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Syntheses of very long chain alkanes terminating in polydeuterium-labelled end-groups and some very large single-branched alkanes including Y-shaped structures

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Abstract

Five alkanes containing very long chains have been synthesised: two deuterium-containing straight chain alkanes $C_{12}D_{25}$–$(CH_2)_m$–$CHDC_{11}H_{23}$ (**A**, $m = 144$ and **B**, $m = 192$); two Y-shaped alkanes $CH_3(CH_2)_{119}CHR(CH_2)_{117}CH_3$ [**C**, R = –$(CH_2)_{60}CH_3$ and **D**, R = –$(CH_2)_{194}CH_3$ *almost symmetrical* molecules; and one alkane with an *asymmetrically branched* methyl group attached to the long chain **E**, $CH_3(CH_2)_{191}CH(CH_3)(CH_2)_{98}CH_3$. Compound D($C_{434}H_{870}$) is the largest hydrocarbon to have been characterised in this work. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Straight and branched alkanes; Polydeuterium; Wittig reactions

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1. Introduction

There is considerable interest in relating the crystallisation processes and crystal morphologies of well defined linear long-chain alkanes to that of commercial polythene [1]; work is also proceeding with specific long-chain alkanes containing one short-chain branch almost symmetrically placed within the molecules. In a previous paper [2], we reported a viable strategy for synthesising these very long chain alkanes based on a chain-doubling procedure starting with 12-bromododecanal ethylene acetal **1** (Scheme 1). The C_{12}-bromoacetal **1** on deprotection gave the aldehyde **2** while reaction with triphenylphosphine gave the salt **3**. Formation of the ylide **4** from **3** with lithium di-*iso*-propylamide (LDA) and a Wittig reaction with **2** in tetrahydrofuran (THF) produced the first chain-doubled C_{24}-bromoacetal **5**. Repetition of this process with **5** gave the second chain-doubled product, the C_{48}-bromoacetal **8** via the bromoaldehyde **6** ($n = 1$) and the ylide acetal **7** ($n = 1$), which in turn was converted into the C_{96}- and C_{192}-bromoacetals **9** and **11**, respectively. Two deuterium-containing straight chain alkanes **A** and **B**, and some single-branched alkanes having small (CH_3–) and large branches (ie Y-shaped molecules) were required for further crystallisation studies and also infra-red, NMR and neutron diffraction work.

$$CD_3(CD_2)_{11}\text{–}(CH_2)_m\text{–}CHD(CD_2)_{10}CD_3$$

A $m = 144(C_{168})$

B $m = 192(C_{216})$.

2. Synthetic work

The starting materials for **A** and **B** were the C_{144}-bromoacetal **10**, a new material prepared via the the C_{96}-bromoaldehyde **6** ($n = 7$) and the C_{48}-ylide acetal **7** ($n = 3$) which in a more general way illustrates the versatility of the chain-extension process, and the C_{192}-bromoacetal **11**, respectively. The acetal end of each of the α,ω-bromoacetals **10** and **11** was labelled with a deuterium-containing terminus starting from 1-bromododecane-d_{25} **12** by conversion to the ylide **13** and reaction in turn with the aldehydes **14** and **15**, the products of the deprotection of the bromoacetals **10** and **11**, to give the end-capped deuterio-derivatives **16** and **17**, respectively (Scheme 2).

Model experiments using the C_{24}-bromoacetal **5** and the Grignard reagent n-$C_{12}H_{25}MgBr$ in THF in the presence of a catalytic amount of CuCN·LiCl [3,4] established the

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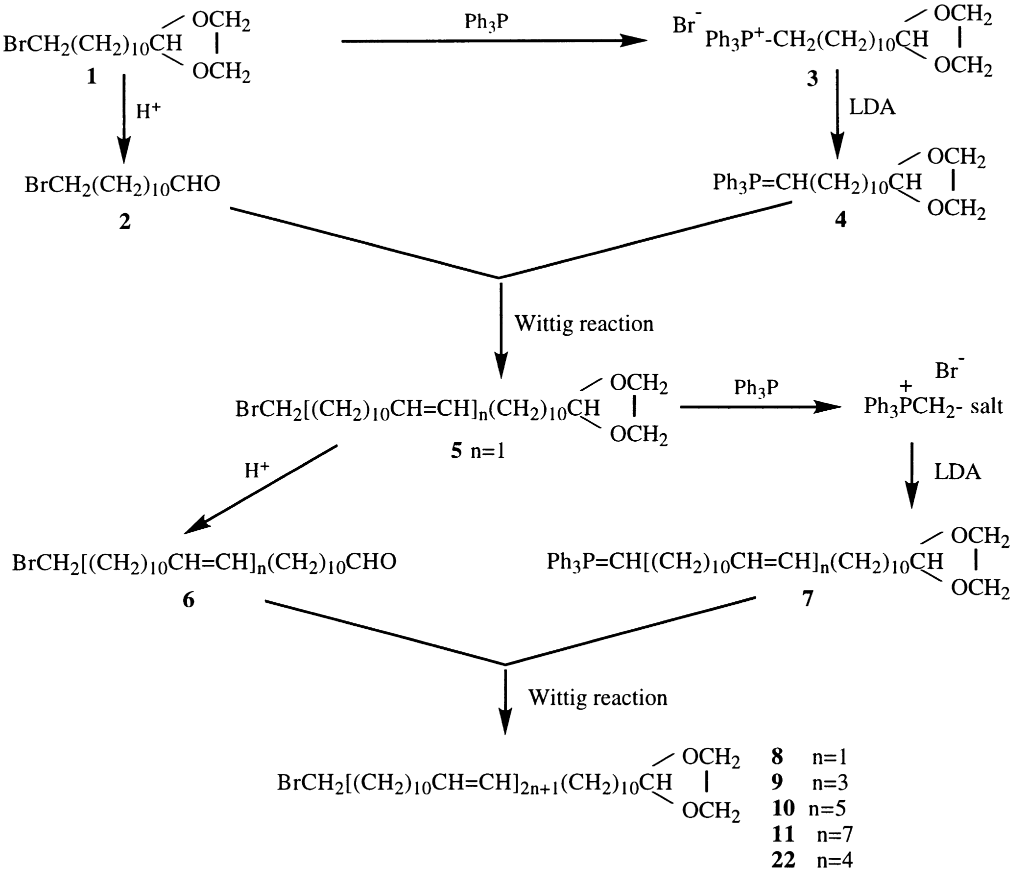
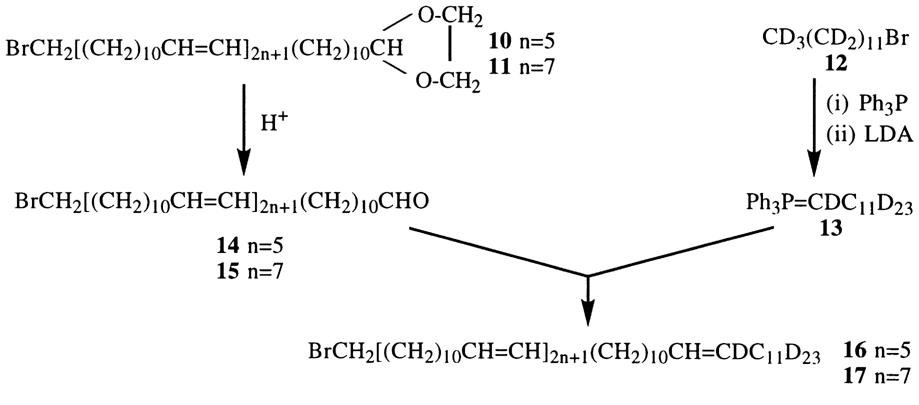


