Tetrahedron Vol 47, No 37, pp 7767-7774, 1991
Printed in Great Britain

0040-4020/91 $3 00+ 00

STEREOSPECIFIC SYNTHESIS OF 1,5-DIEN-3-YNES AND 1,3,5-TRIENES APPLICATION TO THE STEREOCHEMICAL IDENTIFICATION OF TRIENIC SEX PHEROMONES

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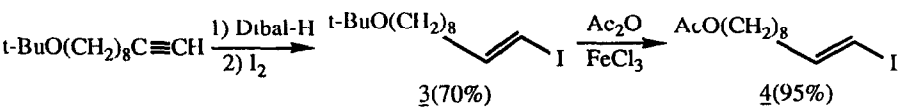
(Received in Belgium 25 June 1991)

Summary *A one-pot stereospecific synthesis of 1,5-dien-3-ynes (Z) or (E) is described, based upon a palladium-catalyzed cross-coupling reaction between butenynylzinc bromide, generated in situ from 1,1-difluoroethylene, and an adequate iodoalkene. These dienynes are converted into the corresponding trienic compounds by (Z) semi-hydrogenation*

Stereo-defined conjugated polyenynes and polyenes containing terminal vinyl units are widely distributed in nature and show interesting biological properties *(1,2)*
In this present publication is reported a one-pot stereoselective synthesis of 1,5-dien-3-ynes (Z) or (E) and their corresponding 1,3,5-trienes (3Z,5Z) or (3Z,5E) which are obtained after a (Z) semi-hydrogenation We have shown the utility of our process by describing the synthesis of trienic hydrocarbons like 1,3,5-undecatriene and of functionalized trienes like 9,11,13-tetradecatrienyl acetate, alcohol and aldehyde
For the past few years, several laboratories *(2-4)* have been interested in the synthesis of isomers of 1,3,5-undecatriene which are reported to exhibit odors highly appreciated in perfumery. Herein is described the synthesis of (Z,E)-1,3,5-undecatriene which occurs with the two other stable isomeric compounds (3E,5E) and (3E,5Z) in the male gametes pheromone of the Hawaiian seaweeds (*Dictyopteris*) *(5)*.
Functionalized terminal conjugated trienic compounds have been recently isolated from the female sex pheromone blend of two species of Lepidoptera, *Ectomyelois ceratoniae* (Pyralidae) *(6)* and *Stenoma cecropia* (Stenomidae) *(7)*. *Ectomyelois ceratoniae* is a widespread pyralid moth of nuts and fruits, including carobs, almonds and dates in North Africa and *Stenoma cecropia* is a serious defoliator of oil palm trees in South America (Z,E)-9,11,13-tetradecatrienyl acetate and the corresponding aldehyde have been

identified as major components of the sex pheromone of these two Lepidoptera species. The synthesis of this isomer has been recently published *(8)* In order to confirm the stereochemistry and to perform laboratory and field bioassays of these pheromonal components, all three stable geometrical isomers were necessary Therefore, we have also applied our method to the synthesis of (E,Z)-9,11,13-tetradecatrienyl acetate and aldehyde

