PERKIN 1

A versatile process for the syntheses of very long chain alkanes, functionalised derivatives and some branched chain hydrocarbons

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An earlier method for synthesising very long straight-chain alkanes of very specific lengths has been improved to give, in some cases, gram amounts of materials. Eleven compounds have been made: $C_{98}H_{198}$, $C_{122}H_{246}$, $C_{162}H_{326}$, $C_{194}H_{390}$, $C_{198}H_{398}$, $C_{210}H_{422}$, $C_{242}H_{486}$, $C_{246}H_{494}$, $C_{258}H_{518}$, $C_{294}H_{590}$ and $C_{390}H_{782}$. The self-condensation reaction of one of the intermediate aldehydes enabled two chain-branched hydrocarbons to be obtained: $C_{96}H_{193}CHRC_{94}H_{189}$ where R = CH_3 and $CH_3(CH_2)_3$. Three long-chain compounds containing carboxylic acid groups have been prepared: $CH_3(CH_2)_{190}CO_2H$, $HO_2C(CH_2)_{48}CO_2H$ and $HO_2C(CH_2)_{192}CO_2H$.

Considerable interest has been shown in recent years in relating the crystallisation processes and crystal morphology of well defined linear long-chain alkanes to that of commercial polyethylene.[1] These materials became available in small quantities from the research work of Wegner[2] and that of Whiting.[3] In the German work,[2] the C_{24} diyne, $HC{\equiv}C(CH_2)_{20}C{\equiv}CH$ was oxidatively coupled with copper(II) acetate to give a mixture of oligomers, $HC{\equiv}C(CH_2)_{20}C{\equiv}C[C{\equiv}C(CH_2)_{20}C{\equiv}C]_nH$ (n = 1–16), which were carefully separated by chromatography. As the chain length increased, the separation of higher homologues became more difficult, although this could be offset by coupling the pure dimer, where $n = 1$. Catalytic hydrogenation gave linear alkanes, of which $C_{384}H_{770}$ was the longest obtained. In this procedure, chain lengths were limited to multiples of C_{24} and only hydrocarbons could be synthesised.

The basis of Whiting's procedure for the synthesis of long chain alkanes is shown in Scheme 1. The starting material was 12-bromododecanal ethylene acetal **1**, which on deprotection gave the aldehyde **3** while reaction with triphenylphosphine gave the phosphonium bromide **5**. The reaction of **3**, **5** and potassium carbonate in the presence of 18-crown-6 to generate the ylide **7** *in situ* in tetrahydrofuran (THF) gave the chain doubled C_{24} bromo acetal **8**. Repetition of the reaction sequence with **8** gave the second chain doubled product, the C_{48} bromo acetal **15**, which in turn was converted into the C_{96} bromo acetal **22** (n = 7), and then into the C_{192} bromo acetal **22** (n = 15); the C_{192} acetal **24** (n = 15) was chain doubled to the C_{384} acetal **24** (n = 31).