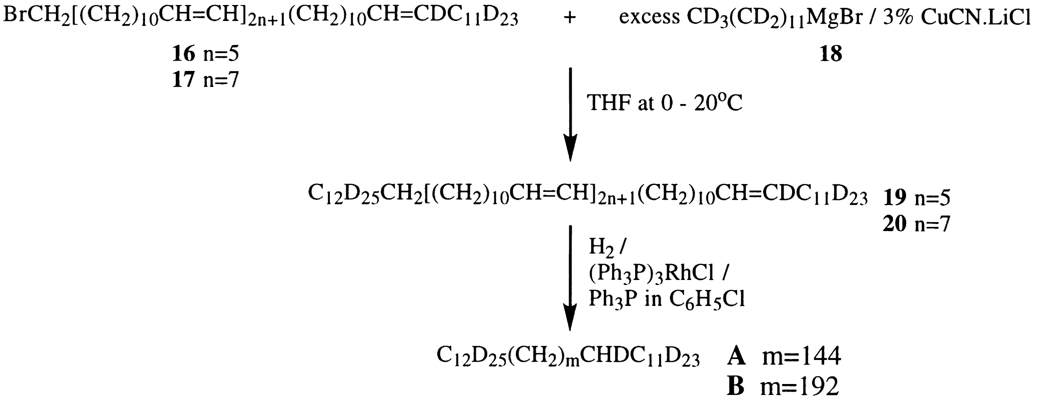
Scheme 1.

conditions required to bring about the replacement of the bromine terminus in each of the compounds **16** and **17** by the $C_{12}D_{25}$- group from $CD_3(CD_2)_{11}MgBr$ **18**, to form the polyalkenes **19** and **20**, respectively. The hydrogenation of these latter two compounds to the target molecules **A** and **B**, respectively, was carried out at 400 psi in chlorobenzene at 132°C using Wilkinson's catalyst $[(Ph_3P)_3RhCl]$ in the presence of >50-fold excess of Ph_3P [5]; this procedure successfully avoided the partial exchange of deuterium by hydrogen [6] which could have occurred under the heterogeneous conditions used previously [2] with Pt on activated carbon (Scheme 3).

In the earlier work [2], the inadvertent conversion of the C_{96}-bromoaldehyde **6** ($n = 7$) to the aldol/dehydration product **21** occurred during the halogen exchange of the C_{96}-chloroacetal to the C_{96}-bromoacetal **9** using (wet) tetra-*n*-butylammonium bromide. Deprotection of the acetal to the aldehyde **6** ($n = 7$) was believed to be due to the

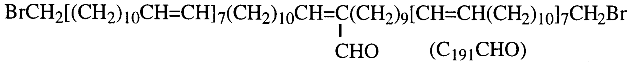


Scheme 2.



Scheme 3.

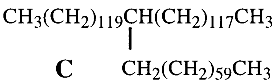
presence of traces of HBr in the wet mixture, which also catalysed the aldol condensation/dehydration reaction. Nevertheless, compound **21** enabled the pendant –CHO group to be converted, ultimately, to CH_3– and $CH_3(CH_2)_3$-containing *singly branched* alkanes, the butyl group resulting from an initial Wittig reaction with $CH_3CH_2CH{=}PPh_3$; these branches are *almost* in the centre of the molecule. Two superbranched Y-shaped alkanes were requested by the material scientists: compounds **C** and **D**. The ultimate precursor to both these materials was the C_{120}-bromoacetal **22** prepared previously [2] via the C_{96}-bromoaldehyde **6** ($n = 7$) and the C_{24}-ylide acetal **7** ($n = 1$) (Scheme 1). Replacement of Br by H in **22** to **23**, followed by deprotection to the aldehyde **24** and a *p*-toluenesulphonic acid-catalysed aldol condensation/dehydration reaction gave the $C_{120}C(CHO)C_{118}$ compound **25** (Scheme 4) capable of reaction with ylides to produce the required branched compounds.

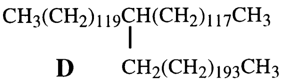

$$BrCH_2[(CH_2)_{10}CH{=}CH]_7(CH_2)_{10}CH{=}\underset{CHO}{C}(CH_2)_9[CH{=}CH(CH_2)_{10}]_7CH_2Br \quad (C_{191}CHO)$$

21

The syntheses of the precursor polyalkenes to the target compounds **C** and **D** required the reaction of C_{60}- (**26**) and C_{194}- (**27**) ylide units, respectively, with the branched aldehyde **25**. The C_{48}-bromoaldehyde **6** ($n = 3$) was capped with the C_{12}-ylide **28** and the product **29** was reacted with triphenylphosphine; the resulting salt **30**, treated with LDA, gave **26** (Scheme 5). Reaction of the C_{194}-bromo compound **31** [2] with triphenylphosphine gave the salt **32** from which the ylide **27** was prepared as before (Scheme 5).

