Tetrahedron Vol. 47, No.20/21, pp. 3347-3352, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

C3-HOMOLOGATION. SYNTHESIS OF C19-SKIPPED POLYENIC PHEROMONES.

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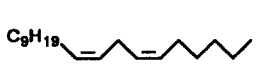
(*Received in Belgium* 2 *January* 1991)

Summary: Total synthesis of three sex pheromone components including an all-*cis* diene or triene unit are described. Starting from decanal, *cis*-Wittig reactions, by using C3 homologating agent **4** and convenient phosphonium salts, allowed us to built up all-*cis* skipped polyenic skeleton of the targets. These syntheses are shorter than those described in the literature and have been performed in better overall yield from starting materials.

Many biological active natural products bear a skipped diene or triene unit with the all *Z* configuration.[1] Sex pheromones of the Lepidoptera have received the widest attention and a large number of structure determinations have been successfully completed.[2] In all the previous synthetic works, the strategies involve the acetylenic coupling reactions followed by partial reduction (possibly associated with Wittig-reaction). [3] Recently, we developed an efficient stereoselective C3-homologation of aldehydes leading to "skipped" *cis* polyenic compounds.[4,5] We report herein an application to the synthesis of three straight-chain C-19 sex attractants **1**, **2**, **3** of the winter moth (*Operophtera brumata* L. (Lepidoptera : Geometridae)).[3]



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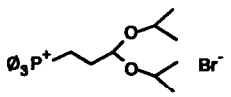

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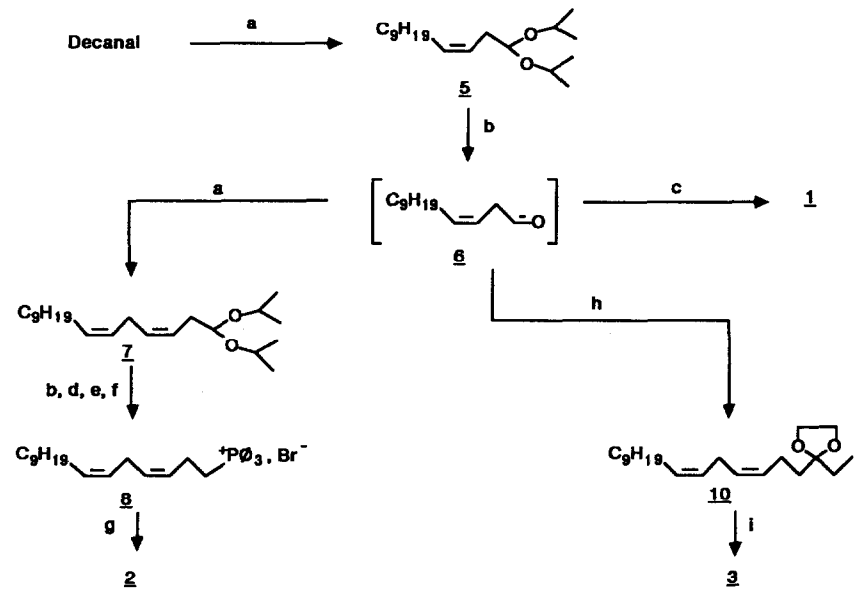
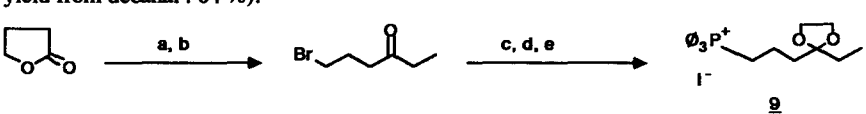
The homologating reagent is the phosphorane resulting from (3,3-diisopropoxypropyl)-triphenylphosphonium bromide **4** treated by sodium hexamethyldisilazane.[4a] The key intermediate of these syntheses is the diisopropyl acetal **5** (from the *cis*-Wittig reaction between n-decanal and **4**), precursor of the *cis* -β,γ-ethylenic aldehyde **6**. *Cis* -configuration of **5** is confirmed by obtention of *Z/E* mixture (8 : 1) with BuLi as base (C_3, C_4 ^{13}C NMR, respectively : *Z*, 132.1, 124.3; *E*, 132.3, 124.0 ppm), while only *Z*-isomer is observed by using sodium hexamethyldisilazane.

