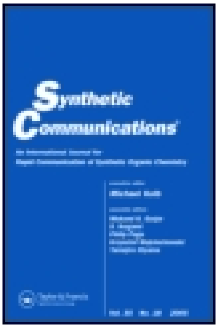

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Sex Pheromone of Chilo Suppressalis: Efficient Syntheses of (Z)-11-Hexadecenal, (Z)-13-Octadecenal And (Z)-9-Hexadecenal

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SEX PHEROMONE OF CHILO SUPPRESSALIS: EFFICIENT SYNTHESES OF (Z)-11-HEXADECENAL, (Z)-13-OCTADECENAL AND (Z)-9-HEXADECENAL

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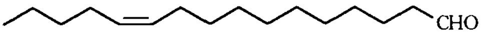
This paper is dedicated to the memory of the late Professor Félix Serratosa

Abstract: The constituents of the sex attractant pheromone of *Chilo suppressalis*: (*Z*)-11-Hexedecenal **1**, (*Z*)-13-octadecenenal **2** and (*Z*)-9-Hexadecenal **3** have been synthesized as their ethylene acetals **19**, **15** and **13**, in six steps from easily available compounds. The synthetic methodology can be applied to preparative scale.

Chilo suppressalis is a serious pest for rice crops all over the world. Only moderate success is achieved in its control with organophosphorate insecticides, because long periods of life of Chilo suppressalis are spent in larval form inside of the rice cane. This feature has fostered the study of its sex attractant pheromone for application as a non contaminant pest-control agent. This pheromone is constituted by a mixture of three unsaturated aldehydes: (*Z*) 11-hexadecenal **1**, (*Z*) 13-octadecenal **2** and (*Z*) 9-hexadecenal **3** in the ratio 250 : 30 : 25. [1]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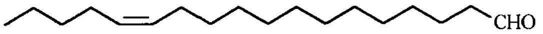
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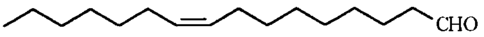
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A good number of syntheses of the first aldehyde have been reported,[2] where the carbon chain is built up in several steps either by alkylation of an alkyne, or by copper catalyzed coupling of organomagnesium reagents. (*Z*)-13-Octadecenal has been prepared from erucic and tetradecanedioic acids through Wittig reaction as (*Z*) double bond forming process,[3] and from myristoleic acid through iteration of malonic alkylation.[4] Similary, (*Z*) 9-hexadecenal **3** has been prepared in nine steps from 1,5 cyclooctadiene by ozonolysis of one of the double bonds, followed by reduction and alkylation reactions to achieve the adequate C_{18} chain and final oxydation to aldehyde.[5]

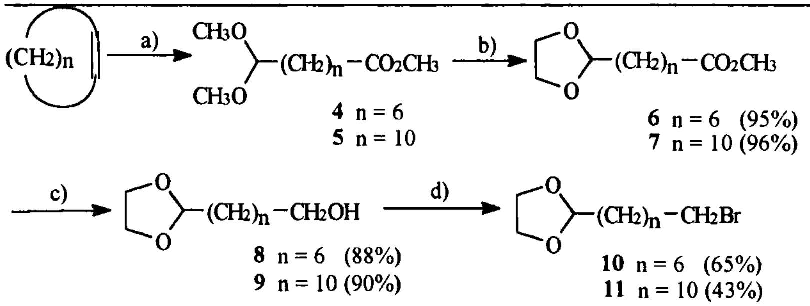
We felt that synthetic procedures easily scaled up and starting from materials commercially available in bulk amounts were required for use of the pheromone as pest-control agent. On the other hand, synthesis of the aldehydes as their ethylene acetals **13**, **15** and **19**,[7] would be advantageous, as oxidation would then be prevented on long storage and the aldehydes would be easily obtained inmediately for laboratory or field application.