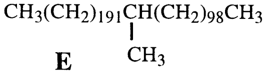
The formation of the Y-branched polyalkenes **33** and **34** by Wittig reactions of the branched α,β-unsaturated aldehyde **25** with the C_{60}-ylide **26** and with the C_{194}-ylide **27**, respectively, and their hydrogenation to the target materials **C** (C_{300}) and **D** (C_{434}), are shown in Scheme 6.


$$CH_3(CH_2)_{119}\underset{CH_2(CH_2)_{59}CH_3}{CH}(CH_2)_{117}CH_3$$


$$CH_3(CH_2)_{119}\underset{CH_2(CH_2)_{193}CH_3}{CH}(CH_2)_{117}CH_3$$

Compound **D** having 434 carbon atoms is the largest alkane yet synthesised in the current work: the $C_{390}H_{782}$ alkane is the longest straight chain alkane which has been synthesised [7,8].

A specific asymmetrically placed methyl-branched long chain alkane **E**, was required by the physicists for their investigations, the route to which is shown in Scheme 7. The synthesis started with the methyl-branched aldehyde **35** analogous to the branched α,β-unsaturated aldehydes **21** and **25** used in the syntheses above, and was prepared by refluxing the C_{192}-aldehyde **36** [9] with the stabilised ylide **37** in THF over 21 days. Reaction of the C_{98}-bromo polyene **38** [2] with triphenylphosphine gave the phosphonium bromide **39** which on treatment with LDA gave the ylide **40**. The Wittig reaction of **35** with **40** produced the methyl-branched polyene **41**, the hydrogenation of which gave the target compound **E**.


$$CH_3(CH_2)_{191}\underset{CH_3}{CH}(CH_2)_{98}CH_3$$

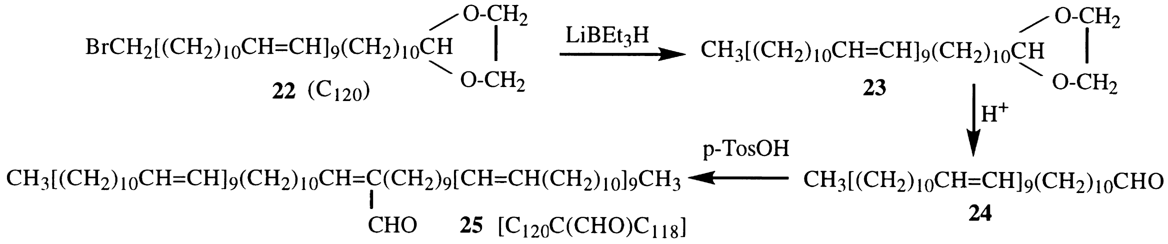
3. Experimental

^1H NMR spectra were recorded on a Bruker AMX 500 (500.139 MHz). Absorption multiplicities have been abbreviated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), b (broad). All chemical shifts are given in ppm with respect to $CHCl_3$ (7.260 ppm) present in the $CDCl_3$ used as solvent unless otherwise stated.

Silica refers to Fluorochem silica gel 60, 40–63 μm.

Analytical HPLC was performed on a Star 5065 instrument fitted with Hypersil 5 SAS 25 cm × 4.6 mm C_1 reverse phase column.

Elemental analyses were performed on an Exeter Analytical Inc CE440 elemental analyser. Compounds containing deuterium were analysed in the usual way and the results recorded for 'hydrogen' are strictly those which treated the deuterium content as hydrogen since the analysis



Scheme 4.

depends on the *number* of water molecules produced in the analyser rather than their molecular weight and so is isotope-independent; the 'theoretical' proportion of hydrogen in the compound is calculated by treating the deuterium content as hydrogen while regarding the molecule as a whole as a deuterium-containing compound. Melting points were determined on a Kofler block melting point apparatus (C. Reichert, Optische Werke AG).

All reaction solvents were dried in the appropriate manner: acetonitrile and dichloromethane (DCM) were freshly distilled from P_2O_5; THF was distilled from sodium wire/benzophenone immediately prior to use. All light petroleum solvents were distilled on a rotary evaporator prior to use.

3.1. NMR analyses

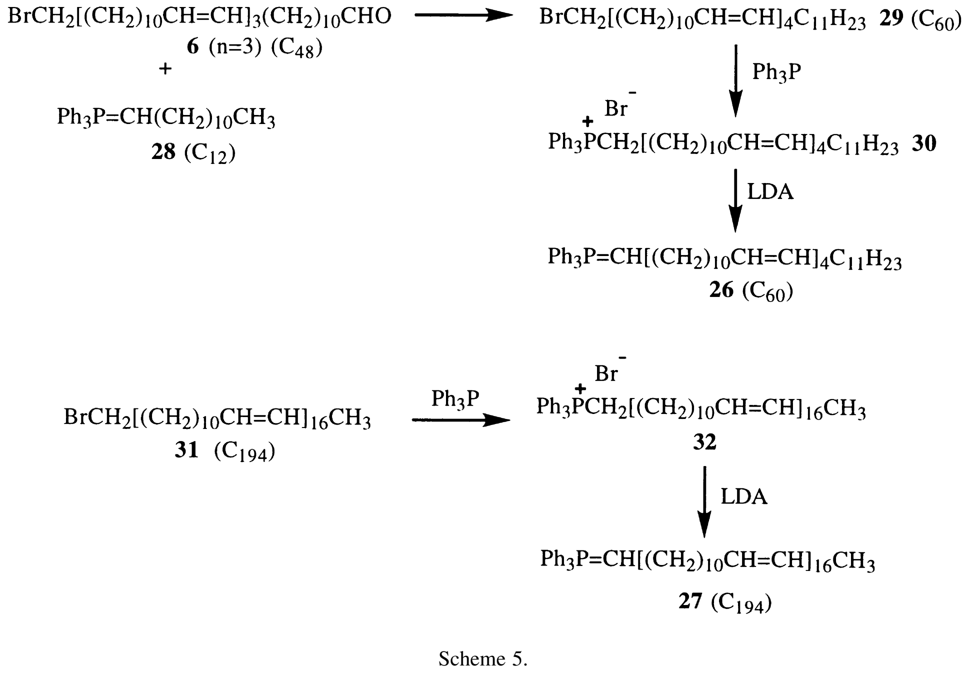
^{1}H NMR was used in the identification of all compounds. The chain length of compounds prepared in this work critically determines the ratio of the number of alkenic protons in the $-CH{=}CH$-groups relative to terminal $-CH_2Br$, $-CH_3$ or $-CH(OCH_2)_2$ (ethylene acetal) groups.