Wittig reaction with hexyltriphenylphosphorane leads to **1** (overall yield from decanal : 86 %). C3-homologation of **6** gives *cis* -"skipped" diene acetal **7**. Conventional inversion of reactivity leads to phosphonium bromide **8** without modification of the diene unit. This conversion is necessary to avoid Wittig reaction of corresponding aldehyde of **7**, with the "moderated" allyltriphenylphosphorane which would provide a mixture of *trans* and *cis* double bond.[6] Wittig condensation of **8** with acrolein furnishes the pure unstable tetraene **2** (overall yield from decanal : 40 %).



a : 4 + $NaN(SiMe_3)_2$; b : TsOH, H_2O / THF ; c : $Ø_3P^+(CH_2)_5CH_3, Br^-$ + $NaN(SiMe_3)_2$; d : $LiAlH_4$, THF, -70 °C ; e : $Ø_3P$, CBr_4 ; f: $Ø_3P$; g : $NaN(SiMe_3)_2$, Acroleine ; h : 9 + $NaN(SiMe_3)_2$; i : H_2SO_4, H_2O / THF.

The 6-bromo-3-hexanone is prepared according to the literature[7] by Claisen condensation of enolate of γ-butyrolactone with ethyl propionate followed by treatment with hydrobromic acid (35%). After phosphorylation, anion exchange with NaI and conversion to ethylene ketal phosphonium salt **9**, Wittig reaction with pivotal aldehyde **6** furnished the ethylene ketal **10**, which was hydrolyzed to the target **3** (overall yield from decanal : 64 %).



a : LDA, CH_3CH_2COOEt ; b : HBr, 48 %, Δ ; c : $Ø_3P$; d : NaI ; e : $HOCH_2CH_2OH$, Δ.

The Wittig reaction conditions that we used with nonstabilized ylids led to *cis*-olefines.[6,8] Structures of **1**, **2** and **3** are consistent with the literature data (^{1}H NMR, IR and Mass analysis). Purity and stereochemistry of targets and key intermediates have been checked, for the first time, by ^{13}C NMR and are above 98 % in *Z* isomers (no trace of *E* double bond in all spectra).

We showed the usefulness of C3-homologating agent **4** for the building up all-*cis*-"skipped" polyene systems, and we can point out that our syntheses are shorter than those described in the literature and have been performed in better overall yield from starting materials.

Experimental Part

General Methods. ^{1}H NMR and ^{13}C NMR spectra of $CDCl_3$ solutions were determined on Bruker AC 200 and Varian XL 200 (50.309 MHz) spectrometers, respectively. For ^{13}C NMR spectra, assignments were confirmed by *J*-modulated spin echo. Mass spectra were obtained on a Varian MAT 311 spectrometer. All reactions were carried out under a positive argon atmosphere. All glassware were dried at 180°C, assembled hot, and cooled in a dessicator under argon atmosphere. All solvents (THF, toluene) were distilled from calcium hydride before being used. Reactions run at -100°C were cooled in 95 % ethanol with liquid nitrogen and slowly warmed up to 0 °C over 4 h. Reaction solutions were dried over anhydrous magnesium sulfate for 5 min. and concentrated with Büchi rotary evaporator at 15-20 mm Hg. After Wittig reaction, two flash chromatographic separations were successively performed by using E. Merck silica gel (70-230 mesh) with 1/10 ether-pentane as eluent and then with 230-400 mesh silica gel with 1/80 ether-pentane as eluent. T.l.c. was done on E. Merck 60 F254 silica plates.