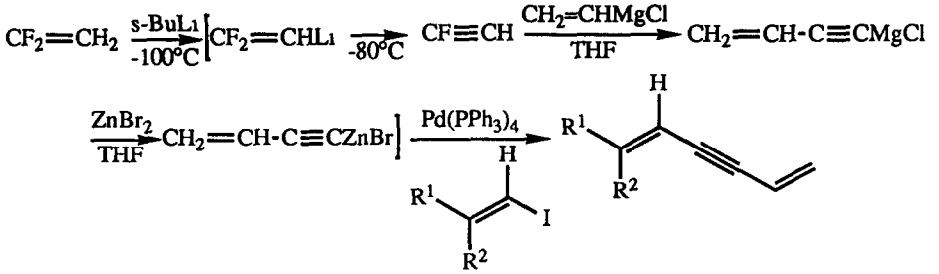
A number of stereoselective methods *(2,9)* for obtaining 1,5-dien-3-ynes have been described, generally, the key steps were two sequential palladium-catalyzed cross-coupling reactions between an acetylenic derivative and two alkenyl units. By this route, Rossi *et al* have obtained (E)-1,5-undecadien-3-yne *(2)*. The strategy which is reported here, involves a direct coupling between an alkenyl unit and a butenynyl moiety which should be the most straightforward method for the construction of a terminal dienyne unit Moreover, the butenynyl moiety is easily generated *in situ* from commercially available 1,1-difluoroethylene. The 2,2-difluorovinyllithium has a restricted thermal stability and it affords fluoroacetylene above -80°C In a previous paper, has been reported the utility of this fluoroderivative that could react according to an addition-elimination reaction with many organometallic compounds to give acetylenes bearing various groups directly in α to the unsaturation *(10)*. The organometallic compound used here was the vinylmagnesium chloride. A first equivalent reacted with fluoroacetylene to give a solution of butenyne and a second equivalent afforded a solution of butenynylmagnesium chloride. A transmetalation drove to butenynylzinc bromide which was coupled with (Z) or (E) iodoalkene in the presence of palladium catalyst to give (Z) or (E) 1,5-dien-3-ynes with more than 99% steric purity (retaining the configuration of the starting alkenyliodide) The pure (Z) alkenyliodide 1 was obtained by carbocupration of acetylene followed by iodolysis according to Normant *et al. (11)* and the pure (E) 2 and 3 by hydroalumination of the corresponding alkynes and reaction with iodine *(12)* (the functionalized alkenyliodide 3 has been obtained by hydroalumination of 1-terbutoxy-9-decyne)



3(70%) 4(95%)

We have chosen to protect the alcoholic function as t-butyl ether because in two recent publications, Alexakis *et al (13)* have pointed out the great advantages of this protective group. Preparation and reactivity of ω-terbutoxy Grignard reagents are exactly the same as non-functionalized ones, and ω-terbutoxyalkynes undergo smooth hydroalumination with diisobutylaluminium hydride in contrast with the other classical protective groups The t-butyl ether 3 could also be cleaved into the corresponding acetate 4 with Ac_2O and $FeCl_3$ in Et_2O without isomerisation This deprotection must be performed before the coupling reaction because the dienynic and trienic systems are unstable in presence of Lewis acid

The synthesis of dienes 5, 6 and 7 is illustrated by the following scheme:

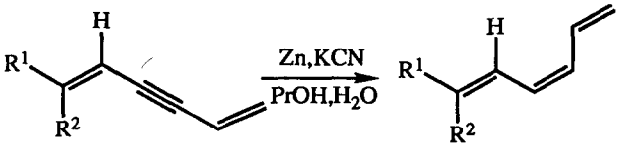


1, 2, 4 5(60%),6(84%),7(70%)

2, 5 R^1=Pent, R^2=H
1, 6 R^1=H, R^2=Pent
4, 7 : R^1=AcO$(CH_2)_8$, R^2=H

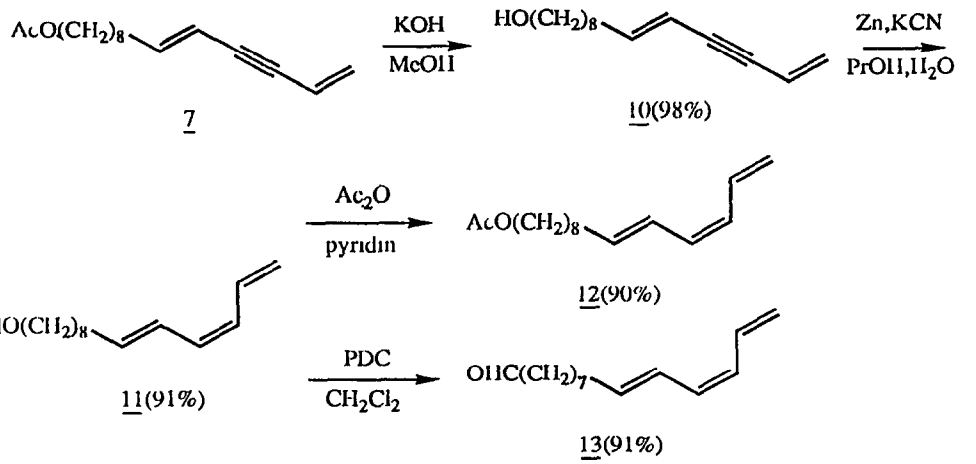
The 2,2-difluorovinyllithium was quantitatively prepared in Et_2O/THF from 1,1-difluoroethylene and s-butyllithium at -100°C *(10,14)*. The temperature was increased and a solution of fluoroacetylene was obtained. The treatment of this gaseous solution with vinylmagnesium chloride in THF led to butenynylmagnesium chloride. The obtained butenynylzinc bromide available via transmetalation with zinc bromide, was successively coupled with iodoalkene 1, 2 and 4 in the presence of Pd° catalyst to afford the desired dienyne 5, 6 and 7. All were obtained with good yield (60 to 80%) and with an isomeric purity more than 99%.