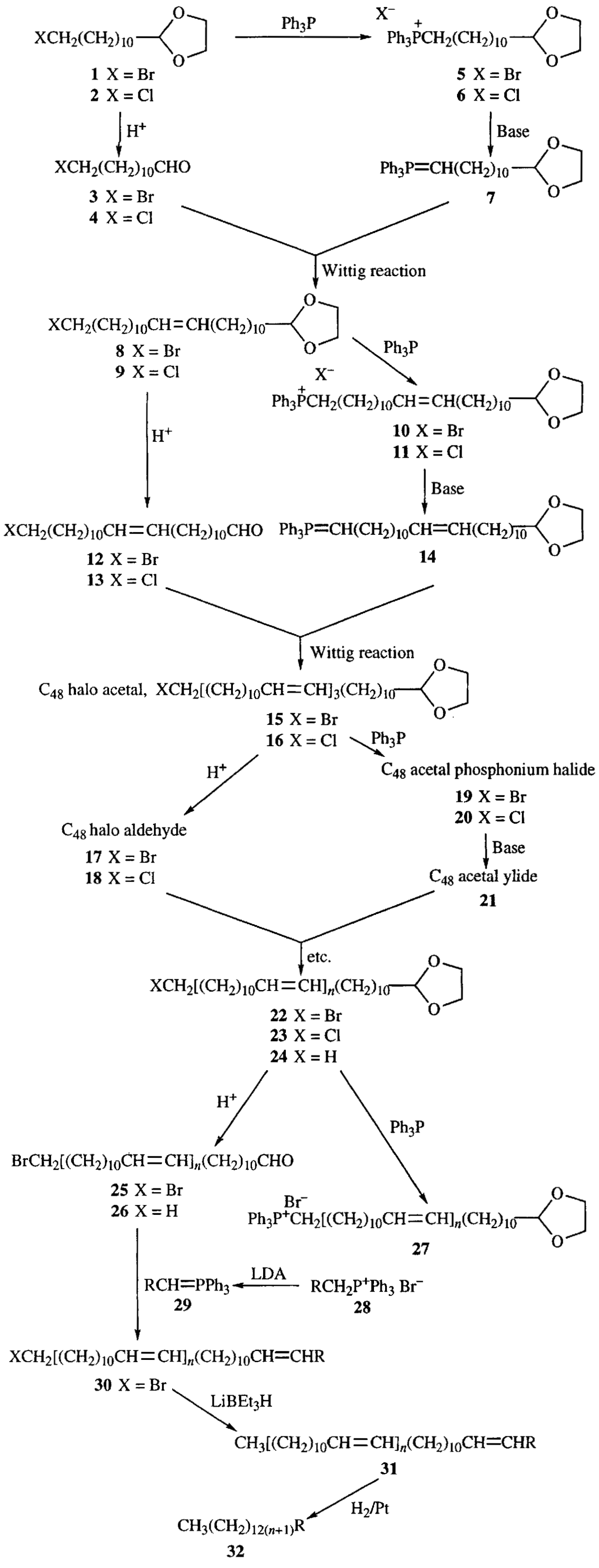
Deprotection of acetals **22** and 'capping' the resulting aldehydes **25** using a Wittig reagent **29** of any desired length, followed by replacement of bromine in **30** by hydrogen using lithium triethylborohydride (or the reverse sequence) and finally hydrogenation of the polyalkene **31**, gave the alkane **32**. The chain lengthening reaction was also carried out using moieties having different chain lengths; *e.g.* the C_{192} aldehyde **26** (n = 15) and the C_{48} acetal ylide **21** gave the C_{240} acetal **24** (n = 19), and ultimately the hydrocarbon $C_{246}H_{494}$ which showed chain-folding properties.[1]

The use of potassium carbonate for generation of the ylides *in situ* was accompanied by a side reaction in which the bromine in some of the product was replaced by carbonate as a nucleophile, producing carbonate esters. Treatment of the reaction product with $LiAlH_4$ converted carbonate to alcohol which was readily removed by chromatography. In order to maximise the efficiency of the Wittig chain coupling, however, we have investigated the use of chloro rather than bromo aldehydes in the reaction: primary chlorides are much less reactive towards nucleophiles than the corresponding bromides.

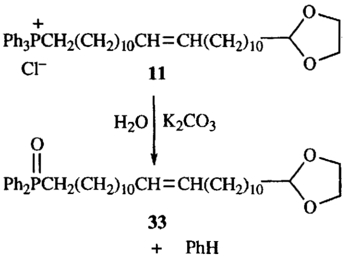
The first perceived major task in the change to 12-chlorododecanal ethylene acetal **2** as the basic starting material, however, was to react this primary chloride with triphenylphosphine to form the phosphonium chloride **6**. The C_{12} chloro acetal **2** and 4 equivalents of triphenylphosphine, when heated and stirred as a melt at 103 °C for 20 days, gave complete removal of the alkyl chloride. Following the work-up, (which included reprotection of some aldehyde which had formed in the procedure), the phosphonium chloride **6** was obtained as a hygroscopic solid (87%) accompanied by the product of hydrolysis of the salt, 12-(diphenylphosphinoyl)dodecanal ethylene acetal, and the β-elimination product, 11-dodecenal ethylene acetal.