Materials. n-Decanal, acrolein, ethyl propionate, γ-butyrolactone (from Aldrich Chemical Co) were distilled before used. (3,3-Diisopropoxypropyl)-triphenylphosphonium bromide **4** was prepared according to the method reported previously.[4a]

(*Z*)-3-Tridecenal Diisopropyl Acetal (5). To a suspension of phosphonium salt **4** (2.6 g, 5.25 mmol, 1.5 equiv) in THF-toluene (14:56 mL) at 0°C was added a 1 M THF solution of sodium bistrimethylsilylamide (5.18 mL, 5.18 mmol, 1.48 equiv). The orange solution of ylid was stirred at room temperature for 1.5 h. The mixture was cooled to -100°C, decanal (0.65 mL, 3.5 mmol, 1 equiv) was added dropwise. The reaction mixture was allowed to warm up to 0°C and then hydrolyzed with saturated NH_4Cl (8 mL) and water (10 mL). After usual work up, the crude material was flash chromatographed twice to pure **5** (1.01 g, 3.39 mmol, 97 %) as a colorless oil : ^{1}H NMR δ : 5.53-5.32 (2, m), 4.54 (1, t, *J* = 5.6 Hz), 3.90 (2, sept, *J* = 6.1 Hz), 2.34 (2, d,d, J = 6.2, 5.6 Hz), 2.03 (2, m), 1.26 (14, br s), 1.19 (6, d, *J* = 6.1 Hz), 1.14 (2, d, *J* = 6.1 Hz), 0.88 (3,t, *J* = 6.4 Hz) ; ^{13}C NMR δ : 132.1 (d), 124.3 (d), 100.2 (d), 67.8 (d)(2C), 33.8 (t), 32.0 (t), 29.7 (t) (2C), 29.5 (t), 29.4 (t)(2C), 27.6 (t), 23.4 (q)(2C), 22.7 (t), 22.6 (q)(2C), 14.1 (q) ; IR (film) 3018, 1650, 1465, 1130, 1040-1030cm^{-1} ; mass spectrum *m/z* 239 (3.5)(HRMS calcd for $C_{16}H_{31}O$ [M - iPrOH] 239.2375, found 239.2367), 131 (50), 89 (100).

(*Z,Z*)-6,9-Nonadecadiene (1). To a suspension of hexyltriphenylphosphonium bromide (2.51 g, 5.15 mmol, 1.52 equiv) in THF-toluene solution (13:54 mL) at 0 °C, was added 1M THF solution of sodium bistrimethylsilylamide (5.1 mL, 5.1 mmol, 1,5 equiv). The orange solution of ylid was stirred at room temperature for 1 h while compound **5** (1.01 g, 3.39 mmol, 1 equiv) was hydrolyzed in refluxing THF (67 mL) with 0.1M aqueous solution of *p*-toluenesulfonic acid (1.7 mL, 0.17 mmol, 0.05 equiv) for 0.3 h. The latter mixture was cooled to 0°C, diluted in pentane (60 mL) and washed with water (3 mL) and

brine (2 x 3 mL). The combined aqueous layers were extracted once with pentane (15 mL). All organic layers were dried over $MgSO_4$, concentrated, transferred into a pear-shaped flask, and then thoroughly dried three times by azeotropic distillation on a rotary evaporator with anhydrous benzene. The residual pivotal aldehyde **6** was diluted in THF (2 mL) and added dropwise to the ylid solution cooled to -100°C. The pear-shaped flask was rinsed twice with THF (1 mL) and the reaction mixture was allowed to warm up to 0°C. After usual work up, the crude material was flash chromatographed twice to give pure **1** (0.72 g, 3.0 mmol, 88 %) as a colorless oil : ^{1}H NMR[3h] δ: 5.46-5.24 (4, m), 2.80 (2, m), 2.10-2.00 (4, m), 1.32 (20, br. s), 0.90 (6, m); ^{13}C NMR δ : 130.1 (d)(2C), 128.0 (d)(2C), 32.1 (t), 31.7 (t), 29.92 (t), 29.83 (t)(2C), 29.77 (t)(2C), 29.73 (t), 29.5 (t), 27.3 (t), 25.7 (t), 22.8 (t), 22.7 (t), 14.2 (q) (2C) ; IR (film) : 3005, 1650, 1465 cm^{-1}; mass spectrum *m/z* 264 (19)(HRMS calcd for $C_{19}H_{36}$ 264.2817, found 264.2835), 110 (37), 95 (67), 81 (87), 67 (100), 55 (87).