3.2. Preparative chromatography and HPLC analysis of 2,4-dinitrophenylhydrazone derivatives

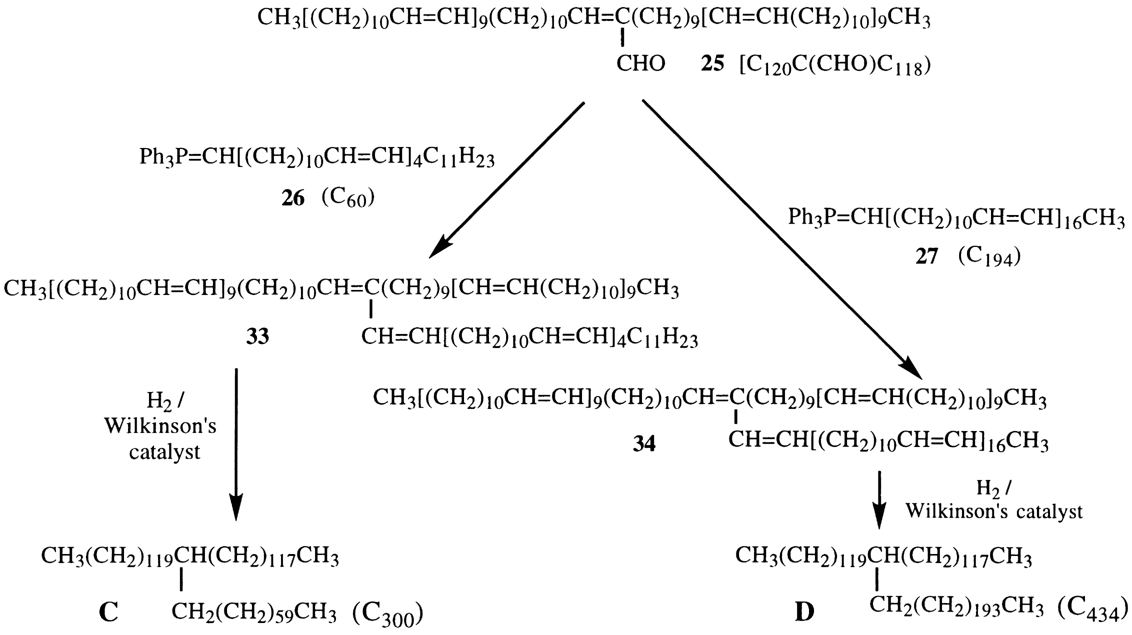
After each chain doubling or chain extension reaction, the resulting α,ω-haloacetals were separated from the *slower*-eluting precursors by preparative chromatography on silica. Nevertheless, it was vital to be able to assess the effectiveness of the separations. ^{1}H NMR analysis is not sensitive to low levels of contamination by homologous compounds, so the 2,4-dinitrophenylhydrazone (DNP) derivative of the product was prepared as before [2] and analysed by HPLC to determine the purity, since homologues of these are well separated.

3.3. Materials

Stocks of the pure C_{24}-phosphonium bromide, the precursor to the C_{24}-ylide **7** ($n = 1$), crude C_{48}-bromoacetal **8** and pure C_{48}-phosphonium bromide, precursor to the C_{48}-ylide **7** ($n = 3$), were available from previous work [2]. The C_{48}-bromoacetal **8** compound was purified as before [2] and used to prepare C_{96}- **9**, C_{120}-**22** [via **7** ($n = 1$) + **9**] and C_{192}-**11**, the purity of each acetal being checked via its DNP derivative; the C_{98}-bromopolyene **38** [2], the



Scheme 5.



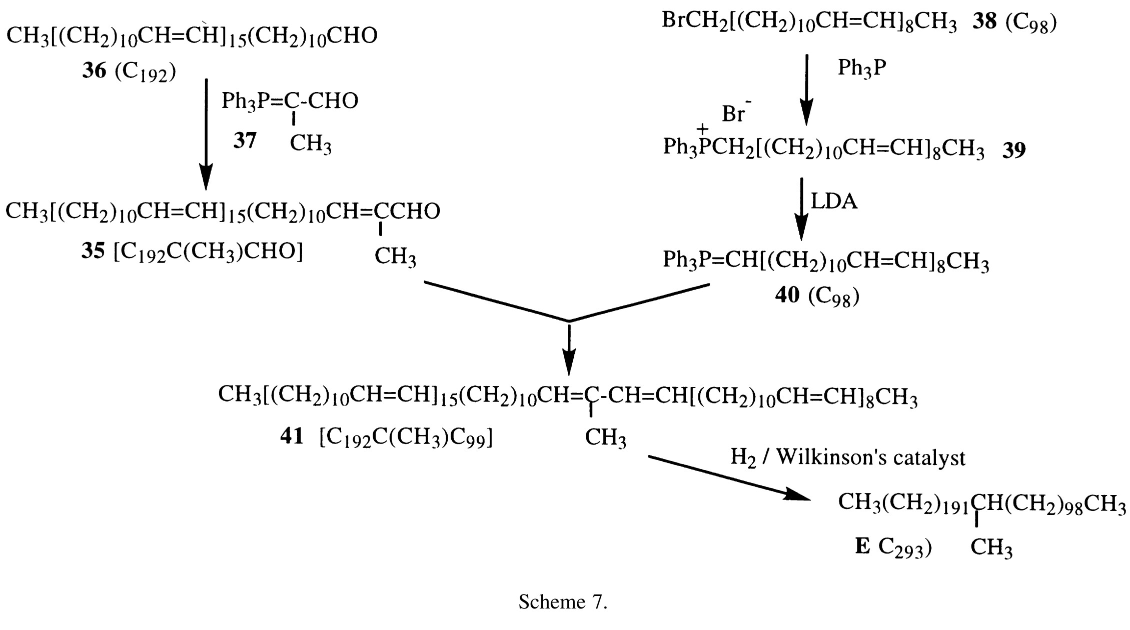
Scheme 6.

