}C NMR and capillary glass chromatography **(OV1,** 20m). According to our synthetic scheme, this compound has to be elongated by six carbon atoms for the obtention of the pheromone 2. The attempted reaction of the chloride 13 with the **functionalised** Grignard reagent 12 under copper(I) catalysis failed completely. The recovered chloro-diene 13 was, then, transformed into the more reactive iodide 14 by the usual **NaI/** acetone (or methanol) method. Unfortunately this reaction was very slow at room temperature and even at reflux temperature it needs two days for completion. However, under these stringent conditions, the obtained iodide 14 was partially **isomerised (8–10%),** probably due to the presence of traces of free iodine which is known to isomerise the conjugated dienic systems.

Another similar synthetic route was also investigated, in which the transhalogenation step preceded the key coupling reaction, according to the following scheme:

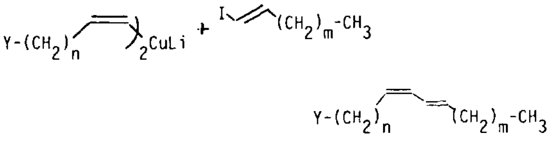


The key coupling reaction between the diiodide 11 and the dialkenyl **cuprate,** previously transmetallated into the zinc species, proceeded quantitatively with ***exclusive*** attack at the alkenyl iodide **group.**[22b] This remarkable selectivity of the palladium catalysed **coupling**[37] contrasts with the above-mentioned copper catalysed coupling at the alkyl iodide group with the Grignard reagent 12. The crude iodide 14 was not further purified and was used directly in the next carbon chain extention step. Thus, the **functionalised** Grignard 12 reacted easily, under copper(I) catalysis, with iodide 14 to **afford** the expected pheromone 2. Crude bombykol 2 was distilled through a **10 cm** Vigreux column to afford a **76%** yield (based on the alkenyl iodide 10) of purified material. This **bombykol** 2 showed a 99.8% stereoisomeric purity upon examination by capillary glass chromatography.

This preparative synthesis of bombyko12 is representative of our general methodology for the synthesis of E-Z dienic pheromones. Although we have not synthesized other pheromones of this type, we may consider that the same route can be applied for the synthesis of many other pheromones using a Z dialkenyl **cuprate** and a functionalised Grignard with the appropriate carbon chain length. In this context, the common intermediate **1,5-diiodo-1(E)-pentene,** easily prepared in bulk and conveniently stored in the refrigerator without noticeable decomposition, is the keystone for various E-Z pheromone syntheses.

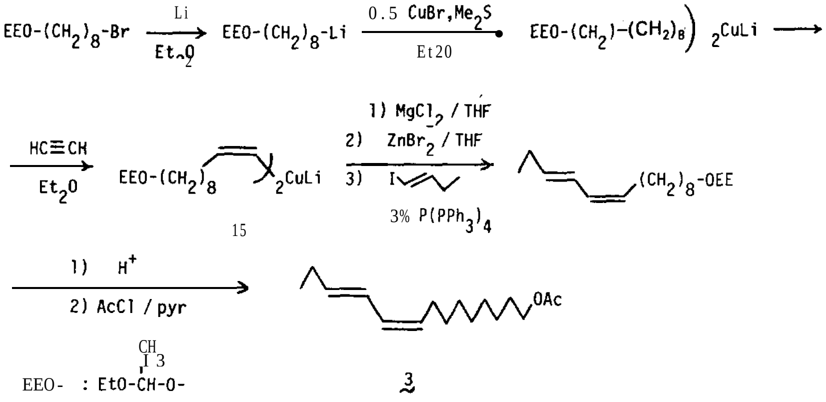
Synthesis of Z-E pheromones

Pheromones with a conjugated dienic system of Z-E type, have the functionality lying on the "Z part" of the molecule. Using our general methodology, this means that the functionality has to be introduced by the Z dialkenyl **cuprate** moiety:



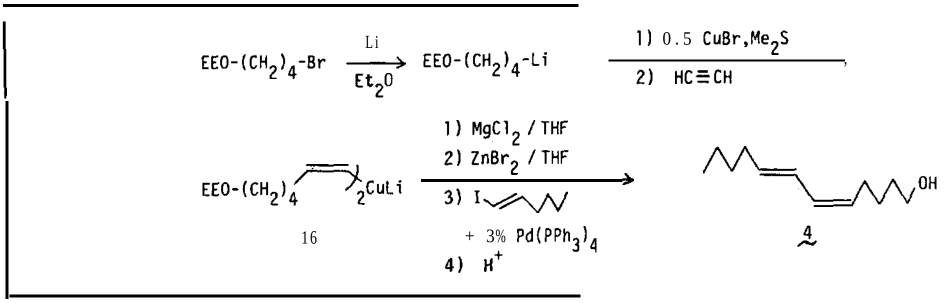
The pheromone of ***Spodopteru littoralis* 3,** the Egyptian cotton leafworm, is the most trivial example of this class of pheromone, and a very large number of syntheses have been **reported.**[39] Our approach is based on the use of **functionalised cuprates**[23] for the preparation of the Z dialkenyl **cuprate,** and is **de-**

picted below:



The easily available **1,8-bromooctanol,** protected as an ethoxyethyl ether, is transformed into the lithium reagent with lithium metal **(1–2%** Na content) in ether under the usual reaction conditions **(−15°)** with an average yield of 65%. This **functionalised** organolithium reagent”' affords a stable **cuprate,** when the complex **$CuBr,Me_2S$**[41] is used, and its addition to acetylene occurs under the standard reaction **conditions.**[14] The **functionalised** Z dialkenyl **cuprate** 15 has, now, to be coupled with **1-iodo-1(E)-butene** to **afford** the required pheromone 3. In contrast to the previous examples of this key coupling reaction, the most valuable of the two partners is, here, **the functionalised** Z dialkenyl **cuprate** and not the non-functional&d alkenyl iodide. Therefore, it is imperative to use efficiently ***both*** alkenyl groups of the **cuprate, and we found in our preliminary study,” that this is indeed possible** when the lithium **cuprate** is first transformed into the magnesium **cuprate** and then transmetallated into the zinc reagent. Under these experimental conditions, the pheromone was obtained in high overall yield (based on the lithium reagent), after removal of the protecting group and acetylation. Distillation of the crude pheromone 3 afforded a product of 97.2% stereoisomeric purity in **60%** overall yield. The stereoisomeric purity is not as high as we wished and it seems that the acidic deprotection step is responsible for that fact. Nevertheless, this purity is high enough for field tests in the case of this pheromone.

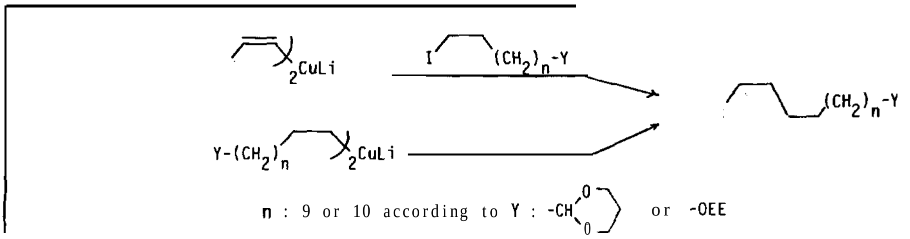
Another example of Z-E type pheromone is compound 4, the pheromone of ***Malascoma disstria,*** the forest tent caterpillar.” The same methodology as above is used for this synthesis as depicted below:



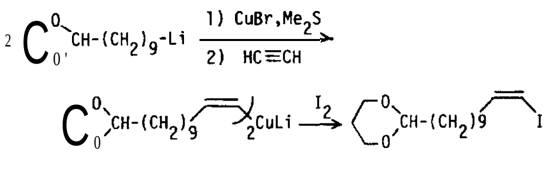
In this case, the functional&d **cuprate** 16 is used and coupled with **1-iodo,(E)1-hexene.** After deprotection of the alcohol, the pheromone is purified by distillation and obtained in 37% yield. The stereoisomeric purity was here, also, lower than we wished: 98.1%. If, however, the crude pheromone was purified by short flash chromatography, the yield is increased to 53%. This different behaviour points to the sensitivity of these compounds to prolonged heating. It is also interesting to note that dienic pheromones bearing an acetate functionality seem to be less sensitive than the ones bearing a free alcohol.

Synthesis of Z-Z and Z 1,3-dienic pheromones

Pheromones with a conjugated dienic system of Z-Z type are less frequently encountered. The main example is the pheromone of ***Amyelois transitella* (Wlk)** 5, the navel orange **worm.**[43] Using our methodology, this kind of pheromone may be synthesised by either of these two ways:

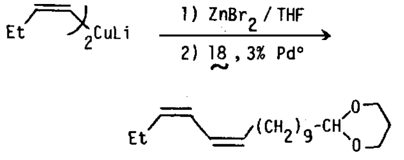


In both of these two ways the Z alkenyl iodide is prepared by iodination of a Z dialkenyl **cuprate.**[23,24] In the first approach we synthesized the functional&d Z alkenyl iodide 18 in the following way:



17 18 71%

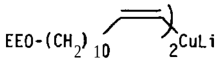
This iodide 18, obtained in 71% yield and with a high isomeric purity (> 99.9%) was coupled with Z **di**butenyl **cuprate** under the usual conditions:



19

The key coupling reaction afforded a 74% crude yield of the diene 19 which was homogeneous by TLC and GLPC. The Z-Z stereoisomeric purity of this diene was estimated to be. **>99%**, according to ^{1}**H** and ^{13}**CNMR** spectra. Capillary glass chromatographic analysis showed a single peak, but since the other stereoisomers were not available, it is hard to appreciate more accurately this purity. The aldehyde functionality of diene 19 had to be deprotected for the obtention of the pheromone 5. Treatment of diene 19 with oxalic acid in methanol at room temperature overnight resulted in an only 10% conversion to the aldehyde 5. On the other hand, treatment with pure anhydrous formic acid afforded, indeed, the expected aldehyde 5 but the pheromone was partially **isomerised** (**~ 5%)** under these vigorous conditions.

These difficulties were circumvented using the second possible approach. According to this scheme we reacted the functionalised **cuprate 20** with I-iodo-i(Z)-butene under the coupling conditions where ***both*** alkenyl groups of the **cuprate** are **used:**[22]



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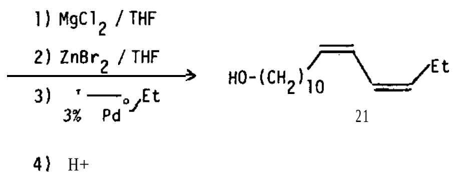


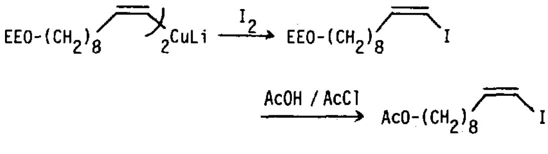
21

After deprotection of the alcohol, the crude dienic alcohol 21 could be either distilled or purified by short filtration through silica gel. Attempted distillation through a **10 cm** Vigreux column **afforded** only a **28%** yield of alcohol 21 which, however, was partially **isomerised (~ 6–7%)**. The Z-Z conjugated dienic system seems to be too sensitive towards prolonged heating. On the other hand, the simple **filtration** through silica gel (10 : 1 ratio of silica gel to product) with elution with pentane, then ether, afforded pure dienic alcohol 21 in 72% yield. This material was homogeneous by TLC and GLPC and showed an isomeric purity > 99% as judged by ^{1}**H** and ^{13}**C** NMR. The obtention of 21 constitutes a formal synthesis of the pheromone 5 since its **con**vertion to the aldehyde by pyridinium **chloro**chromate oxidation is already **described.**[43a] Thus, we can consider that our general methodology may be easily extended to the synthesis of Z-Z dienic pheromones.

Another example of synthesis of Z-Z dienic systems is the preparation of (Z, Z), 1 **1-tridecadien-1-yl** acetate 22. This compound has been shown to give a higher response on the antennae of males of some processionary moths than their corresponding pheromones, and more material was needed for further tests?

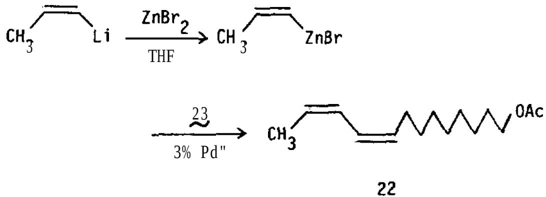
22

This compound was synthesized, also, by coupling of two alkenyl moieties one of which is a Z propenyl group and the other one a functionalised Z alkenyl iodide. The previously used functionalised Z **di**alkenyl **cuprate** 15 was iodinated and the crude product was deprotected and acetylated with **AcOH/AcCl:**[33]



23

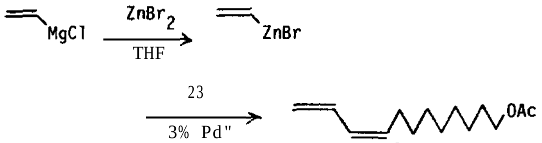
The iodide 23 was obtained in 70% isolated yield and its **isomeric** purity was > 99.9% as usually found for all Z alkenyl iodides obtained by carbocupration of acetylene. The needed organometallic partner of the key coupling reaction is, in the present case, the Z propenyl moiety, which, unfortunately cannot be prepared by carbocupration of acetylene, since lithium **dimethyl cuprate** does not add satisfactorily to this **alkyne.**[14] Therefore we prepared the required **1-bromo-1(Z)-propene** with 96.4% Z **isomeric** purity from trans. crotonic **acid.**[47] This bromide was converted into the lithium **reagent**[48] (Li metal, **Et$_2$O, −15°**, 85% yield) which was transmetallated into the zinc reagent for the coupling reaction with 22 in the presence of a catalytic amount of **Pd°:**[49]