We have already described the conversion of cyclododecanone to (*Z*) 11-hexadecenal **1** and (*Z*) 13-octadecenal **2** as the dioxolanes **19** and **15.**[6] We wish to report here that easily available starting materials, namely, cyclooctene, cyclododecene and 10-undecen-1-ol, enable shorter syntheses and higher yields for these acetals and for the acetal **13** of the minor aldehyde **3**.

The starting materials should undergo a facile conversion into ω-bromoaldehyde acetals [2-(ω-bromoalkyl)-1,3-dioxolanes] for alkylation of the convenient 1-alkynes and thus lead to C_{16} and C_{18} acetylenic compounds, with the triple bond placed at the right position for conversion into the Z-olefinic aldehyde acetals **13**, **15** and **19** by Lindlar hydrogenation.

The ω-bromo alkyl dioxolanes **10** and **11** are prepared in 42 and 35% yields, respectively, by ozonolysis of cyclooctene and cyclododecene to the corresponding ω-methyl carboxylate aldehyde acetals **6** and **7**, reduction of the ester moiety to the alcohols **8** and **9**, and final substitution of the hydroxyl group **(Scheme 1)**. The alternative ozonolysis to the monoacetal of a dialdehyde and reduction to the corresponding ω-hydroxy aldehyde acetal led to less pure crudes that on purification afforded lower global yields.

Initial protection of aldehyde moiety as dimethoxyl acetal (**4**, **5**) was achieved by performing the ozonolysis in methanol.[8] Unfortunately, these acetals were partly cleaved

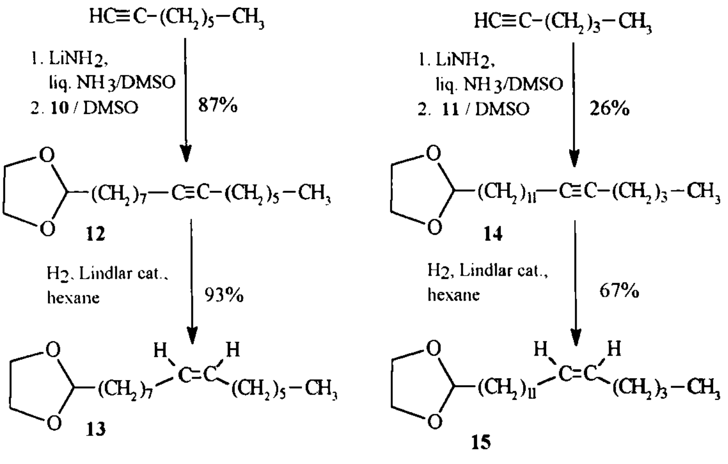


a) 1 O_3, MeOH, CH_2Cl_2; 2 p-TsOH; 3 $NaHCO_3$; 4 Et_3N, Ac_2O;
b) ethylene glycol, ac. p-TsOH (cat.), benzene 2 h reflux; c) $LiAlH_4$, ethyl ether;
d) 1 CBr_4, Ph_3P, dry CH_2Cl_2; 2 ethylene glycol, ac. p-TsOH (cat.), benzene 2 h reflux.

Scheme 1

under the conditions for replacement of the hydroxyl group of the alcohol resulting from reduction of the esters **4** and **5**, and transacetalation in order to have more stable hydroxydioxolanes **8** and **9** was required. Even thus, the latter underwent occasional cleavage on treatment with triphenylphosphine in carbon tetrabromide, and small amounts of ω-bromoaldehyde (< 10%) were observed in the products (^1H NMR). Reprotection *in situ* became then easier and gave better yields than purification.