The triple bond of dienynes 5 and 6 was (Z) semi-hydrogenated over zinc powder, according to Morris *(15)* to furnish the corresponding (ZE) and (ZZ) trienes



8 R^1=Pent, R^2=H (92%)
9 R^1=H, R^2=Pent

In the case of the functionalized triene, acetate 7 should be saponified into alcohol 10, before semi-hydrogenation of the triple bond

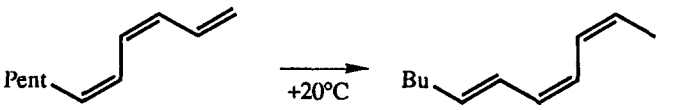


The alcohol 11 was either acetylated or oxidized by PDC in CH_2Cl_2 to afford respectiv the acetate 12 or the aldehyde 13.

All the trienes 8, 11, 12 and 13 were obtained with an isomeric purity of 99%.

Näf *et al* have studied the stability of terminal conjugated trienes *(3)*. (ZZ) 1 isomer has proved extremely difficult to obtain, due to its tendency to undergo a the [1,7] hydrogen shift at slightly above room temperature to yield (Z,Z,E)-2,4,6-triene a highly stereoselective manner.

In our case, (Z,Z)-1,3,5-undecatriene 9 underwent a rapid isomerisation to (Z,Z,E) 2 undecatriene 14 at room temperature.



9 14

The (Z,E)-1,3,5-trienes are more stable, but upon heating (150°C), they undergo electrocyclic reaction to give 5-alkyl-1,3-cyclohexadienes *(3)*.

The stereochemistry of the double bonds has been ascertained by high resolution NMR IR which were in good agreement with those previously reported in the literature *(2* The stereoisomeric purity of the trienes was evaluated by gas chromatographic analysi capillary columns.

In conclusion, this route allowed us to prepare products of very high stereoisom purity, with excellent overall yields and in few steps from readily available star materials This reaction appears to be a general and highly stereoselective method the obtention of conjugated dienynes and their corresponding trienes, and we have s that this procedure could be used for the synthesis of functionalized products (E,Z)-9,11,13-tetradecatrienyl acetate and aldehyde, the geometrical isomers of m components of two sex pheromones of Lepidoptera, *Stenoma cecropia* and *Ectomye ceratoniae*.

Experimental section

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer ($CDCl_3$,δ(ppm) TMS, J(Hz)). Mass spectra were obtained by using a Nermag R10x10 Infrared spectra measured on a Perkin-Elmer 397 spectrometer (neat, cm^{-1}). Gas chromatographic anal were performed on a model 2900 Carlo Erba instrument equipped with fused silica p capillary column (25 m WCOT FFAP 0.32 id, H_2 carrier gas flow 25 ml/min, 1.2 b)

(Z)-iodo-1-heptene 1

It was prepared according to Normant *(11)*, by carbocupration of acetylene usin etheral solution of pentLi followed by iodolysis (80% yield). Bp 54°C/10 Torr.