22

After distillation through a 10 cm Vigreux column the required diene 22 was isolated in 92% yield and its purity was found to be **91.7%,** almost as high as that of the starting Z bromopropene. This loss in **stereoisomeric** purity is due to the slight isomerisation which **occured** during the preparation of the Z **propenyl** lithium.%. In the synthesis of the **"pseudo**-pheromone" 22 the carbocupration reaction has been used only for the preparation of the required functional&d Z alkenyl iodide. This class of compounds is very usefull for the synthesis of a large variety of natural products, including of course pheromones.

A last example of the use of such functionalised Z alkenyl iodides is given by the synthesis of the pheromone of ***Diparopsis castanea*** (Hamps) 6 the red **bollworm moth.**[51] This pheromone is the typical example of a terminal conjugated dienic system of Z configuration. Our synthesis requires the same **al**kenyl iodide 23 which was needed for the above "pseudo-pheromone" 22. In the present case the coupling reaction was performed with the vinyl zinc reagent obtained by transmetallation of the vinyl Grignard reagent, according to:



6

The pheromone 6 is obtained in 67% distilled yield and also with a high stereo-isomeric purity 99%. Due to difficulties in the separation of the two **stereo**isomers on capillary glass gas chromatography this purity was determined by ^{1}**H** and ^{13}**C NMR spec**trometry.

CONCLUSION

From the syntheses shown above, it is clear that our general methodology is applicable to the synthesis of a large array of pheromones bearing a conjugated dienic system of Z-E, E-Z, or Z-Z configuration. This general methodology is based on a pool of three useful reactions: (1) the **carbo**cupration of acetylene; (2) the coupling of the obtained Z alkenyl **cuprates** with alkenyl iodides, and (3) the iodination of the functionalised Z dialkenyl **cuprates** which **affords** the often required **func**tionalised Z alkenyl iodides. Each of these reactions is completely stereoselective and the whole methodology **affords** products of very high **stereo-isomeric** purity. In all the cases where the final pheromone was sufficiently stable, the purification method was a simple distillation, which is necessary when a large amount of material is needed. The preparative potential of this methodology is also emphasized since all the above syntheses were performed on multigram scale. We believe finally, that many other pheromones and, of course, many other natural products may be efficiently synthesized following the same general methodology.

EXPERIMENTAL

^{1}**H** NMR spectra were recorded on **Jeol** MH 100 **(CCl_4;** δ ppm from TMS), ^{13} C NMR on Jeol FX 90 Q **($CDCl_3$;** δ ppm) spectrometers. IR spectra were obtained on a **Perkin–Elmer** model 457 spectrometer. GLPC analyses were performed on a Carlo Erba gas **chromatograph** (models G 1 and 2150) using a 3 m glass **column** (10% SE 30 or 10% LAC 860 on **silanized** chromosorb **G80/100** mesh) and a **50 m** capillary glass **column** (OV 101). The gas **chro**matograph was coupled to an integrator LTT 9400. All reactions are performed under nitrogen in a **250 ml** flask equipped with a low temperature thermometer, a mechanical stirrer and a pressure **equalizing** addition funnel. **l-Iodo**-1(Z)-butene was prepared according to Ref. **13b.** 1-Iodo-1(E)-butene and **1-iodo-1(E)-hexene** are prepared according to Ref. 28.

Preparation of Z-dialkenyl cuprates[13b,14,23]

The organolithium reagent (50mmol) prepared in ether (from the corresponding bromide and lithium metal) was added to a suspension of copper(I) iodide (5.35 g, 28 mmol) or (in the case of **functionalised** organolithium reagent) copper(I) bromide-dimethyl sulphide **complex**[41] (1 : 1 complex; 5.75 g, 28 mmol) in ether (100 ml) at – 35". The mixture was stirred for 20 min at – 35" until a clear solution is obtained. Acetylene, from which acetone was removed by passage through a dry ice cooled trap was measured in a water gasometer (50 **mmol :** 1.2 L) and bubbled into the reaction mixture after being dried over a column packed with calcium chloride. The temperature was allowed to rise from -50" (at the start) to -25". Stirring of the greenish solution was maintained for 30 min at **–25°,** whereupon the solution of **Z-dialkenyl cuprate** (25mmol) was ready for further use.