It is known that terminal triple bond alkylation of long chain derivatives usually requires use of HMPA as a co-solvent.[9-11] We have reported [6] that HMPA can be succesfully replaced by DMI for that purpose. However, use of any of these solvents at larger scale can be troblesome. Replacement of those solvents by pure DMSO is only succesfull for highly stabilized lithium alkynides as otherwise deprotonation of the solvent is a major competing process.[12] Use of DMSO as co-solvent in liquid ammonia has been reported for alkylation of sodium acetylide,[10] but low yields are obtained for higher lithium or sodium alkynides.[11] We have found now that use of solid $LiNH_2$ as a base in liquid ammonia containing 15% DMSO allows alkylation of 1-alkynes with alkyl halides, up to 8 carbon atoms for each reagent in good yields at gram scale (70 to 90%). For longer chain alkyl halides, the system must be cooled at -78°C prior to addition of the alkyl halide **(Scheme 2)**. Otherwise, substitution of the halogen atom by ammonia interferes, and

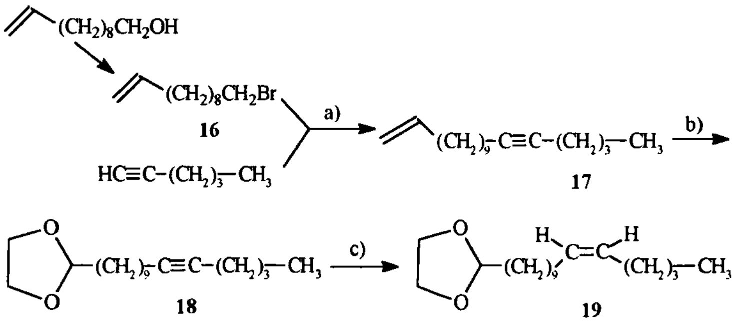


Scheme 2

some amounts of the alkyl amines are obtained. However, this present finding is limited as well by the number of the carbon atoms of the alkylating agent, as the method fails again when the chain becomes too long. Thus, for the 2-(ω-bromodecyl)-1,3-dioxolane **11** alkylation of 1-hexyne according to this method gave the alkynyldioxolane **14** in only 26% yield, far below the result obtained by us (83%) when the alkylation was carried out with BuLi in DMI.[6]

10-Undecen-1-ol showed to be a convenient starting material for the synthesis of the acetal **19** of the major component of the pheromone, as a shorter sequence is required than by the methodology applied for the acetals **13** and **15** of the minor components of the pheromone, and is based on a cheaper starting material. This unsaturated alcohol was easily converted into the ω-bromo alquene **16** [13] which, after alkynylation and ozonolysis, led to the appropriate C_{16} chain with the triple bond at C-11 (**Scheme 3**). A lower yield was obtained when ozonolysis of **16** was done before alkynylation.

An alternative to alkylation of a commercialy available 1-alkyne was envisaged based on the sequential alkylation of acetylene in DMSO/NH_3 first with bromoaldehyde acetal, and then with an alkyl halide. This method enabled us to obtain the acetylenic acetal **18** in 70 % yield from the corresponding halide compounds. Although this strategy does



a) 1. $LiNH_2$, liquid NH_3 / DMSO (69%)
b) 1. O_3, CH_2Cl_2; 2. SMe_2, ethylene glycol, p-TsOH (cat.), benzene (90%)
c) H_2, Lindlard catalyst, hexane (72%)

Scheme 3

not improve the results attained by alkylation of 1-hexyne, it may be useful for the synthesis of related compounds requiring non commercially available alkynes.

Hydrogenations with Lindlar catalyst were easily achieved, and led to good yields of the spectrocopically (^{1}H and ^{13}C NMR) pure *Z* isomers. GC analysis was hampered by product descomposition. Compounds **19**, **15** and **13** were thus obtained in 45, 6 and 34 % global yields, respectively, from cheap starting materials. Global yield for compound **15** can be rised to 20% if DMI is used for the alkylation step.[6]

As a conclusion, we think that the present findings provide valuable methods for preparation of the components of the sex pheromone of *Chilo suppressalis* that improve former procedures, and can be the basis for commercially useful prepartions.