C_{192}-acetal **36** [9] and the C_{194}-bromopolyene **31** were prepared as described in the references. 1-Bromododecane-d_{25} **12** was obtained from UNIVAR PLC, Priestley Road, Basingstoke, Hants, RG24 9QB.

3.4. Replacement of bromine by hydrogen

*Cosahecta-12,24,36,48,60,72,84,96,108-nonaenal ethylene acetal **23**.* The C_{120}-bromoacetal **22** (4.85 g, 2.68 mmol) in THF (13 ml) was treated with lithium triethylborohydride in THF (1 M, 5.5 ml, 5.5 mmol) at room temperature for 4 h, worked up as described previously [2] and purified by chromatography on silica to give the C_{120}-acetal **23** (3.93 g, 85%) mp 40–42°C (Found: C, 85.05; H, 13.39. $C_{122}H_{226}O_2$ requires C, 84.94; H, 13.21%); δ_H ($CDCl_3$), 5.36 [m, 9 × (CH=CH)], 4.84 [t, $-C\mathit{H}O_2(CH_2)_2$], 3.9 [d of m, $-CHO_2(C\mathit{H}_2)_2$] and 0.88 (t, CH_3-) with intensities in the ratio 18.2: 0.97: 4.00: 3.17, respectively.

*Acid-catalysed aldol/dehydration reaction of the C_{120}-aldehyde **24** derived from the acetal **23**.* The acetal **23** (6.125 g) was deprotected by passage through a silica column (120 g) impregnated with *p*-toluenesulphonic acid (3.6 g) and water (10 ml) using light petroleum (bp 40–60°C)–DCM (75: 25% v/v) as the eluent, and the resulting



Scheme 7.

aldehyde **24** was heated under reflux with *p*-toluenesulphonic acid monohydrate (1.5 g) in THF (50 ml) for 27 days. The reaction mixture was filtered through a short silica column with light petroleum (bp 40–60°C)–diethyl ether (60: 40% v/v) and 2.5 g of the crude product (5.27 g) was chromatographed twice on silica using first light petroleum (bp 40–60°C)–diethyl ether (95: 5% v/v) then changing the same solvent system to (92: 8% v/v), to give the pure branched α,β-unsaturated $C_{239}CHO$ product *2-(octadecahecta-10,22,34,46,58,70,82,94,106-nonaenyl)-dodocosahecta-2,14,26,38,50,62,74,86,98,110-decaenal* **25** (0.865 g, 15%) mp 41.5–43°C (Found: C, 86.11; H, 13.39. $C_{240}H_{442}O$ requires C, 86.20; H, 13.32%); δ_H ($CDCl_3$) 9.36 (CHO), 6.43 ppm [t, $-CH_2C\mathit{H}{=}C(CHO$]; 5.36[m, $8\times(CH{=}CH)$] were in the ratio 0.99:1.00:38, respectively.

3.5. Phosphonium salts

Dodecyl(triphenyl)phosphonium bromide. 1-Bromododecane (3.00 g) and triphenylphosphine (7.86 g) were heated together under reflux in acetonitrile (10 ml) for 64 h, the solvent evaporated in vacuo and the residue separated by chromatography on silica using DCM–methanol (95: 5 → 90: 10% v/v) to give the solid product (6.06 g, 98%).

Dodecyl-d_{25}-(triphenyl)phosphonium bromide. 1-Bromododecane-d_{25} **12** (1.27 g) and triphenylphosphine (3.08 g) were heated together under reflux in acetonitrile (20 ml) for 67 h, and the product worked up as before to give the salt (2.48 g, 99%).

Hexaconta-12,24,36,48-tetraenyl(triphenyl)phosphonium bromide ***30***. The C_{60}-bromo compound **29** (3.733 g) (see below), triphenylphosphine (2.273 g) were heated together in acetonitrile (40 ml) over 160 h as before to give the salt **30** (4.715 g, 98%).

Octanonaconta-12,24,36,48,60,72,84,96-octaenyl(triphenyl)phosphonium bromide ***39***. The C_{98}-bromo compound **38** [2] (2.486 g), triphenylphosphine (3.505 g) and acetonitrile (35 ml) were heated together under reflux for 11 days and worked up as before to give the salt **39** (2.364 g, 80%).

Tetranonacontahecta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192-hexadecaenyl(triphenyl)phosphonium bromide ***32***. The C_{194}-bromo compound **31** [2] (0.715 g), triphenylphosphine (0.372 g), acetonitrile (30 ml) and dry toluene (5 ml) were heated under reflux for 37 days and worked up as before to give the salt **32** (0.575 g, 73%).

3.6. Wittig reactions

144-Bromotetratetracosahecta-12,24,36,48,60,72,84,96,108,120,132-undecaenal ethylene acetal ***10***. The C_{96}-bromoacetal **9** (7.6 g, 5.16 mmol) was deprotected on silica (116 g) impregnated with *p*-toluenesulphonic acid monohydrate (6.04 g) and water (10 ml) using light petroleum (bp 40–60°C)–DCM (75:25% v/v) to give the aldehyde **6** ($n = 7$). The C_{48}-(triphenyl)phosphonium bromide (8.2 g, 7.67 mmol), dissolved in THF (80 ml) and cooled to −5° with stirring, was treated with lithium di-*iso*-propylamide (LDA) in THF (1.5 M, 1.3 ml) until a faint orange-yellow colour of the ylide **7** ($n = 3$) persisted, and a further amount of LDA was added (1.5 M, 4.3 ml, 6.45 mmol). After 50 m at −5°C, the aldehyde **6** ($n = 7$) in THF (40 ml) was added to the ylide over 15 m during which the temperature was maintained at <5°C and then allowed to warm to room temperature. The mixture was washed through a short column of silica with light petroleum (bp 40–60°C)-diethyl ether (60:40 v/v) and the crude product (12.4 g) chromatographed on silica with light petroleum (bp 40–60°C)-diethyl ether (95: 5 v/v) to give the C_{144}-bromoacetal **10** (8.445 g, 76%) mp 40–41.5°C (Found: C, 81.97; H, 12.77. $C_{146}H_{269}BrO_2$ requires C, 82.07; H, 12.69%); δ_H ($CDCl_3$): 5.35 [m, $11\times-CH{=}CH-$], 4.84 [t, $-C\mathit{H}O_2(CH_2)_2$], 3.905 [m, $-O-(CH_2)_2-O-$], 3.405 [t, $-CH_2Br$] were observed in the ratio 22.6:0.97:4.00:2.00, respectively.