(E)-1-iodo-1-heptene 2

This product was obtained by hydroalumination of heptyne followed by iodolysis *(12)* synthesis of product 3) (60% yield) Bp. 41°C/10 Torr

(E)-1-terbutoxy-10-iodo-9-decene 3

To a solution of 1-t-butoxy-9-decyne *(8)* (21.0 g, 0.1 mol) in 20 ml of anhydrous hexane were added dropwise 100 ml (0.1 mol) of 1 M diisobutylaluminium hydride solution in hexane at room temperature. The reaction mixture was stirred at 50°C for 4 h, then cooled to -70°C. 50 ml of THF followed by iodine (25.4 g, 0 1 mol) in 50 ml of THF were added The stirred mixture was allowed to warm up to room temperature for 1 h, cooled again to -50°C, hydrolyzed with a 1 N H_2SO_4 solution and extracted with Et_2O. The organic phase was washed successively with $Na_2S_2O_3$, $NaHCO_3$ and NaCl sat. aq. solutions It was then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was distilled over Cu powder to afford 23 7 g of 3 (70% yield). Bp. 115°C/0.1 Torr (E) steric purity (⩾99%). m/z : 323 (M-15)
IR : 1600, 1190, 940.
^1H NMR . 1.15 (s,9H), 1.4 (m,12H), 2.05 (m,2H), 3.3 (t,2H), 5.9 (d,1H), 6.4 (dt,1H) (J=14 and 7)
^{13}C NMR . 26.2, 27.5, 28.3, 28.8, 29.3, 30.6, 36.0, 61 4, 72.1, 74.3, 146.4.
Note : This product contained two impurities : (1) t-BuO$(CH_2)_{10}$I, this iodoalkane was removed by treatment with n-butylamine *(16)*.
(2) t-BuO$(CH_2)_8$C≡CI, this iodoalkyne can be removed by treatment with 20% of HeptCu (HeptLi+CuI in Et_2O (-40°C/30 min), then THF for 2 h at -40°C) (t-BuO$(CH_2)_8$C≡CHept was obtained and removed by distillation)

(E)-1-acetoxy-10-iodo-9-decene 4

Ac_2O (9.4 ml, 0.1 mol) and anhydrous $FeCl_3$ (0.8 g, 0.005 mol) were successively added to a solution of t-butylether 3 (16.9 g, 0.05 mol) in Et_2O (100 ml). The stirred solution was left at room temperature for 6 h. A sat. aq. solution of $NaHPO_4$ was added and the mixture was stirred for 1 h The solid $FePO_4$ precipitate was filtered off. After usual work up 15.4 g of acetate 4 were obtained (95% yield). Bp. 112°C/0.1 Torr. (E) steric purity (⩾99%) m/z : 281 (M-43). IR . 1730, 1595, 1235, 945.
^1H NMR : 1.32 (m,12H), 2 03 (m,5H), 4 05 (t,2H), 5.96 (d,1H), 6.51 (dt,1H) (J= 14 4 and 7).
^{13}C NMR : 20.9, 25 9, 28 3, 28 6, 28.8, 29.1, 29.2, 36.0, 64.3, 74.5, 146.4, 170.4.

Preparation of dienynes 5, 6, 7

To a solution of CF_2=CH_2 (3 8 g, 0 06 mol) in THF (80 ml) and Et_2O (20 ml) were added at -100°C, 0.05 mol of s-BuLi in cyclohexane. The reaction mixture was stirred at -90°C for 20 min, and then at -100°C were added 0.08 mol of vinylmagnesium chloride in THF The stirred mixture was allowed to warm up to room temperature After 1.5 h, 3-buten-1-ynyl magnesium chloride was obtained To this reagent were added at 0°C an anhydrous $ZnBr_2$ solution (11.3 g, 0.05 mol/50 ml THF) The mixture was warmed to 20°C for 20 min and at 0°C were then added successively a solution of $Pd(PPh_3)_4$ (2%) (0 5 g/20 ml THF) and 0.02 mol of the iodoalkenes 1, 2 or 4. Stirring was maintained at room temperature 30 min The reaction mixture was hydrolyzed by H_2SO_4 solution (1 N). After usual work up, the crude residue was filtered through a small column packed with silicagel in order to remove the palladium catalyst (eluting with cyclohexane). The solvent was evaporated and the products 5, 6 or 7 were obtained.