EXPERIMENTAL PART

IR spectral data were obtained for liquid film or KBr discs, with a Bio Rad FTS-7 spectrophotometer. NMR spectra were recorded for $CDCl_3$ solutions, with Varian Unity 300 or Unity 400 spectrometer. Mass spectra were determined with a VG Autospec Spectrometer. Elemental analyses were determined by "Servicio de Semimicroanálisis del

Centro de Investigación y Desarrollo (CSIC) de Barcelona". Silica gel Merck 60 (230-400 mesh) was used for flash column chromatography, with hexane/ether mixtures as eluent. Dry ethyl ether and tetrahydrofuran (THF) were distilled from blue sodium diphenylketyl, immediatelly before use. Dry CH_2Cl_2 was distilled from anhydrous $CaCl_2$ and stored over 4A molecular sieves. Triethylamine was dried over CaH_2 and distilled before use. Acetic anhydride was dried over P_2O_5 and distilled before use. $LiNH_2$ was purchased from Aldrich and stored under Ar. Methyl 12,12-dimethoxydodecanoate **5** [14] and methyl 8,8-dimethoxy-octanoate **4** [14] were obtained from cyclododecene and cyclooctene according to the procedure of the literature.[8] 11-Bromo-1-undecene **16** was prepared from 10-undecen-1-ol, as described in the literature.[13]

2-(6-methoxycarbonylhexyl)-1,3-dioxolane 6.- Methyl 8,8-dimethoxyoctanoate (8.847 g, 40.6 mmol), ethylene glycol (3.019 g, 48.7 mmol) and p-toluenesulfonic acid monohydrate (779 mg, 4.1 mmol) in benzene (85 ml) were heated under reflux for 3 h in a Dean-Stark apparatus. The solution was washed with aqueous sodium bicarbonate and water, and dried over $MgSO_4$. Evaporation of the solvent gave 2-(6-methoxycarbonylhexyl)-1,3-dioxolane **6** (8.379 g, 95%) as a yellow oil; HRMS: Found M^+ 216.131441, $C_{11}H_{20}O_4$ requires 216.136159; ν_{max} (NaCl) 2940, 2860, 1738 (C=O), 1440 and 1170 cm^{-1}; δ_H 4.79 (1H, t, J 4.8 Hz, 2-H), 4.0-3.7 (4 H, m, 4-H and 5-H), 3.62 (3 H, s, CH_3 ester), 2.26 (2 H, t, J 7.5 Hz, 6'-H) and 1.70-1.20 (10 H, m, $-(CH_2)_5-$) ppm; δ_C 174.18 (C=O), 104.57 (C_2), 64.81 (C_4 and C_5), 51.39 (CH_3 ester), 34.03, 33.79, 29.11, 29.01, 24.80 and 23.82 ppm.

2-(7-hidroxyheptyl)-1,3-dioxolane 8.- The ester **6** (8.031 g, 37.2 mmol) was added during 20 min to stirred lithium aluminum hydride (987 mg, 26 mmol) in dry ethyl ether (40 ml), the mixture was stirred for 30 min, and water was added dropwise. The mixture was poured into HCl 0.1 N (30 ml) and extracted with ethyl ether. The organic layer was washed with aqueous sodium bicarbonate and water, and dried. Evaporation of the solvent yielded 2-(7-hidroxyheptyl)-1,3-dioxolane **8** (6.127 g, 88%) as a yellow oil; HRMS: Found M^+ 188.140437, $C_{10}H_{20}O_3$ requires 188.141245; ν_{max} (NaCl) 3600-3200 (OH), 2930, 2860, 1450, 1120, 1060 and 950 cm^{-1}; δ_H 4.82 (1 H, t, J 4.9 Hz, 2-H), 4.0-3.8 (4 H, m, 4-H and 5-H), 3.61 (2 H, t, J 6.5 Hz, 7'-H) and 1.70-1.20 (12 H, m, $-(CH_2)_6-$) ppm; δ_C

104.62 (C_2), 64.81 (C_4 and C_5), 62.97 ($C_{7'}$), 33.82, 32.72, 29.45, 29.27, 25.58 and 23.97 (6 CH_2) ppm.