The chain doubling reaction involving the C_{12} chloro aldehyde **4** and the C_{12} acetal phosphonium chloride **6** under Whiting's conditions gave very crude C_{24} chloro acetal **9** (86%); accumulated material was carefully distilled under controlled conditions in a short path distillation unit, enabling large quantities of the pure compound **9** to be obtained with ease. In the original work, the assessment of purity was carried out using high temperature analytical vapour phase chromatography, but it was clear that this method would not be applicable to the involatile C_{48} chloro acetal **16** and higher homologues. An HPLC analysis of the 2,4-dinitrophenylhydrazones (DNPs) of the haloaldehydes derived directly from the acetals has been developed, and represents an important advance in determining the effectiveness of the purification processes undertaken: the DNPs derived from the C_{12}, C_{24}, (and from higher homologues which were prepared later in the work) C_{36}, C_{48}, C_{72}, C_{96}, C_{144} and C_{192} haloacetals (Cl or Br), were all well resolved from each other. Potential impurities in the C_{24} chloro acetal **9** were the C_{12} chloro aldehyde **4**, and the C_{36} chloro acetal **23** (n = 2) formed *via* deprotection of **9** followed by further reaction with C_{12} acetal ylide **7**; both were shown to be absent in the distilled product.

The reaction of the C_{24} chloro acetal **9** with triphenylphosphine required 28 days to give the C_{24} acetal phosphonium chloride **11**, which was hygroscopic, and so was stored as a standard solution in anhydrous tetrahydrofuran. The reaction of the ylide **14** from this salt with the C_{24} chloro aldehyde **13** under the original conditions gave only *ca.* 1% C_{48} chloro acetal **16**, and it became clear that the use of potassium carbonate, in our hands, under long reaction times (> 200 h) brought about

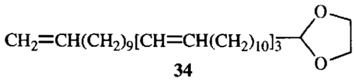


Scheme 1

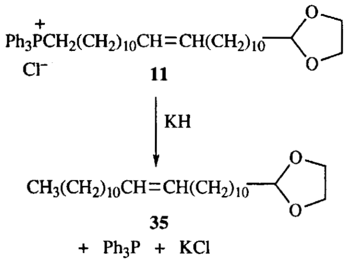


Scheme 2

self-condensation reactions of the aldehyde **13**, and also hydrolytic cleavage of benzene from the salt **11** to give the unreactive diphenylphosphinoacetal **33** (Scheme 2); water is inevitably formed in any base-catalysed reaction with potassium carbonate. These problems were overcome by pre-forming the ylide **14**, as in a conventional Wittig reaction, using potassium hydride as the base with 18-crown-6 again as the phase-transfer agent in refluxing tetrahydrofuran. The progress of the reaction was followed by ^{31}P NMR spectroscopy until no phosphonium salt remained, and then the chloroaldehyde **13** was added to the deep orange–black solution of the ylide. The yields of C_{48} chloro acetal **16** were $>80\%$, and the product was of high purity [free from **13** and C_{72} chloro acetal **23** ($n = 5$) by HPLC of DNPs]. However, two minor by-products formed from **11** by loss of Ph_3P were identified in the crude product: (a) the vinyl acetal **34** (from an elimination reaction), a compound which would present no problems in subsequent chain-doubling reactions; it would merely appear as a terminal vinyl-containing contaminant of the same overall chain length as the major chain extended product from the Wittig reaction; and (b) the terminal hydrocarbon acetal **35** formed by nucleophilic replacement by hydrogen (Scheme 3) rationalised the presence. These two processes of triphenylphosphine (detected by ^{31}P NMR) accompanying the formation of the ylide. This would cause contamination of the final products with shorter chain hydrocarbons. Removal of the C_{24} acetal **35** from the C_{48} chloro acetal **16** was achieved by a combination of sublimation at 190 °C and 0.05 mmHg, and column chromatography, but the same problem was expected to arise in subsequent chain-doubling reactions where purification using sublimation would not be applicable: only very difficult chromatography for the removal of this non-halogen containing compound could be used. Consequently, we sought to find an alternative powerful base to generate the ylide, and yet which was also non-nucleophilic. Preliminary experiments with lithium diisopropylamide (LDA) fulfilled these requirements admirably. Moreover, the ^{13}C NMR spectrum of the C_{24} chloro acetal **9** from **2** and **6** showed a high *cis* to *trans* ratio of 4:1, similar to the material prepared in the original potassium carbonate-induced Wittig reaction,[2] so that potential problems of compound solubility with higher homologues were not expected. In general, ylide formation is essentially instantaneous at −10 to −25 °C, as is the subsequent reaction with aldehydes.