1-*Iodo*-(*E*)1-*octen*-8-*yl acetate* 8[32,33]

To a **soln** of **1-octyn-8-ol,**[52] protected as THP ether (50mmol) in 50 ml THF, was added, at **–20°,** 50mmol of **MeLi** (ethereal solution). After **10 min, tri**methylchlorosilane (100 mmol) was added in **soln** in 50 ml THF. The mixture was stirred for 2 h at room temp, then hydrolysed with aq ammonium chloride. After usual workup and evaporation of the solvent, the crude alkynylsilane was added, in another flask, to a soln of diisobutyl aluminum hydride (55 mmol) in 55 ml hexane containing 55**mmol** THF. The mixture was heated 4 h at **35°,** then cooled to **–78°,** and a soln of iodine (50 mmol) in 40ml THF was slowly added. After this addition, the mixture. is brought to 0" for 30 min, then hydrolysed with 250 ml **6N** aqs sodium hydroxide. The organic layer is washed twice with water, once with aqs sodium thiosulphate and then with sat aq sodium chloride. After evaporation of the solvents, the crude product is dissolved in 45 ml methanol and added to a solution of 13 **g sodium** hydroxide in 45 ml methanol. The mixture is heated at 40" for 4 h, whereupon 300 ml of**icecold** water are added. The product is extracted 4-5 times with ether, then washed once with sat aqs sodium chloride, and dried over magnesium sulphate. After evaporation of the solvents, the crude product is added to a 10 **:** 1 mixture of **AcOH/AcC1** (50ml) and left at room temperature overnight. This mixture is then added to 200ml **icecold** water and 200ml hexane and partitioned. The organic phase is washed with **10%** aq sodium bicarbonate, then with water, dried over magnesium sulphate and concentrated in ***vacuo.*** The residue is distilled through a 10 cm Vigreux column to afford 2.67 **g** of pure acetate 8. Yield 18%.**B.p. 92°/10**$^{-2}$ mm Hg; n_D^{20}: 1.4965; IR (neat) cm^{-1}: 3050, 1740, 1655, 1240, 950; ^{1}**H NMR (CCl_4, δ)** 6.86 **(CH=, dt, 1H),** 6.33 (CH=, **d, 1H),** $J_{H\text{-}Htrans}$**: 16 Hz,** 4.21 **(CH_2–O,** t, **2H),** t, **2H),** 2.09 **(CH_3COO, s,** 3H): ^{13}**C** NMR **($CDCl_3$, δ)** 170.9 (COO), 146.3 (CH=), 74.5 **(ICH=),** 64.3 **(CH_2O).**

(*E*, *Z*)7,9-*Dodecadien*-1-*yl acetate* 1

An ethereal **soln** (100 ml) of Z dibutenyl **cuprate** (**12** mmol) is prepared as described above. 40 ml of THF***are*** added at **–40°,** followed by 2.7 **g** (12 mmol) of **zinc** bromide dissolved in 25ml THF. A mixture of **2.67 g** (9mmol) of acetate 8 and 0.31 **g** (0.27 mmol) of **Pd(PPh_3)$_4$** in 30 ml THF is then added at -20” and the whole mixture is stirred at + 10” for 1 h, then hydrolysed with 60 ml aq ammonium chloride. The salts am **filtered** and the aq layer extracted twice with ether. The combined organic phases are concentrated *in vacuo* and **150 ml** of pentane is added to the residue. The salts am **filtered** again, the organic phase washed with aq ammonia, then with aq ammonium chloride and finally dried over magnesium sulphate. After evaporation of the solvents, the residue is distilled through a 10 cm Vigreux column to afford 1.58 g of the title pheromone **1**. Yield 78%. **B.p. 95°–96°/10** $^{-2}$ mm Hg; n_D^{20}: 1.4739; **IR(neat) cm** $^{-1}$: 3020, 1745, 1650,980, 725; ^1H NMR (CCl_4, 6): 6.48 (CH=, dd, **1H**), 6.04 **(CH=**, dd, **1H)**, 5.76 (CH=, dt, **1H)**, 5.42 (CH=, dt, **1H)**, $J_{H\text{-}Htrans}$: **15HZ**, $J_{H\text{-}Hcis}$: **11HZ**, 4.18 **(CH_2O–, t, 2H)**, 2.06 **(CH_3COO–, s,** 3H); ^{13}C NMR (CDCI,, 6): 170.9 (COO), 134.2 131.6, 128.1, 125.8 (CH=), 64.5 **(CH_2O–)**.