2-(7-bromoheptyl)-1,3-dioxolane 10.- Triphenyl phosphine (10.428 g, 40 mmol) was added in small portions to a solution of carbon tetrabromide (13.202 g, 40 mmol) and the alcohol **8** (5.748 g, 30.6 mmol) in dry CH_2Cl_2 (30 ml) and the mixture was stirred for 30 min. The solvent was evaporated, and the residue diluted with 50 ml of hexane, and the precipitate filtered off. Evaporation of the solvent gave a yellow oil which was added to a solution of ethylene glycol (186 mg, 3 mmol) and p-toluenesulfonic acid monohydrate (57 mg, 0.3 mmol) in benzene (45 ml). The mixture was heated under reflux for 3 h in a Dean-Stark apparatus, and then washed with aqueous sodium bicarbonate, water, and dried. Evaporation of the solvent gave a yellow oil which was purified by flash column chromatography with hexane:diethyl ether (9:1), to give 2-(7-bromoheptyl)-1,3-dioxolane **10** (4.331 g, 56%) as a colourless oil; ν_{max} (NaCl) 2930, 2870, 1130, 1040 and 950 cm^{-1}; δ_H 4.82 (1 H, t, J 3.6 Hz, 2-H), 4.0-3.8 (4 H, m, 4-H and 5-H), 3.38 (2 H, t, 7'-H), 1.8 (2 H, m, 6'-H), 1.6 (2 H, m, 1'-H) and 1.5-1.2 (8 H, m, $-(CH_2)_4-$) ppm; δ_C 104.56 (C_2), 64.81 (C_4 and C_5), 33.94, 33.80, 32.75, 29.29, 28.63, 28.01 and 23.92 ppm.

2-(8-pentadecynyl)-1,3-dioxolane 12.- $LiNH_2$ (372 mg, 16.2 mmol) and 2 ml of dry DMSO were added to liquid NH_3 (14 ml). Then 1-octyne (1.485 g, 13.5 mmol) was added dropwise and the mixture was stirred for 30 min. The solution was cooled to -78 °C under argon atmosphere, and compound **10** (2.257 g, 9 mmol) was added dropwise.The cooling bath was removed and the solution stirred for 3 h. The mixture was diluted with ethyl ether and poured into 30 ml of cool water.The aqueous layer was extracted with ethyl ether, and the organic extract was washed with aqueous NH_4Cl, water, and dried. The solvent was evaporated to give 2-(8-pentadecynyl)-1,3-dioxolane **12** (2.177 g, 87%) as a yellow oil; HRMS: Found M^+ 280.239503, $C_{18}H_{32}O_2$ requires 280.240230; ν_{max} (NaCl) 2930, 2860, 1460, 1140, 910 and 730 cm^{-1}; δ_H 4.80 (1 H, t, J 4.8 Hz, 2-H), 4.0-3.7 (4 H, m, 4-H and 5-H), 2.1 (4 H, m, 7'-H and 10'-H), 1.6 (2 H, m, 1'-H), 1.5-1.1 (18 H, m, $-(CH_2)_9-$) and 0.85 (3 H, t, J 6.6 Hz, 15'-H) ppm; δ_C 104.66 (C_2), 80.25 ($C_{8'}$ or $C_{9'}$), 80.15 ($C_{8'}$ or $C_{9'}$), 64.81 (C_4 and C_5), 33.89, 31.38, 29.44, 29.13, 29.06, 28.73, 28.54, 24.05, 22.57, 18.75, 18.73 and 14.05 ($C_{15'}$) ppm.