Hexaconta-12,24,36,48-tetraenyl bromide ***29***

The C_{48}-bromoacetal **8** (4.29 g, 5.32 mmol) was deprotected as in the previous experiment and the resulting aldehyde **6** ($n = 3$) was reacted with the ylide **28** prepared from the dodecyl-(triphenyl)phosphonium bromide (4.1 g, 8.02 mmol) and LDA (1.5 M, 4.5 ml, 6.75 mmol). The crude product (5.26 g) was worked up and purified by chromatography on silica using light petroleum (bp 40–60°C) as eluent to give the C_{60}-bromo compound **29** (3.75 g, 77%) mp 30.5–34°C (Found: C, 78.49; H, 12.67. $C_{60}H_{113}Br$ requires C, 78.81; H, 12.46%); δ_H ($CDCl_3$) 5.35 (m, $4\times-CH{=}CH-$), 3.4 (t, $-CH_2Br$ were observed in the ratio 7.95: 2.0, respectively.

143-[2-Undecyl-d_{23}-2-d_1-(ethenyl)]-triatetracontahecta-12,24,36,48,60,72,84,96,108,120,132-undecaenyl bromide ***16*** *($BrC_{143}-CH{=}CD-C_{11}D_{23}$)*. The C_{144}-bromoacetal **10** (6.63 g, 3.1 mmol) was deprotected as in the previous experiment and the resulting aldehyde **14** was reacted with the ylide **13** prepared from dodecyl-d_{25}-(triphenyl)phosphonium bromide (2.5 g, 4.65 mmol) and LDA [1.5 M, (0.3 ml) + 2.6 ml, 3.9 mmol]. The crude product (6.864 g) was worked up and purified as before to give **16** (4.7 g, 67%) mp 40–43°C (Found: C, 82.83; H, 13.07. $C_{156}H_{265}D_{24}Br$ requires C, 82.58; H, 12.84%); δ_H ($CDCl_3$) 5.35 [m, $11\times-CH{=}CH-$ + $1\times-CH{=}CD-$], 3.4 (t, $-CH_2Br$) were observed in the ratio 23.4: 2.0, respectively; δ_D ($CHCl_3$) 5.38 [bs, $1\times-CH{=}C\mathit{D}-CD_2-$], 1.96 [bs,$-CH{=}CD-C\mathit{D}_2-$], 1.20 [bs, $-(C\mathit{D}_2)_9CD_3$] and 0.82 [bs, $-(CD_2)_9C\mathit{D}_3$] were observed in the ratio 0.8: 2.0: 18.00: 3.22, respectively.

191-[2-Undecyl-d_{23}-2-d_1-(ethenyl)]-unnonacontahecta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180-pentadecaenyl bromide ***17*** *($BrC_{191}-CH{=}CD-C_{11}D_{23}$)*. The C_{192}-bromoacetal **11** (5.98 g, 2.13 mmol) was deprotected as in the previous experiment and the resulting aldehyde **15** was reacted with the ylide **13** prepared from dodecyl-d_{25}-(triphenyl)phosphonium bromide (1.782 g, 3.32 mmol) and LDA [1.5 M, (0.05 ml) + 1.85 ml, 2.77 mmol]. The crude product (6.2 g) was worked up and purified as before to give **17** (5.297 g, 85%) mp 36–40°C (Found: C, 83.63; H, 13.17. $C_{204}H_{353}D_{24}Br$ requires C, 83.50; H, 12.95%); δ_H (CDCl$_3$) 5.35 [m, 15 × –CH=CH– + 1 × –CH=CD–], 3.4 (t, –CH$_2$Br) were observed in the ratio 31.1: 2.0, respectively.

119-(Unhexaconta-1,13,25,37,49-pentaenyl)-nonatriacontadicta-12,24,36,48,60,72,84,96,108,119,131,143,155,167,179,191,203,215,227-nonadecaene ***33*** *[C$_{120}$CH(C$_{61}$)C$_{118}$].* The branched α,β-unsaturated aldehyde **25**, C$_{239}$CHO (2.227 g, 0.666 mmol) was reacted with the ylide **26** prepared from the C$_{60}$-(triphenyl)phosphonium bromide **30** (4.8 g, 4.08 mmol) amd LDA [1.5 M, (4.4 ml) + 2.17 ml, 3.26 mmol]. The crude product (2.259 g) was purified as in the previous experiment using light petroleum (bp 40–60°C) as eluent to give **33** (2.018 g, 73%) mp 33.5–34°C (Found: C, 86.40; H, 13.54. $C_{300}H_{554}$ requires C, 86.58; H, 13.42%); δ_H (CDCl$_3$) 5.92 and 5.74 (d and d part of –CH=C–CH=CH–) and 5.35 (m, 22 × –CH=CH– and remainder of –CH=C–CH=CH–), 0.88 (t, 3 × –CH$_3$) were observed in the ratio 47.3 (total alkenic H): 9.00, respectively.