1-Iodo, 5-chloro, (E)1-pentene 10[35]

100 ml of a **1** M **soln** of diisobutyl **aluminum** hydride (DIBAH) in hexane **(100** mmol) are added to a solution of 12.25 g (100 mmol) of **1-chloro,4-pentyne**[52] in 50 ml of **hexane** at room temperature. After heating at 50” for 2 h, the mixture is cooled to **– 40°** and 50 ml of THF are added, followed by a **dropwise** addition of iodine **(25.4 g,** 1OOmmol)in **100 ml THF. The mixture is warmed to** -10” and hydrolysed with dilute **sulphuric** acid. The organic layer is washed with aq sodium **thiosulphate,** then with sat aq sodium chloride and dried over magnesium sulphate. The solvents are removed *in vacuo* and the residue **distilled. Pure iodo-alkene 10** is obtained in an average of **70–80%** yield. **B.p. 54°/10** $^{-2}$**mm** Hg; IR (neat) cm-‘: 3050, 1610, 950; ^1H NMR **(CCl_4, δ)$_{13}$**: 6.69 **(CH=, dt, 1H),** 6.25 (ICI-I=, d, **1H),** $J_{H\text{-}Htrans}$: 16 **Hz,** 3.64 **(CH_2–Cl)**; ^{13}C NMR (CDCI,, 6): 144.2 (CH=), 71.1 (ICH=), 43.7 **(CH_2–Cl).**

1,5-Diiodo,(E)1-pentene 11

11.5 **g** (50 **mmol)** of alkenyl iodide **10** are added, at room **temperature,** to a **soln** of **37 g** (250 mmol) of sodium iodide in **100 ml** acetone. The mixture is stirred at reflux for two days (at room temperature during the night) whereupon the conversion was essentially complete. To the cooled mixture (+ **20°**) are added 100 **ml** of pentane in order to precipitate most of the inorganic salts which are filtered on a sintered glass funnel. The filtrate is concentrated *in vacuo* and 100 ml of pentane am again added in order to precipitate all the residual inorganic salts. This filtrate is concentrated in *vacuo* to **afford,** quantitatively, the diiodide **11** which is used as such. ^1H NMR **(CCl_4,** 6): 6.62 (CH=, dt, **1H),** 6.23 (ICH=, **d, 1H),** $J_{H\text{-}Htrans}$: **16 Hz,** 3.23 **(CH_2I,** t, 2H); ^{13}C NMR **($CDCl_3$, δ)**: 137.1 **(CH=)**, 69.9 **(I** CH=), -0.7 **(CH_2I)**.

(E,Z)10,12-Hexadecadien,1-ol 12 “bombykol”

An ethereal soln (150 ml) of Z **dipentenyl cuprate** (25 mmol) is **prepared** as described above. 40 ml of THF are added at **–40°, followed** by 5.7 g (25 mmol) of zinc bromide dissolved in 40 ml THF. A mixture of 6.45 g (20 mmol) of diiodide **11** and *0.7 g (0.6 mmol)* of **$Pd(PPh_3)_4$** in 50 ml THF is then added at -20” and the whole mixture is stirred at + 10” for **30 min,** then hydrolysed and worked-up as described above for 1. The obtained crude **1-iodo,(E,Z)4,6-decadiene** 14 is dissolved under nitrogen in a separate flask in 100 **ml** THF and 0.15 g (0.1 mmol) of **copper(I)** bromide is added. This mixture is cooled to **–** 15” **and** a **freshly** prepared **soln** of functionalised **Grignard** reagent **12**[36] (40 **mmol) (prepared** from **1,6-chloro** hexanol) is added dropwise. After-the-end of the addition, the mixture is stirred 30 min at + **10°**, then hydrolysed, at **– 10°**, with aq ammonium chloride. The organic phase is concentrated in *vacuo* and 200ml of pentane are added to the residue in order to precipitate the **diols** (formed during the preparation of the **Grignard** reagent 12). The organic phase is washed **with aq** ammonia, then with aq ammonium chloride and dried over magnesium sulphate. After evaporation of the solvents the residue is distilled through a **10 cm** Vigreux column to afford 3.65 g of pure “bombykol” 2. Yield 76%. **B.p. 128–129°/10** $^{-2}$**mm** Hg; n_D^{20}: 1.4722; IR (neat) **cm** $^{-1}$: 3320, 3020, 1650, 980, 945, 720; ^1H NMR **(CCl_4, δ)**: 6.46 (CH=, dd, **1H)**, 6.10 **(CH=**, dd, **1H)**, 5.78 **(CH=**, dt, **1H)**, 5.44 (CH=, dt, **1H)**, $J_{H\text{-}Htrans}$: **16Hz**, $J_{H\text{-}Hcis}$: 11 Hz, 3.68 **(CH_2OH, t,** 2H); ^{13}C NMR (CDCI,, 6): 134.5, 129.7, 128.9, 125.7 (CH=), 67.2 **(CH_2OH)**.