(*Z*)-2-(8-pentadecenyl)-1,3 dioxolane 13.- A mixture of Lindlar catalyst (8 mg), quinoline (0.08 ml) and acetylene **12** (449 mg, 1.6 mmol) in hexane (2 ml) was stirred under hydrogen at 1 atm for 1 h. The mixture was poured into a flash chromatography column and washed with hexane-ethyl ether (24:1). Evaporation of the solvent yielded (*Z*)-2-(8-pentadecenyl)-1,3-dioxolane **13** (437 mg, 93%) as a colourless oil; HRMS: Found M$^+$ 282.255422, $C_{18}H_{34}O_2$ requires 282.2558805; ν_{max} (NaCl) 2920, 2860, 1460, 1140, 910 and 730 cm^{-1}; δ_H 5.3 (2 H, m, 8'-H and 9'-H), 4.80 (1 H, t, J 4.8 Hz, 2-H), 4.0-3.8 (4 H, m, 4-H and 5-H), 2.0 (4 H, m, 7'-H and 10'-H), 1.6 (2 H, m, 1'-H), 1.5-1.2 (18 H, m, -$(CH_2)_9$-) and 0.85 (3 H, t, J 6.8 Hz, 15'-H) ppm; δ_C 129.91 (C_8 or C_9), 129.81 (C_9 or C_8), 104.69 (C_2), 64.81 (C_4 and C_5), 33.92, 31.78, 29.74, 29.53, 29.46, 29.44, 29.18, 28.98, 27.21, 27.18, 24.08, 22.65 and 14.09 ($C_{15'}$) ppm.

2-(10-methoxycarbonyldecyl)-1,3-dioxolane 7.- This was obtained from methyl 12,12-dimethoxydodecanoate (11.268 g, 41.1 mmol) by the same procedure as above for **6** as a yellow oil (10.832 g, 96%); HRMS: Found (M$^+$-1) 271.190766, $C_{15}H_{27}O_4$ requires 271.190935; ν_{max} (NaCl) 2930, 2860, 1740, 1440, 1170 and 940 cm^{-1}; δ_H 4.81 (1 H, t, J 4.8 Hz 2-H), 4.0-3.7 (4 H, m, 4-H and 5-H), 3.63 (3 H, s, CH_3 ester), 2.36 (2 H, t, J 7.7 Hz, 10'-H) and 1.7-1.2 (18 H, m, -$(CH_2)_9$-) ppm; δ_C 174.32 (C=O), 104.70 (C_2), 64.82 (C_4 and C_5), 51.42 (CH_3 ester), 34.11, 33.91, 29.53, 29.49, 29.43, 29.39, 29.23, 29.14, 24.95 and 24.07 ppm.

2-(11-hidroxyundecyl)-1,3-dioxolane 9.- This was obtained from **7** (10.635 g, 39.1 mmol) according to the procedure employed for **8** as a yellow oil (8.687 g, 90%); HRMS: Found M$^+$ 244.200979, $C_{14}H_{28}O_3$ requires 244.203845; ν_{max} (NaCl) 3600-3200 (-OH), 2920, 2850, 1450, 1430, 1130 and 1030 cm^{-1}; δ_H 4.78 (1 H, t, J 4.8 Hz, 2-H), 4.0-3.7 (4 H, m, 4-H and 5-H), 3.59 (2 H, t, J 6.6 Hz, 11'-H), 1.6 (2 H, m, 1'-H), 1.5 (2 H, m, 10'-H) and 1.4-1.2 (16 H, m, -$(CH_2)_8$-) ppm; δ_C 104.63 (C_2), 64.77 (C_4 and C_5), 63.03 ($C_{11'}$), 33.85 , 32.74, 29.52, 29.48, 29.43, 29.36, 25.67 and 24.04 ppm.

2-(11-bromoundecyl)-1,3-dioxolane 11.- By the same procedure as for **10**, **9** (8.280 g, 33.9 mmol) gave crude 2-(11-bromoundecyl)-1,3-dioxolane **11** which purified by flash column chromatography with hexane:diethyl ether (9:1) gave pure **11** (4.494 g, 43%) as a colourless oil (Lit.^{15}); ν_{max} (NaCl) 2930, 2860, 1140, 1040 and 950 cm^{-1}; δ_H 4.82

(1 H, t, J 3.6 Hz, 2-H), 4.0-3.7 (4 H, m, 4-H and 5-H), 3.38 (2 H, t, J 5.1 Hz, 11'-H), 1.8 (2 H, m, 10'-H), 1.6 (2 H, m, 1'-H) and 1.5-1.2 (16 H, m, -$(CH_2)_8$-) ppm; δ_C 104.55 (C_2), 64.79 (C_4 and C_5), 34.01, 33.87, 32.81, 29.51, 29.48, 29.46, 29.43, 29.38, 28.73, 28.15 and 24.05 ppm.