121-(Octadecahecta-10,22,34,46,58,70,82,94,106-nonaenyl)-hexadecatricta-12,24,36,48,60,72,84,96,108,120,122,134,146,158,170,182,194,206,218,230,242,254,266,278,290,302,314-heptacosaene ***34*** *[C$_{120}$CH(C$_{118}$)C$_{195}$].* The branched α,β-unsaturated aldehyde **25**, C$_{239}$CHO (0.865 g, 0.259 mmol) was reacted with the C$_{194}$-ylide **27** prepared from the C$_{194}$-(triphenyl)phosphonium bromide **32** (0.575 g, 0.190 mmol) amd LDA [1.5 M, (0.20 ml) + 0.13 ml, 0.20 mmol]. The crude product was purified on five thick layer silica plates using light petroleum (bp 40–60°C)-diethyl ether (98: 2% v/v) as eluent to give **34** (0.613 g, 39%) mp 35–37°C (Found: C, 86.63; H, 13.52. $C_{434}H_{798}$ requires C, 86.63; H, 13.37%); δ_H (CDCl$_3$) 5.92 and 5.74 (d and d part of –CH=C–CH=CH–) and 5.35 (m, 34 × –CH=CH– and remainder of –CH=C–CH=CH–), 0.88 (t, 2 × –CH$_3$ but *not* including –CH=CHC*H*$_3$ which occurs at higher frequencies) were observed in the ratio 71.1: 6.00, respectively.

2-Methyl-tetranonacontahecta-2,14,26,38,50,62,74,86,98,110,122,134,146,158,170,182-hexadecaenal ***35*** *[C$_{192}$C(CH$_3$)CHO].* The C$_{192}$-aldehyde **36**, prepared by deprotection of the parent acetal [9] (2.139 g, 0.798 mmol)) was heated under reflux with the stabilised ylide **37** (2.501 g, 7.86 mmol) in THF (20 ml) for 21 days. The product was worked up as before and purified by chromatography on silica using light petroleum (bp 40–60°C)-diethyl ether (96: 4% v/v) to give the branched α,β-unsaturated aldehyde **35** (1.936 g, 90%) mp 42–44°C (Found: C, 86.17; H, 13.30. $C_{195}H_{358}O$ requires C, 86.14; H, 13.27%); δ_H (CDCl$_3$) 9.40 (s, CHO), 6.49 (t, –CH$_2$C*H*=C–CHO), 5.35 (m, 15 × –CH=CH–) were observed in the ratio 1.00: 0.97: 31.5, respectively.

100-Methyl-dononacontadicta-2,14,26,38,50,62,74,86,98,100,112,124,136,148,160,172,184,196,208,220,232,244,256,268,280-pentacosaene ***41*** *[C$_{192}$CH(CH$_3$)C$_{99}$].* The α,β-unsaturated aldehyde **35** [C$_{192}$C(CH$_3$)CHO] (1.00 g, 0.368 mmol) was reacted with the ylide **40** prepared from the C$_{98}$(triphenyl)phosphonium bromide **39** (0.814 g, 0.478 mmol) and LDA [1.5 M, (0.4 ml) + 0.204 ml, 0.31 mmol, followed by a further 0.2 ml after 24 h]. The crude product was purified by chromatography on silica using light petroleum (bp 40–60°C)-diethyl ether (98: 2% v/v) as eluent to give **41** (0.471 g, 32%) mp 36.5–37.5°C (Found: C, 86.42; H, 13.50. $C_{293}H_{538}$ requires C, 86.65; H, 13.35%); δ_H (CDCl$_3$) 6.05 and 5.79 (d and d part of –CH=C–CH=CH–) and 5.35 (m, 23 × –CH=CH– and remainder of –CH=C–CH=CH–) 0.88 (t, 1 × –CH$_3$ but *not* including *two* –CH=CC*H*$_3$ which occur at higher frequencies) were observed in the ratio 47.8 (*all* alkenic –CH=): 3.00, respectively.

3.7. Alkylation reactions of terminal –CH$_2$Br with CD$_3$(CD$_2$)$_{11}$MgBr/3% CuCN·LiCl

(i) Formation of 1-(Undecyl-d$_{23}$)-145-(dodecyl-d$_{25}$)-1-d$_1$-pentatetracontahecta-1,13,25,37,49,61,73,85,97,109,121,133-dodecaene ***19*** *(C$_{12}$D$_{25}$–C$_{144}$=CDC$_{11}$D$_{23}$).* 1-Bromododecane-*d*$_{25}$ **12** (1.602 g, 5.847 mmol) in THF (7 ml) was added to magnesium turnings (0.47 g, 19.33 mmol) in THF (6 ml) under argon at room temperature over 15 m. The exothermic reaction was maintained at <34°C by external cooling, the mixture was stirred at room temperature for 3.5 h, and filtered under argon using a canular tipped with a Whatman glass microfibre GF A filter. The solution was cooled to 1°C, treated with a standard solution of CuCN and LiCl in THF (0.878 M in CuCN, 200 μl, 0.176 mmol) [made from CuCN (1.10 g, 12.29 mmol), LiCl (0.534 g, 12.59 mmol) in THF (14 ml)] for 1.3 h at 0–5°C to give **18**, and the BrC$_{143}$–CH=CD–C$_{11}$D$_{23}$ compound **16** (2.48 g, 1.09 mmol) in THF (14 ml) was added over 15 m, the temperature being kept at <5°C. The mixture was allowed to warm to room temperature overnight and was filtered through silica using light petroleum (bp 40–60°C)-diethyl ether (60:40% v/v) as solvent. The ^{1}H NMR of the crude product showed the presence of 7% of unreacted starting material **16** which was removed as the quaternary ammonium bromide by heating at 115°C with piperidine (5 ml) under argon for 17 h by chromatography on silica using light petroleum (bp 40–60°C)-diethyl ether (92: 8% v/v) as eluent to give the pure polyalkene **19** (2.146 g, 82%) mp 39–41.5°C (Found: C, 84.96; H, 13.67. $C_{168}H_{265}D_{49}$ requires C, 84.65; H, 13.28%); δ_H (CDCl$_3$) 5.35 [m, 11 × –CH=CH– + 1 × –CH=CD–]; δ_D (CHCl$_3$) 5.38 [bs, 1 × –CH=C*D*–CD$_2$–], 1.96 [bs, –CH=CD–C*D*$_2$–], 1.20 [bs, –(C*D*$_2$)$_9$CD$_3$ and –(C*D*$_2$)$_{11}$CD$_3$] and 0.83 [bs, –(CD$_2$)$_9$C*D*$_3$ and –(CD$_2$)$_9$C*D*$_3$] were observed in the ratio 0.9: 2.16: 40.00: 6.57, respectively.