(*Z, Z*)-3,6-Hexadecadienal Diisopropyl Acetal (7). As the latter procedure using phosphonium salt **4** (3.08 g, 6.15 mmol, 1.5 equiv), acetal **5** (1.22 g, 4.1 mmol, 1 equiv) led to the pure **7** (1.33 g, 3.9 mmol, 95 %) as a colorless oil : ^{1}H NMR δ : 5.47-5.32 (4, m), 4.55 (1, t, *J* = 5.6 Hz), 3.87 (2, sept, *J* = 6.2 Hz), 2.80 (2, m), 2.37 (2, m), 2.05 (2, m), 1.26 (14, br s), 1.19 (6, d, *J* = 6.1 Hz), 1.14 (6, d, *J* = 6.1 Hz), 0.88 (3,t, *J* = 6.5 Hz) ; ^{13}C NMR δ : 130.4 (d), 130.2 (d), 127.6 (d), 124.6 (d), 100.0 (d), 67.8 (d)(2C), 33.8 (t), 31.9 (t), 29.7 (t), 29.6 (t)(2C), 29.3 (t)(2C), 27.3 (t), 25.9 (t), 23.4 (q)(2C), 22.7 (t), 22.6 (q)(2C), 14.1 (q) ; IR (film) : 3005, 1465, 1120, 1030 cm^{-1}; mass spectrum *m/z* 278 (1.2)(HRMS calcd for $C_{19}H_{34}O$ [M - iPrOH] 278.2609, found 278.2610), 131 (51), 89 (100), 43 (57).

(*Z,Z*)-3,6-hexadecadienyltriphenylphosphonium bromide (8). The acetal **7** (1.66 g, 4.95 mmol, 1 equiv) was hydrolyzed according to the previous procedure into (*Z,Z*)-3,6-hexadecadienal. The crude aldehyde, diluted in THF (1 mL) was slowly added to a suspension of $LiAlH_4$ (200 mg, 4,95 mmol) in THF (50 mL) at -70°C. The reaction mixture was allowed to warm at -20°C and hydrolyzed with hydrochloric acid (2N, 16 mL) and water (30 mL). After usual work up, the crude alcohol was purified by flash chromatography on silica gel (230-400 mesh)(ether-pentane 1/80) giving pure (*Z, Z*)-3,6-hexadecadienol (1.13 g, 4.75 mmol, 96 %) as colorless oil : ^{1}H NMR[3h] δ : 5.56-5.27 (4, m), 3.64 (2, t, *J* = 6.5 Hz), 2.80 (2, m), 2.34 (2, m), 2.03 (2, m), 1.24 (14, br s), 0.86 (3, t, *J* = 6.4 Hz) ; ^{13}C NMR δ : 131.3 (d), 130.6 (d), 127.4 (d), 125.3 (d), 62.2 (t), 31.9 (t)(2C), 30.8 (t), 29.6 (t)(2C), 29.4 (t)(2C), 27.3 (t), 25.8 (t), 22.7 (t), 14.1 (q); IR (film) : 3320, 3010, 1465, 1040 cm^{-1}.

To a mixture of hexadecadienol (900 mg, 3.78 mmol, 1 equiv) and tetrabromomethane (1.88 g, 5.67 mmol, 1.5 equiv) in anhydrous methylene chloride (6 mL) at -5°C was added triphenylphosphine (1.488 g, 5.67 mmol, 1.5 equiv) in methylene chloride (6 mL). Alcohol disappearing was checked by t.l.c. (ether-pentane 1/4 ; R_f = 0.55). The reactive mixture was added to ether-pentane 1/1 (100 mL), filtered, washed with ether. The solvent was removed in *vacuo* and the crude product was purified by flash chromatography on silica gel (230-400 mesh, ether-pentane 1/10) giving the pure (*Z,Z*)-1-bromo-3,6-hexadecadiene (1.09, 3.6 mmol, 95%) : ^{1}H NMR[3e,3h] δ : 5.55-5.28 (4, m), 3.34 (2, t, *J* = 7,1 Hz), 2.79 (2, m), 2.65 (2, m), 2.04 (2, m), 1.27 (14, br. s), 0.88 (3, t, *J* = 6.4 Hz) ; ^{13}C NMR δ : 131.30 (d), 130.79 (d), 127.06 (d), 126.06 (d), 32.32 (t), 31.93 (t)(2C), 30.85 (t), 29.63 (t)(2C), 29.35 (t)(2C), 27.31 (t), 25.82 (t), 22.70 (t), 14.13 (q); IR (film) : 3010, 1650, 1460 cm^{-1}.