2-(12-heptadecynyl)-1,3-dioxolane 14.- By the same procedure as for **12**, 1-hexyne (1.107g, 13.5 mmol) and **11** (2.777 g, 9 mmol) gave starting material (21%) and 2-(12-heptadecynyl)-1,3-dioxolane **14** (720 mg, 26%) as a yellow oil; Found: C, 77.71; H, 11.88. $C_{20}H_{36}O_2$ requires C, 77.85; H, 11.77 %; ν_{max} (NaCl) 2927, 2860, 1458, 1137 and 1040 cm^{-1}; δ_H 4.82 (1 H, t, J 4.8 Hz, 2-H), 4.0-3.8 (4 H, m, 4-H and 5-H), 2.1 (4 H, m, 11-H and 14-H), 1.7-1.2 (24 H, m, -$(CH_2)_{12}$-) and 0.88 (3 H, t, J 7.0 Hz, 17-H) ppm; δ_C 104.69 (C_2), 80.17 (C_{12} or C_{13}), 80.11 (C_{13} or C_{12}), 64.79 (C_4 and C_5), 33.90, 31.26, 29.52, 29.49, 29.15, 29.13, 28.83, 24.06, 21.89, 18.72, 18.41 and 13.59 (C_{17}) ppm.

(*Z*)-2-(12-heptadecenyl)-1,3-dioxolane 15.- A mixture of Lindlar catalyst (0.9 mg), quinoline (0.01 ml) and acetylene **14** (55 mg, 0.18 mmol) in hexane (1 ml) was stirred under hydrogen at 1 atm for 1 h. The mixture was poured into a flash chromatography column and washed with hexane-ethyl ether (24:1). The solvent was evaporated to give a yellow oil (48 mg), which was purified by HPLC chromatography to give 2 ((*Z*)-12'-heptadecenyl) 1,3-dioxolane **15** (37 mg, 67%) as a colorless oil; Found: C, 77.20; H, 12.33. $C_{20}H_{38}O_2$ requires C, 77.35; H, 12.34 %; ν_{max} (NaCl) 2925, 2860, 1457, 1335 and 1040 cm^{-1}; δ_H 5.33 (2 H, t, J 4.8Hz, 12'-H and 13'-H), 4.82 (1 H, t, J 4.8 Hz, 2-H), 4.00-3.80 (4 H, m, 4-H and 5-H), 1.99 (4 H, m, 11'-H and 14'-H), 1.70-1.20 (24 H, m, -$(CH_2)_{12}$-) and 0.88 (3 H, t, J 7.0 Hz, 18-H) ppm; δ_C 129.89 ($C_{12'}$ or $C_{13'}$), 129.82 ($C_{12'}$ or $C_{13'}$), 104.68 (C_2), 64.80 (C_4 and C_5), 33.91, 31.98, 31.95, 29.76, 29.61, 29.54, 29.32, 29.30, 27.21, 27.18, 26.90, 24.09, 22.33 and 13.99 ($C_{17'}$) ppm.