(E)-1,5-undecadien-3-yne 5

Yield (60%). Bp 42-44°C/0.5 Torr. (E) steric purity (99%). Anal. calcd. for $C_{11}H_{16}$: C, 89 12; H, 10 88. Found: C, 89.29; H, 10.67 m/z : 148 (M^+, 1%), 78 (100%).

IR 3090, 3005, 2920, 2850, 2185, 1600, 1180, 950, 910.

^1H NMR · 0.85 (t,3H), 1.3 (m,6H), 2.07 (q,2H), 5.41 (dd,1H) H^1, 5.56 (dd,1H) $H^{1'}$, 5 5ε (dm,1H) H^5, 5.88 (ddd,1H) H^2, 6.14 (dt,1H) H^6; $JH^1/H^{1'}$=2.0, $JH^{1'}/H^2$=17.6, JH^1/H^2=10.8, JH^2/H^5=2.1, JH^5/H^6=15.8, JH^6/H^7=7.1.

^{13}C NMR 14.1, 22 6, 28.6, 31 5, 33.3, 86.85, 89.2, 109.7, 117.6, 125.7, 145.1

(Z)-1,5-undecadien-3-yne 6

Yield (84%). Bp. 31-33°C/0.01 Torr. (Z) steric purity (99%). Anal. calcd. for $C_{11}H_{16}$. C 89.12, H, 10.88. Found: C, 88.91; H, 10.53. m/z : 148 (M^+,2%), 78 (100%).

IR · 3090, 3010, 2950, 2920, 2845, 2180, 1600, 1460, 1155, 965, 910, 730.

^1H NMR · 0.9 (t,3H), 1.3 (m,6H), 2.3 (qd,2H), 5.40 (dd,1H) H^1, 5.54 (ddt,1H) H^5, 5.5 (dd,1H) $H^{1'}$, 5.89 (dt,1H) H^6, 5.92 (ddd,1H) H^2; $JH^1/H^{1'}$=2.0, JH^1/H^2=10.9, $JH^{1'}/H^2$=17 5 JH^2/H^5=2.3, JH^5/H^6=10.7, JH^6/H^7=7 5, JH^5/H^7=1 5.

^{13}C NMR : 14 1, 22.7, 28.8, 30.4, 31 6, 87 2, 92.35, 109.2, 117.7, 125.8, 144.2.

(E)-1-acetoxy-9,13-tetradecadien-11-yne 7

Yield (70%). Bp. 113-117°C/0 1 Torr (E) steric purity (99%). Anal. calcd. for $C_{16}H_{24}O_2$ C, 77.38, H, 9 74. Found: C, 77.10, H, 9.82 m/z · 248 (M^+,1%), 78 (100%).

IR · 3100, 3010, 2920, 2850, 2190, 1740, 1600, 1460, 1365, 1240, 1035, 950, 910

^1H NMR : 1 3 (m,12H), 2.02 (s,3H), 2.15 (q,2H), 4.04 (t,2H), 5.41 (dd,1H) H^{14}, 5.5 (dd,1H) $H^{14'}$, 5.57 (dd,1H) H^{10}, 5.88 (ddd,1H) H^{13}, 6.13 (dt,1H) H^9, $JH^{14}/H^{14'}$=2.0 JH^{14}/H^{13}=10.8, $JH^{14'}/H^{13}$=17 6, JH^{13}/H^{10}=2 0, JH^{10}/H^9=15.8, JH^9/H^8=7 1.

^{13}C NMR : 20 7, 25.9, 26.9, 28.8, 29 0, 29 2, 29.3, 33 1, 64 4, 86 8, 89.05, 109.75 117 5, 125 6, 144 8, 170.6

(E)-9,13-tetradecadien-11-yn-1-ol 10

This product was prepared by saponification of the corresponding acetate 7 with 2 N KO in MeOH.