A mixture of bromohexadecadiene (760 mg, 2.5 mmol, 1 equiv) and triphenylphosphine (1.18 g, 4.5 mmol, 1.8 equiv) in acetonitrile (15 mL) was refluxed for 36 h. Bromide disappearing was checked by

t.l.c. (ether-pentane 1/4 ; R_f = 0.73). Solvent was removed and the crude material was purified by flash chromatography on silica gel (230-400 mesh) (ether-pentane 1/1 to methanol-dichloromethane 1/20) giving pure salt **8** as pale yellow viscous oil (1.01 g, 1.79 mmol, 74 %) : ^{1}H NMR δ : 7.90-7.61 (15, m), 5.63-5.15 (4, m), 3.90-3.64 (4, m), 2.57-2.35 (4, m), 1.87 (2, m), 1.24 (14, m), 0.87 (3, m, *J* = 6.4 Hz).

(*Z,Z,Z*)-1,3,6,9-nonadecatetraene (2). To a solution of phosphonium bromide **8** (1.74 g, 2.98 mmol, 1 equiv) in THF-toluene (12/50 mL) at 0°C was added 1 M THF solution of sodium bistrimethylsilylamide (2.86 mL, 2.86 mmol, 0,96 equiv). The solution was stirred for 1.5 h at room temperature. After cooling at -100°C, acrolein (197 µL ; 2.95 mmol, 0.95 equiv) in THF (1 mL) was added. After usual work up, two flash chromatographic purifications gave pure **2** as colorless oil (476 mg, 1.83 mmol, 62 %) : ^{1}H NMR[3b,3c,3g,3h] δ : 6.66 (1, d,d,d,d, *J* = 17.0, 10.8, 10.2, 0.9 Hz), 6.02 (1, br t, *J* = 10.8 Hz), 5.46-5.29 (5, m), 5.20 (2, br d, *J* = 17.0 Hz), 5.11 (1, br d, *J* = 10.2 Hz), 2.96 (2, m), 2.81 (2, m), 2.05 (2, m), 1.25 (14, br s), 0.88 (3, t, *J* = 6.4 Hz) ; ^{13}C NMR δ : 132,0 (d), 130.5 (d), 130.4 (d), 129.3 (d), 129.0 (d), 127.4 (d), 127.3 (d), 117.3 (t), 32.0 (t), 29.7 (t)(2C), 29.6 (t), 29.4 (t)(2C), 27.3 (t), 26.1 (t), 25 7 (t), 22.7 (t), 14.1 (t) ; IR (film) : 3005, 1645, 1465, 990, 900 cm^{-1}; mass spectrum[3b, 3h] *m/z* 260 (1)(HRMS calcd for $C_{19}H_{32}$ 260.2504, found 260.2510), 206 (13), 78 (100).

(4-Oxo-hexyl)triphenylphosphonium iodide ethyleneketal (9). To a solution of diisopropylamine (4.8 mL, 34 mmol, 1.2 equiv) in THF solution (56 mL) at - 40 °C was added a 1.5 M hexane solution of butyl lithium (20.7 mL, 31 mmol, 1.1 equiv). The mixture was stirred from - 40 °C to - 20 °C for 0.75 hr, then was cooled down to - 80 °C. Butyrolactone (2.16 mL, 28.2 mmol, 1 equiv) was added and stirring was maintained for 2 hr. Then ethyl propionate (9.6 mL, 84.6 mmol, 3 equiv) was added. The reaction mixture was slowly warmed to room temperature over 10 hr. Hydrolysis with 15 mL saturated NH_4Cl and 10 mL H_2O, extraction with ether, washing of organic layers with brine, drying over $MgSO_4$ and concentration led to a crude product. Flash chromatography over silica gel (70 - 230 mesh) with ether - pentane : 1 / 4 to 1 / 1 gave pure 2-propionyl-γ-butyrolactone (1.36 gr, 9.57 mmol, 34 %). This latter was vigorously stirred in a mixture of toluene (18 mL) and 48 % hydrobromic acid (20 mL) for 45 min. Extraction with ether (330 mL), washing until neutral with brine, drying over $MgSO_4$ and concentration gave 6-bromo-3-hexanone in quantitative yield. ^{1}H NMR δ : 3.45 (2, t, *J* = 7.3 Hz), 2.61 (2, t, *J* = 6.9 Hz), 2.44 (2, q, *J* = 7.3 Hz), 2.12 (2, t,t, *J* = 7.3, 6.9 Hz), 1.06 (2, t, *J* = 7.3 Hz).