(ii) Formation of 1-(Undecyl-d$_{23}$)-193-(dodecyl-d$_{25}$)-1-d$_1$-trianonacontahecta-1,13,25,37,49,61,73,85,97,109,121,133,

145,157,169,181-hexadecaene **20** *($C_{12}D_{25}–C_{192}{=}CDC_{11}D_{23}$).* The Grignard reagent from 1-bromododecane-d_{25} **12** (1.305 g, 4.76 mmol) was treated with the solution of CuCN·LiCl in THF (0.878 M in CuCN, 160 μl, 0.140 mmol) and the mixture **18** reacted with the $BrC_{191}–CH{=}CD–C_{11}D_{23}$ compound **17** ((2.656 g, 0.905 mmol). Isolation of the product as in the previous experiment gave **20** (1.467 g, 53%) mp 39–43°C (Found: C, 85.37; H, 13.70. $C_{216}H_{353}D_{49}$ requires C, 85.09; H, 13.29%); δ_H ($CDCl_3$) 5.35 [m, 11 × –CH=CH– + 1 × –CH=CD–]; δ_D ($CHCl_3$) 5.4 [bs, 1 × –CH=C*D*–CD_2–], 1.96 [bs, –CH=CD–CD_2–], 1.19 [bs, –$(CD_2)_9CD_3$ and –$(CD_2)_{11}CD_3$] and 0.83 [bs, –$(CD_2)_9CD_3$ and –$(CD_2)_9CD_3$] were observed in the ratio 0.95: 2.31: 40.00: 6.79, respectively.

3.8. Hydrogenation reactions of polyenes

(i) Formation of $C_{12}D_{25}(CH_2)_{144}CHDC_{11}D_{23}$ ***A***. The C_{168}-polyene **19** (2.094 g), triphenylphosphine (6.06 g, 23.1 mmol), Wilkinson's catalyst, $[(C_6H_5)_3P]_3RhCl$ (0.368 g, 0.398 mmol) and chlorobenzene (15 ml) were sealed in a stainless steel autoclave (capacity 86 ml) with hydrogen at 400 psi and heated with rocking at 133°C for 48 h. The apparatus was cooled to room temperature and the contents filtered using chlorobenzene as solvent. The filtered solid was washed with light petroleum (bp 40–60°C), placed in a cellulose extraction thimble and extracted with boiling light petroleum (bp 120–160°C) (150 ml) in an apparatus which allowed the hot vapours to heat the thimble through which was passing condensed solvent vapours. After cooling the extract slowly to room temperature, the white solid was filtered, washed with light petroleum (bp 40–60°C), and finally heated at 110°C and 0.01 mm Hg overnight to give the *octahexacontahectane-d_{49}* **A** (2.03 g, 95%) mp 114–116°C (Found: C, 84.05; H, 14.55. $C_{168}H_{289}D_{49}$ requires C, 83.80; H, 14.15%); δ_H ($CDCl_2CDCl_2$ at 120°C) showed a solvent resonance at 5.85, *no* alkene resonances, and –CH_2– resonances at 1.21.

(ii) Formation of $C_{12}D_{25}(CH_2)_{192}CHDC_{11}D_{23}$ ***B***. The C_{216}-polyene **20** (1.447 g) was hydrogenated as in (**i**) to give the *hexadecadictane-d_{49}* **B** (1.171 g, 80%) mp 114–115°C (Found: C, 84.19; H, 14.48. $C_{216}H_{385}D_{49}$ requires C, 84.20; H, 14.20%); δ_H ($CDCl_2CDCl_2$ at 120°C) showed a solvent resonance at 5.99, *no* alkene resonances, and –CH_2– resonances at 1.35.

(iii) Formation of $CH_3(CH_2)_{119}–CH[(CH_2)_{60}CH_3]–(CH_2)_{117}CH_3$ ***C***. The C_{300}- polyene **33** (1.985 g) was hydrogenated as in (i) to give *119-henhexacontyl-nonatriacontadictane* **C** (1.714 g, 85%) mp 112–112.5°C (Found: C, 85.51; H, 14.52. $C_{300}H_{602}$ requires C, 85.59; H, 14.41%); δ_H ($CDCl_2CDCl_2$ at 120°C) 5.99 (solvent), *no* alkene resonances, 1.35 [$(CH_2)_{296}$ and one CH] and 0.96 (t, 3 × CH_3), the latter two being in the ratio 594: 9.

(iv) Formation of $CH_3(CH_2)_{119}–CH[(CH_2)_{117}CH_3]–(CH_2)_{194}CH_3$ ***D***. The C_{434}- polyene **34** (0.613 g) was hydrogenated as in (i) to give *196-octadecahectyl-hexadecatrictane* **D** (0.512 g, 82%) mp 122–123°C (Found: C, 85.61; H, 14.53. $C_{434}H_{870}$ requires C, 85.60; H, 14.40%); δ_H ($CDCl_2CDCl_2$ at 120°C) 5.99 (solvent), *no* alkene resonances, 1.35 [$(CH_2)_{430}$ and one CH] and 0.96 (t, 3 × CH_3), the latter two being in the ratio 885: 9.

(v) Formation of $CH_3(CH_2)_{191}–CH(CH_3)–(CH_2)_{98}CH_3$ ***E***. The C_{293}- polyene **41** (1.242 g) was hydrogenated as in (**i**) to give *100-methyl-dononacontadictane* **E** (1.018 g, 81%) mp 120–122°C (Found: C, 85.57; H, 14.54. $C_{293}H_{588}$ requires C, 85.59; H, 14.41%); δ_H ($CDCl_2CDCl_2$ at 120°C) 5.99 (solvent), *no* alkene resonances, 1.35 [$(CH_2)_{289}$ and one CH] and 0.96 (overlapping t, 3 × CH_3), the latter two being in the ratio 581: 9.

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