Crude yield (98%). (E) steric purity (99%) m/z. 206 (M^+,2%), 78 (100%)

IR 3350, 2190, 1600, 1585, 980, 955, 915

^1H NMR · 1.35 (m,12H), 2 09 (q,2H), 3 5 (t,3H), 5.40 (dd,1H) H^{14}, 5.557 (dd,1H) $H^{14'}$ 5 563 (dd,1H) H^{10}, 5.88 (ddd,1H) H^{13}, 6.13 (dt,1H) H^9, $JH^{14}/H^{14'}$=2.0, JH^{14}/H^{13}=10.9 $JH^{14'}/H^{13}$=17 5, JH^{13}/H^{10}=2 0, JH^{10}/H^9=15 7, JH^9/H^8=7.1

^{13}C NMR · 25 9, 28.8, 29 1, 29.5, 32.7, 33.2, 62.35, 86.8, 89 1, 109 6, 117 45, 125 ε 145 05

Preparation of trienes 8, 9, 11

A mixture of dienynes 5, 6 or 10 (0.014 mol), 1-propanol/water (1/1) (600 ml), zin powder (200 g) and potassium cyanide (10 4 g, 0 16 mol) was stirred at room temperatu for 24 h under argon in the dark The reaction product was filtered through celite, a the filtrate was extracted with Et_2O. After usual work up, the trienes 8, 9 or 11 we obtained 9 is extremely unstable and fastly, around 25°C it gives the triene 14

(Z,E)-1,3,5-undecatriene 8

Crude yield (92%). (EZ) steric purity (99%). Anal. calcd. for $C_{11}H_{18}$: C, 87.93, H, 12.07. Found: C, 87.73; H, 11.83. m/z : 150 (M^+,14%), 79 (100%).

IR 1630, 1610, 1460, 1430, 1000, 970, 935, 895.

^1H NMR : 0.9 (t,3H), 1.3 (m,6H), 2.15 (q,2H), 5.08 (dd,1H) H^1, 5.16 (dd,1H) $H^{1'}$, 5 72 (dt,1H) H^6, 5.90 (m,2H) H^3 and H^4, 6.49 (ddt,1H) H^5, 6.79 (ddd,1H) H^2; $J_{H^1/H^{1'}}$=2.0, $J_{H^{1'}/H^2}$=16.8, J_{H^1/H^2}=10 2, J_{H^2/H^3}=10.3, J_{H^4/H^5}=10 3, J_{H^5/H^6}=14.9, J_{H^5/H^7}=1.5, J_{H^6/H^7}=7 0, J_{H^3/H^4}~11.

^{13}C NMR : 14.1, 22 7, 29.1, 31 6, 33.0, 116.9, 125.7, 127 9, 130 4, 132.4, 136.6

(Z,Z)-1,3,5-undecatriene 9

^{13}C NMR · 14.1, 22.7, 27 6, 29.4, 31.6, 117.8, 123.6, 125.0, 129.5, 132.2, 133.8.

(E,Z)-9,11,13-tetradecatrienol 11

Crude yield (91%). Mp. 36°C. (EZ) steric purity (99%). Anal. calcd. for $C_{14}H_{24}O$: C, 80 71; H, 11.61 Found C, 80.65, H, 11.47. m/z : 208 (M^+,11%), 79 (100%).

IR · 3200, 1635, 1615, 1455, 1435, 995, 970, 940, 895, 850, 830, 790, 745, 720.

^1H NMR : 1.3 (m,10H), 1.5 (m,2H), 2.1 (q,2H), 3.45 (m,1H), 3.5 (t,2H), 5.07 (dd,1H) H^{14}, 5.17 (dd,1H) $H^{14'}$, 5 71 (dt,1H) H^9, 5.90 (m,2H) H^{11} and H^{12}, 6.47 (ddt,1H) H^{10}, 6 78 (ddd,1H) H^{13}; $J_{H^{14}/H^{14'}}$=2.0, $J_{H^{14'}/H^{13}}$=16.8, $J_{H^{14}/H^{13}}$=10.1, $J_{H^{13}/H^{12}}$=10.3, $J_{H^{11}/H^{10}}$=10.3, J_{H^{10}/H^9}=15.0, J_{H^{10}/H^8}=1.5, J_{H^9/H^8}=7, $J_{H^{11}/JH^{12}}$~11.

^{13}C NMR : 25 8, 29.2, 29 3, 29.4, 29.5, 32 7, 33.0, 62 6, 117 1, 125.6, 127.8, 130 3, 132 3, 136.7.