(Z,E)9,11-Tetradecadien,-yl acetate 3

An ethereal **soln** (150 ml) of functionalised Z **dialkenyl cuprate 15** is **prepared** as described above (15 **mmol)**. 40 **ml** of THF are added at **– 40°,** followed by a THF **soln** of magnesium chloride (15 mmol) (freshly prepared by **reaction** of **1,2-dichloroethane** on magnesium turnings). To the obtained magnesium **cuprate** is added a THF **soln** of **zinc** bromide **(3.4 g,** 15 mmol) at -30”. A mixture of 6.0 g **(33 mmol)** of **1-iodo,(E)1-butene** and 1.05 g **(0.9 mmol)** of **$Pd(PPh_3)_4$** in 50ml THF is then added and the whole mixture is stirred at **+10°** for one hour, then hydrolysed and worked-up as described above for **1. The** obtained crude product is dissolved in 30 **ml** methanol and added to 1.2 ml acetic acid in 40 ml methanol and 30 ml water. The mixture is stirred at room temperature overnight. Most of the solvents are then removed at reduced pressure and **200 ml** of pentane am added along with **50 ml** water. The aqueous layer is washed twice with 50 **ml** pentane and the combined organic phases are washed with aq sodium bicarbonate, then with sat aq sodium chloride and then dried over magnesium sulphate. After evaporation of the solvents the crude residue is dissolved in 50 ml dry pyridine, cooled to **0°**, and 5.4 ml (75 mmol) of **acetyl** chloride are added dropwise. The mixture is stirred 2 h at room temperature whereupon 200 ml pentane and **100 ml icecold** water are added. The organic layer is washed once with dilute hydrochloric acid, then with aq sodium bicarbonate, then with aq sodium bicarbonate, then with sat aq sodium chloride and finally dried over sodium sulphate. After evaporation of the solvents the residue is distilled through a **10 cm** Vigreux **column** to **afford 4.54 g** of pure pheromone 3. Yield **60%. B.p. 112–114°/10** $^{-2}$**mm** Hg; n_D^{20}: 1.4581; IR (eat) **cm** $^{-1}$ 3020, 1745, 1650, **1240, 980, 945, 720;** ^1H HNMR **(CCl_4,** 6): 6.42 **(CH=**, dd, **1H)**, 6.08 **(CH=**, dd, **1H)**, 5.80 (CH=, dt, **1H)**, 5.48 (CH=, **dt, 1H)**, $J_{H\text{-}Htrans}$: 16 Hz, $J_{H\text{-}Hcis}$: 11 **Hz,** 4.16 **(CH_2O–, t, 2H)**, 2.07 **(CH_3COO–**, s, 3H): ^{13}C NMR **($CDCl_3$, S). 171.0 (COO), 136.0, 129.9, 128.7, 124.8 (CH=), 64.6 (CH_2O).**

(Z,E)5,7-Dodecadien,1-ol 4

Same procedure as for 3 using fimctionahsed **cuprate** 16 and I-iodo,(E)l-hexene. The acetylation step is omitted, **B.p. 76°/10** $^{-2}$**mm**; n_D^{20}: 1.4891: IR (neat) cm-‘: 3350, 3020, 1650, 1620, 980,945, 730; ^1H NMR **(CCl_4, δ)**; 6.48 (CH=, dd, **1H)**, 6.05 (CH=, dd, **1H)**, 5.72 (CH=, dt, **1H)**, 5.38 (CH=, dt, **1H)**, $J_{H\text{-}Htrans}$: 16 Hz, $J_{H\text{-}Hcis}$: 11 **Hz**, 3.64 **(CH_2O–,)**; ^{13}C NMR (CDCI,, 6): 134.8, 129.4, 129.1, 125.6 (CH=), 62.4 **(CH_2OH)**.

(Z,Z) 11,13-Hexadecadien, 1 *-ol* 21

Same procedure as for 3 using fimctionahsed **cuprate 20** and **1-iodo,(Z)1-butene.** The acetylation step is omitted. **B.p. 103–105°/10** $^{-3}$**mm Hg**; n_D^{20}: 1.4757; IR (neat) cm-‘: **3350, 3040,** 3810, 1640, **1600, 910, 720;** ^1H NMR **(CCl_4,** S): 6.28 **(CH=**, d, **2H)**, 5.50 **(CH=**, m, **2H)**, 3.64 **(CH_2O)**; ^{13}C NMR **($CDCl_3$,** 6): 133.3, 131.8, 123.6, 123.1 (CH=), 62.4 **(CH_2OH)**.