34



Scheme 3

The reaction of the C_{48} chloro acetal **16** with triphenylphosphine at 100–103 °C to form the phosphonium chloride **20** was incomplete after 60 days. Consequently, half of the stock of **16**

Table 1 'Capping' reactions to form bromo polyenes and polyenes

Aldehyde	Ylide	Product
C_{96} bromo aldehyde **25** (n = 7)	C_2 ylide **29** (R = CH_3)	C_{98} bromo polyene **46**
C_{120} bromo aldehyde **25** (n = 9)	C_2 ylide **29** (R = CH_3)	C_{122} bromo polyene **47**
C_{96} bromo aldehyde **25** (n = 7)	C_{66} ylide **45**	C_{162} bromo polyene **48**
C_{192} bromo aldehyde **25** (n = 15)	C_2 ylide **29** (R = CH_3)	C_{194} bromo polyene **49**
C_{192} bromo aldehyde **25** (n = 15)	C_{18} ylide **43**	C_{210} bromo polyene **50**
C_{192} aldehyde **26** (n = 15)	C_{50} ylide **44**	C_{242} polyene **51**
C_{192} bromo aldehyde **25** (n = 15)	C_{66} ylide **45**	C_{258} bromo polyene **52**
C_{384} aldehyde **26** (n = 31)	C_6 ylide **29** (R = C_5H_{11})	C_{390} polyene **53**

$CH_3(CH_2)_4CH{=}CH(CH_2)_{10}CH_2X$
37 X = Br
38 X = $P^+Ph_3Br^-$

$CH_3[CH{=}CH(CH_2)_{10}]_4CH_2X$
39 X = Br
40 X = $P^+Ph_3Br^-$

$CH_3(CH_2)_4[CH{=}CH(CH_2)_{10}]_5CH_2X$
41 X = Br
42 X = $P^+Ph_3Br^-$

$CH_3(CH_2)_4CH{=}CH(CH_2)_{10}CH{=}PPh_3$
43

$CH_3[CH{=}CH(CH_2)_{10}]_4CH{=}PPh_3$
44

$CH_3(CH_2)_4[CH{=}CH(CH_2)_{10}]_5CH{=}PPh_3$
45

which had been prepared was converted into the C_{48} bromo acetal **15** using tetrabutylammonium bromide in 1-bromopropane,[3] for reaction with triphenylphosphine in acetonitrile, which with the addition of 2,2-dimethyl-1,3-dioxolane, formed the phosphonium bromide **19** unaccompanied by any deprotected acetal, in only 3.5 days. Unlike the chlorides **6** and **11**, the phosphonium bromides **5**, **10**, **19** and, subsequently, all the bromides were non-hygroscopic, and so presented no difficulties in handling.