A mixture of 6-bromo-3-hexanone (1.864 g, 10.3 mmol, 1 equiv) and triphenylphosphine (5.4 g, 20.6 mmol, 2 equiv) in 60 mL acetonitrile was refluxed for 36 h. Reaction is checked by disappearing of bromide (ether -pentane 1/4 ; R_f = 0.52). After concentration, reaction mixture is diluted in 100 mL CH_2Cl_2 and washed twice 1M solution of NaI. Drying over $MgSO_4$, concentration and addition to 350 mL ether gave a precipitate wich was recrystallized ($CHCl_3$/AcOEt : 1/1) leading to pure (4-Oxo-hexyl)triphenylphosphonium iodide (3.74 g, 7.66 mmol, 74 %) : ^{1}H NMR δ : 7.92-7.63 (15, m), 3.91-3.77 (2, m), 3.10 (2, t, *J* = 5.7 Hz), 2.53 (2, q, *J* = 7.3 Hz), 1.97-1.81 (2, m), 1.04 (2, t, *J* = 7.3 Hz).

Ketalization of the last compound was performed by refluxing through a Dean-Stark apparatus containing molecular sieve (4 Å), a mixture of the oxo-phosphonium salt, *p*-toluenesulfonic acid (0.3 g), ethylene glycol (1 g) and $CHCl_3$ (40 mL) for 36 hr. After dilution in CH_2Cl_2 (100 mL), the mixture is successively washed with 1M solution of $NaHCO_3$ (20 mL), NaI (20 mL) and $Na_2S_2O_3$ (20 mL) ; drying over $MgSO_4$, concentration, addition to 350 mL ether and stirring gave a precipitate which was recrystallized ($CHCl_3$ / AcOEt) leading to pure salt **9** (3.75 g, 7 mmol, 92 %) : ^{1}H NMR δ : 7.87-7.32 (15, m), 3.87 (4, br. s), 3.79-3.65 (2, m), 2.00 (2, t, *J* = 7.21), 1.92-1.70 (2, m), 1.51 (2, q, *J* = 7.4 Hz), 0.82 (3, t, *J* = 7.4 Hz).

(*Z, Z*)-6,9-nonadecadiene-3-one ethyleneketal (10). As in a previous procedure,

phosphonium salt **9** (1.38 g, 2.6 mmol, 1.2 equiv) and acetal **5** (0.64 g, 2.17 mmol, 1 equiv) led to pure **10** (0.47 g, 1.48 mmol, 70 %) as a colorless oil : ^{1}H NMR δ : 5.28 (4, m), 3.93 (4, br. s), 2.77 (2, m), 2.17-2.02 (4, m), 1.69-1.58 (4, m), 1.24 (14, br. s), 0.90 (3, t, J = 7.4 Hz), 0.86 (3, t, J = 6.5 Hz); IR (film) : 3010, 1460, 1060 cm^{-1}.