1-Iodo,(Z)1-decen,10-yl acetate 23

An ethereal **soln** of functionalised **cuprate 15** is prepared as described above (50 mmol). To this cooled **soln** (**– 40°)** are added, in ten portions, **25.4 g (100 mmol)** of finely crushed iodine. The mixture is warmed, carefully, to **–10°**, stirred for 30 min and then hydrolysed with **100 ml** aq ammonium chloride. After filtration of the salts, the organic layer, to which 150 ml of pentane have been added, is washed successively with aq sodium thiosulphate, then with aq ammonia and with aq ammonium chloride, then dried over magnesium sulphate. After removal of the solvents the residue is added to 100 ml of a mixture of AcOH/AcCl (10 : 1) and left at room temperature overnight. The mixture is then added to 400 ml icecold water and 400 ml hexane and partitioned. The organic phase is washed with 10% aq sodium bicarbonate, then with water, dried over magnesium sulphate and concentrated in *vacuo*. The residue is distilled through a 10 cm Vigreux column to afford 22.7 g of the title product 23. Yield 70%. B.p. 95–97°/10^{-2}mm Hg; n_D^{20}: 1.4942; IR (neat) cm^{-1}: 3065, 1740, 1610, 1240, 725, 690; ^1H NMR (CCl_4, δ), 6.16 (CH=, m, 2H), 4.07 (CH_2O–, t, 2H), 2.03 (CH_3COO–, s, 3H); ^{13}C NMR ($CDCl_3$, 6): 170.6 (COO), 141.1 (CH=), 82.4 (ICH=), 64.3 (CH_2O).

(Z,Z)9,11-Tridecadien, 1*-yl* acetate 22

To an ethereal solution of Z propenyl lithium (30 mmol) (prepared from 1-bromo,(Z)1-propene and lithium metal) are added 50 ml THF and then a soln of 30 mmol of zinc bromide in 30 ml THF, at -20”. After stirring for 10 min, the iodide 23 ((8.1 g, 25 mmol) admixed with 0.9 g (0.75 mmol) $Pd(PPh_3)_4$ in 30ml THF is added and the mixture is warmed to room temperature for 30 min, then hydrolysed with aq ammonium chloride. The organic phase is dried over magnesium sulphate and after removal of the solvents under vacuum, the residue is distilled to afford 5.5 g of the title compound 22. Yield 92%. B.p.102°/10^{-2}mm Hg; n_D^{20}: 1.4924; IR (neat) cm^{-1}: 3020, 1740, 1650, 1600, 1240, 700; ^1H NMR (CCl_4, 6): 6.20 (CH=, d, 2H), 5.41 (CH=, m, 2H), 4.01 (CH,O-, t, 2H), 1.98 (CH_3COO–, s, 3H), 1.76 (CH_3–C=, d, 3H); ^{13}C NMR ($CDCl_3$, 6): 171.0 (COO), 131.7, 125.7, 124.7, 123.4 (CH=), 64.6 (CH_2O).

(Z)9,11-Dodecadien,1-yl acetate 6

To a THF solution of vinyl magnesium chloride (40mmol) are added at 0° a solution of zinc bromide (40mmol) in 50ml THF. After stirring for 15 min, the iodide 23 (8.1 g, 25 mmol), admixed with 0.9 g (0.75 mmol) $Pd(PPh_3)_4$ in 30ml THF, is added and the mixture is warmed to room temperature and stirred for 2 h. The mixture is hydrolysed with 80 ml aq ammonium chloride, the aqueous phase extracted once with 100 ml ether and the combined organic phases washed with aq ammonium chloride, dried over magnesium sulphate and concentrated *in vacuo*. The residue is distilled to afford 3.8 g of pure pheromone 6. Yield: 67%. B.p. 84–85°/10^{-2}mm Hg; n_D^{20}: 1.4705: Ir (neat) cm-‘: 3080, 3010, 1745, 1645, 1595, 1240, 995, 965; ^1H NMR (CCl_4, δ): 6.68 (CH=, ddd, 1H), 6.02 (CH=, dd, 1H),5.42 (CH=, dt, 1H), 5.18 (CH=, d, 1H), 5.07 (CH=, d, 1H), $J_{H\text{-}Hcis}$: 11 HZ, 4.08 (CH_2O–, t, 2H), 2.03 (CH_3COO, s, 3H); ^{13}C NMR ($CDCl_3$, δ): 170.8 (COO), 132.6, 132.3, 129.4 (CH=), 116.6 (CH_2=), 64.5 (CH_2O).

Acknowledgements-*The* authors gratefully acknowledge support from the Centre National de la Recherche Scientifique (A.T.P. “Mediateurs chimiques” and E.R.A. 825).

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