The C_{96} chloro acetal **23** (n = 7) was prepared in 77% yield from the C_{48} chloro aldehyde **18** and the C_{48} acetal ylide **21** generated from bromide **19** and LDA. All of this material was subjected to the trans-halogenation reaction with tetrabutylammonium bromide to give the C_{96} bromo acetal **22** (n = 7) so that future reactions could be carried out using bromo compounds only, as in the original Whiting procedure.[3] The reaction did not proceed as expected, due to contamination of the solvent/reagent by water, and faulty technique. The product consisted of the C_{96} bromo aldehyde **25** (n = 7) (3 parts) and the self-condensation product of this compound **36** (2 parts), readily identified by ^1H NMR spectroscopy. Closer inspection of the spectra of both of these materials showed that *ca.* 25% contained the equivalent of the addition of one molecule of HBr to one C=C bond in the C_{96} chain to form CHBr. The mixture was subjected to reprotection of the aldehyde functions with ethylene glycol–toluene-*p*-sulfonic acid: only the saturated aldehyde **25** (n = 7) reacted. The bromo acetal **22** (n = 7) was separated from the α,β-unsaturated aldehyde **36** by chromatography for subsequent reactions. Triphenylphosphine reacted exclusively with the primary alkyl bromide group of **22** (n = 7) to give the C_{96} phosphonium bromide **27** (n = 7): a model experiment of triphenylphosphine with the secondary bromide 6-bromododecane occurred very slowly, and the characteristic shift of the $CH{-}P^+Ph_3$ was absent from **27** (n = 7), so no branched chain impurities could be introduced subsequently.

$BrCH_2[(CH_2)_{10}CH{=}CH]_7(CH_2)_{10}$
$CH{=}C(CHO)(CH_2)_9[CH{=}CH(CH_2)_{10}]_7CH_2Br$
36

The chain doubled compound, the C_{192} bromo acetal **22** (n = 15) was formed in 77% yield from the C_{96} bromo aldehyde **25** (n = 7) and the ylide derived from the C_{96} acetal phosphonium bromide **27** (n = 7). The bromo acetal **22** (n = 15) was deprotected and the resulting bromo aldehyde **25** (n = 15) was 'capped' with the C_6 unit **29** (R = C_5H_{11}). Treatment of the C_{198} bromo polyene **30** (n = 15, R = C_5H_{11}) with lithium triethylborohydride gave the C_{198} polyene **31** (n = 15, R = C_5H_{11}) still containing the secondary bromide functionality: this was removed by dehydrobromination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and the product hydrogenated to give the known hydrocarbon[3] $C_{198}H_{398}$ **32** (n = 15, R = C_5H_{11}), in much larger quantities.

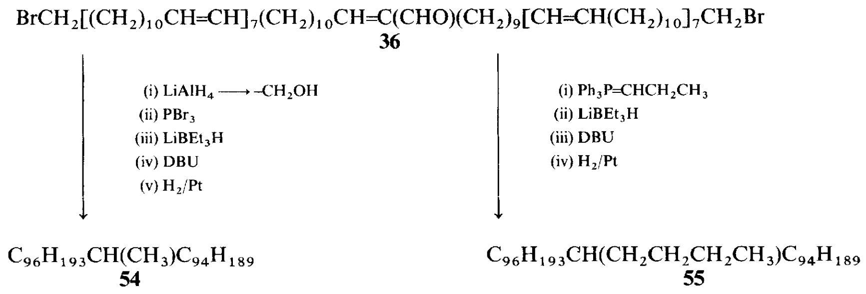
The C_{192} bromo aldehyde **25** (n = 15) underwent Wittig reactions with the C_{48} acetal ylide **21** and with the ylide from the C_{96} acetal phosphonium bromide **27** (n = 7) to give the C_{240} bromo acetal **22** (n = 19) and the C_{288} bromo acetal **22** (n = 23), respectively. Both in turn were 'C_6-capped', hydrodebrominated, dehydrobrominated and hydrogenated as before to give the hydrocarbons[3] $C_{246}H_{494}$ **32** (n = 19, R = C_5H_{11}) and $C_{294}H_{590}$ **32** (n = 23, C_5H_{11}), respectively.