(Z,Z,E)-2,4,6-undecatriene 14

m/z : 150 (M^+,13%), 79 (100%).

IR : 1630, 1620, 1460, 1000, 980, 960, 935, 920, 910, 900, 890, 835, 700, 690.

^{13}C NMR : 13.1, 14.0, 22.4, 31.6, 32.8, 122 1, 124.8, 125.8, 126 2, 129 3, 136 1

(E,Z)-1-acetoxy-9,11,13-tetradecatriene 12

Ac_2O (1.4 ml, 15 mmol) were added to a stirred mixture of 1.0 g (5 mmol) of alcohol 11 and 1 2 ml of pyridin Stirring was maintained for 3 h at room temperature and the mixture was poured in crushed ice. After usual work up, the acetate 12 was obtained.

Crude yield (90%). (EZ) steric purity (99%). Anal. calcd for $C_{16}H_{26}O_2$. C, 76 75, H, 10 47 Found: C, 76.88, H, 10.43. m/z · 250 (M^+,15%), 79 (100%).

IR . 1735, 1460, 1450, 1430, 1360, 1240, 1035, 970, 960, 940, 930, 900.

^1H NMR : 1.3 (m,10H), 1 6 (m,2H), 2.01 (s,3H), 2 10 (q,2H),4.03 (t,2H), 5.08 (dd,1H) H^{14}, 5.17 (dd,1H) $H^{14'}$, 5.71 (dt,1H) H^9, 5.90 (m,2H) H^{11} and H^{12}, 6.48 (ddt,1H) H^{10}, 6.78 (ddd,1H) H^{13}; $J_{H^{14}/H^{14'}}$=2 0, $J_{H^{14'}/H^{13}}$=16.8, $J_{H^{14}/H^{13}}$=10.2, $J_{H^{13}/H^{12}}$=10 3, $J_{H^{11}/H^{10}}$=10 4, J_{H^{10}/H^9}=15.0, J_{H^{10}/H^8}=1.5, J_{H^9/H^8}=7 0, $J_{H^{11}/JH^{12}}$~11.

^{13}C NMR : 20 9, 25 95, 28 7, 29.2, 29 25, 29 4, 32.95, 64 5, 117.0, 125.7, 127 85, 130.3, 132 3, 136 5, 170 8.

(E,Z)-9,11,13-tetradecatrienal 13

To a solution of alcohol 11 (1 0 g, 5 mmol) in CH_2Cl_2 (20 ml), were added 5.6 g (15 mmol) of PDC (pyridinium dichromate) The reaction mixture was stirred at room temperature for

8 h, admixed with Et_2O and filtered through a small column packed with florisyl to after evaporation of solvents the desired aldehyde 13.
Crude yield (91%). (EZ) steric purity (99%). m/z : 206 (M^+,14%), 79 (100%).
IR · 2710, 1720, 1630, 1610, 1460, 1450, 1430, 1000, 970, 955, 940, 925, 900.
^1H NMR : 1.3 (m,10H), 1 6 (m,2H), 2 1 (m,2H), 2.38 (td,2H), 5.08 (dd,1H) H^{14}, (dd,1H) $H^{14'}$, 5.71 (dt,1H) H^9, 5.90 (m,2H) H^{11} and H^{12}, 6.48 (ddt,1H) H^{10}, 6 78 (dd H^{13}; $JH^{14}/H^{14'}$=2.0, $JH^{14'}/H^{13}$=16.8, JH^{14}/H^{13}=10.2, JH^{13}/H^{12}=10.3, JH^{11}/H^{10}= JH^{10}/H^9=15.0, JH^{10}/H^8=1.5, JH^9/H^8=7.1, JH^{11}/JH^{12}~11; 9.7 (t,1H).
^{13}C NMR · 22.0, 29.0, 29.1, 29.2, 32.9, 43.8, 117.1, 125.6, 127 8, 130.3, 132.3, 1 202 2

Acknowledgements: *The authors thank Prof J.F. Normant for helpful discussions ar Baudry for NMR spectral data This work was supported by INRA and CNRS. We are ind to Atochem for a generous gift of* CF_2=CH_2.

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