12-heptadecyn-1-ene 17.- It was obtained from 1-hexyne (1.107g, 13.5 mmol) and 11-Bromo-1-undecene (2.097 g, 9 mmol) as described for the preparation of **12**. On the scale indicated there was obtained 12-heptadecyn **17** (1.453 g, 69%) as a yellow oil; Found: C, 86.92; H, 12.99. $C_{17}H_{30}$ requires C, 87.09; H, 12.91 %; ν_{max} (NaCl) 2930, 2860, 1636, 1450, 990 and 910 cm^{-1}; δ_H 5.8 (1 H, m, 2-H), 4.9 (2 H, m, 1-H), 2.1 (4 H, m, 11-H and 14-H), 2.0 (2 H, m, 3-H), 1.5-1.2 (18 H,.m, -$(CH_2)_9$-) and 0.88 (3 H, t, J 7.2

Hz, 17-H) ppm; δ_C 139.20 (C_1), 114.08 (C_2), 80.19 (C_{12} or C_{13}), 80.15 (C_{13} or C_{12}), 33.81 (C_3), 31.29, 29.48, 29.44, 29.18, 29.14, 28.94, 28.85, 21.93, 18.75, 18.45 and 13.62 (C_{17}) ppm.

2-(10-pentadecynyl)-1,3-dioxolane 18.- A solution of **17** (500 mg, 2.1 mmol) in dry CH_2Cl_2 (8 ml) was cooled to -78°C and a stream of ozone bubbled into it. The ozonolysis reaction was followed by tlc and dimethylsulfide (0.4 ml) added upon the disappearance of **17**. The mixture was warmed to room temperature and the solvent evaporated to gave a yellow oil which was added to a solution of ethylene glycol (286 mg, 4.6 mmol) and p-toluenesulfonic acid monohydrate (38 mg ,0.2 mmol) in toluene (10 ml). The mixture was heated under reflux for 2 h in a Dean-Stark apparatus and washed with aqueous sodium bicarbonate and water, and dried. Evaporation of the solvent gave 2-(10-pentadecynyl)-1,3-dioxolane **18** (532 mg, 90%) as a yellow oil; HRMS: Found M^+ 280.240029, $C_{18}H_{32}O_2$ requires 280.240231; ν_{max} (NaCl) 2930, 2860, 1450, 1140 and 1040 cm^{-1}; δ_H 4.83(1 H, t, J 5 Hz, 2-H), 4.0.8 (4 H, m, 4-H and 5-H), 2.1 (4 H, m, 9'-H and 12'-H), 1.6 (2 H, m, 1'-H), 1.5-1.1 (18 H, m, -$(CH_2)_9$-) and 0.89 (3 H, t, J 7 Hz, 15-H) ppm; δ_C 104.6 (C_2), 80.14 (C_{10} or C_{11}), 80.11 (C_{11} or C_{10}), 64.8 (C_4 and C_5), 33.8, 31.2, 29.5, 29.3, 29.3, 29.1, 28.8, 24.0, 21.9, 18.7, 18.4 and 13.6 (C_{15}) ppm.

(*Z*)-2(10-pentadecenyl)-1,3-dioxolane 19.- A mixture of Lindlar catalyst (1.8 mg), quinoline (0.02 ml) and acetylene **18** (100 mg, 0.36 mmol) in hexane (2 ml) was stirred under hydrogen at 1 atm for 1 h. The mixture was poured into a flash chromatography column and washed with hexane-ethyl ether (24:1). Evaporation of the solvent yielded (*Z*)-2-(10-pentadecenyl)-1,3-dioxolane **19** (74 mg, 72%) as a yellow oil (Lit.[5]); ν_{max} (NaCl) 2920, 1460 and 1030 cm^{-1}; δ_H 5.3 (2 H, m, 10-H and 11-H), 4.8 (1 H, t, J Hz, 2-H), 4-3.8 (4 H, m, 4-H and 5-H), 2.0 (4 H, m, 9-H and 12-H), 1.7-1.2 (20 H, m, -$(CH_2)_{10}$-) and 0.9 (3 H, t, J 3.4 Hz, 15-H) ppm; δ_C 129.87 (C_{10} or C_{11}), 129.82 (C_{11} or C_{10}), 104.7 (C_2), 64.8 (C_4 and C_5), 33.9, 31.9, 29.7, 29.54, 29.52, 29.49, 29.3, 27.2, 26.9, 24.1, 22.3 and 13.99 (C_{15}) ppm.

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