(*Z,Z*)-6,9-nonadecadiene-3-one (3). A mixture of compound **10** (0.16 g, 0.49 mmol) , 2M solution of sulfuric acid (1 mL) in THF (21 mL) was refluxed for 0.5 hr. After cooling, dilution in pentane (21 mL), washing with 3 x 10 mL brine and concentration under *vacuo* , crude material was chromatographed giving pure ketone **3** (0.14 g; 0.5 mmol ; 99 %) as a colorless oil. ^{1}H NMR[3e] δ : 5.43-5.26 (4, m), 2.77 (2, m), 2.48-2.30 (6, m), 2.04 (2, m), 1.26 (14, br. s), 1.05 (3, t, J = 7.32) Hz, 0.88 (3, t, J = 6.5 Hz) ; ^{13}C NMR δ : 210.8 (s), 130.5 (d), 129.3 (d), 128.1 (d), 127.5 (d), 42.1 (t), 36.0 (t), 31.0 (t), 29.7 (t), 29.6 (t)(2C), 29.4 (t)(2C), 27.3 (t), 25.6 (t), 22.7 (t), 21.8 (t), 14.4 (q), 7.8 (q) ; IR (film) : 3005, 1720, 1650, 1460, 1260 cm^{-1}; mass spectrum *m/z* 278 (2)(HRMS calcd for $C_{19}H_{34}O$ 278.2609, found 278.2624), 206 (56), 80 (100).

References

1 (a) Green, R. H. ; Lamberts, P.F. *Tetrahedron* **1983**, *39*, 1687.
(b) Hart, T. W. *Nat. Prod. Rep.* **1984**, *1*, 409.

2 (a) Baker, R. ; Evans, D. A. *J. Chem. Soc. Ann. Reports (London)* **1977**, *74B*, 367.
(b) K. Mori in *"Total Synthesis of Natural Products"*, ed. J. ApSimon, Wiley-Interscience, New York, Vol 4, p.1.

3 (a) Jain, S.C. ; Dussourd, D.E. ; Conner, W.E. ; Eisner, T. ; Guerrero, A. ; Meinwald, J. *J. Org. Chem.* **1983**, *48*, 2266.
(b) Huang, W. ; Pulaski, S. P. ; Meinwald, J. *J. Org. Chem.* **1983**, *48*, 2270.
(c) Jain, S. C. ; Roelofs, W. L. ; Meinwald, J. *J. Org. Chem.* **1983**, *48*, 2274.
(d) Becker, D. ; Kimmel, T. ; Cyjon, R. ; Moore, I. ; Wysoki, M. ; Bestmann, H. J. ; Platz, H. ; Roth, K. ; Vostrowsky, O. *Tetrahedron Lett* **1983**, *24*, 5505.
(e) Buser, H. R. ; Guerin, P. M. ; Toth, M.; Szöcs, G. ; Schmid, A. ; Francke, W. ; Arn, H. *Tetrahedron Lett.* **1985**, *26*, 403.
(f) Bestmann, H. J. ; Dötzer, R. ; Manero-Alvarez, J. *Tetrahedron Lett.* **1985**, *26*, 2769.
(g) Millar, J. G. ; Underhill, E. W. *Can. J. Chem.* **1986**, *64*, 2427.
(h) Bestmann, H. J. ; Roth, K. ; Michaelis, K. ; Vostrowsky, O. ; Schäfer, H. J. ; Michaelis, R. *Liebigs Ann. Chem.* **1987**, 417.
(i) Kovalev, B.G. ; Sorochinskaya, A.M. *Zh. Org. Khim.* **1989**, *25*, 1180.

4 (a) Viala, J. ; Santelli, M. *Synthesis* **1988**, 395 ;
(b) Viala, J. ; Santelli, M. *J. Org. Chem.* **1988**, *53*, 6121.

5 For an alternative method, see : Wilson, S.R.; Zucker, P.A. *J. Org. Chem.* **1988**, *53*, 4682.

6 Vedejs, E. ; Marth, C.F. *J. Am. Chem. Soc.* **1988**, *110*, 3948.

7 Rathke, M. W. ; Deitch, J. *Tetrahedron Lett* **1971**, 2953.

8 (a) Bestmann, H.J. ; Stransky, W. ; Vostrowsky, O. *Chem. Ber.* **1976**, *109*, 1694.
(b) Reitz, A.B. ; Nortey, S.O. ; Jordan, A.D. ; Mutter, M.S. ; Maryanoff, B.E. *J. Org. Chem.* **1986**, *51*, 3302.
(c) Eya, B.K.; Otsuka, T.; Kubo, I.; Wood, D.L. *Tetrahedron* **1990**, *46*, 2695.