The work described above was carried out starting with 12-chlorododecanal ethylene acetal **2** derived from 1 kg of 12-chlorododecanol *via* a Swern oxidation to the aldehyde **4** which was then converted to the stable 12-chlorododecanal acetal **2**;[3] on standing at room temperature, the aldehyde **4** began to trimerise within 24 h, so it was always used as quickly as possible in Wittig reactions. New work was started with **2** derived from 3 kg of 12-chlorododecanol. It was first converted to 12-bromododecanal ethylene acetal **1** by the trans-halogenation reaction,[3] and then chain extension reactions were carried out to give C_{24}, C_{36}, C_{48}, C_{96} and C_{192} bromo acetals as before, while reaction of the C_{96} bromo aldehyde **25** (n = 7) with the C_{24} acetal ylide **14** gave the C_{120} bromo acetal **22** (n = 9). The C_{384} acetal[3] **24** (n = 31) was formed from the C_{192} aldehyde **26** (n = 15) and the ylide from the C_{192} acetal phosphonium bromide **27** (n = 15).

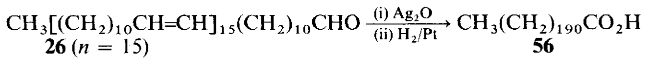
Three new primary bromides were prepared for incorporation into 'capping' agent precursors: (a) the C_{18} bromo compound **37** from the C_{12} bromo aldehyde **3** and the C_6 ylide **29** (R = C_5H_{11}); with triphenylphosphine it gave the C_{18} phosphonium bromide **38**, *i.e.* **28** [R = $CH_3(CH_2)_4CH{=}CH(CH_2)_{10}$]; (b) the C_{50} bromo compound **39** from the C_{48} bromo aldehyde **17** and the C_2 ylide **29** (R = CH_3); it was converted into the C_{50} phosphonium bromide **40**, *i.e.* **28** {R = $CH_3[CH{=}CH(CH_2)_{10}]_4$} with triphenylphosphine; and (c) the C_{66} bromo compound **41** from the C_{48} bromo aldehyde **17** and the C_{18} ylide from **38**; it gave the C_{66} phosphonium bromide **42**, *i.e.* **28** {R = $CH_3(CH_2)_4[CH{=}CH(CH_2)_{10}]_5$} with triphenylphosphine. The three new 'capping' agents **43**, **44** and **45**, and their use, are given in Table 1.

Bromopolyenes were converted to polyenes with lithium triethylborohydride, and the resulting polyenes hydrogenated. Seven new straight chain hydrocarbons were obtained: $C_{98}H_{198}$, $C_{122}H_{246}$, $C_{162}H_{326}$, $C_{194}H_{390}$, $C_{210}H_{422}$, $C_{242}H_{486}$ and $C_{258}H_{518}$ as they were required for the physical study of phase changes;[4] $C_{390}H_{782}$ (12 mg) had been prepared earlier.[3]

Two branched chain hydrocarbons $C_{96}H_{193}CH(CH_3)C_{94}H_{189}$ **54** and $C_{96}H_{193}CH(CH_2CH_2CH_2CH_3)C_{94}H_{189}$ **55** were prepared from the branched C_{192} dibromo α,β-unsaturated aldehyde **36**, as shown in Scheme 4. Although

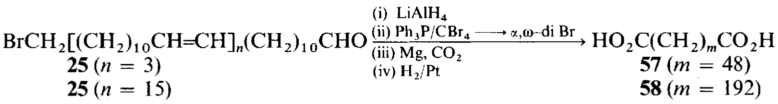


Scheme 4



$$\underset{\mathbf{26}\ (n\,=\,15)}{CH_3[(CH_2)_{10}CH{=}CH]_{15}(CH_2)_{10}CHO} \xrightarrow[\text{(ii) } H_2/Pt]{\text{(i) } Ag_2O} \underset{\mathbf{56}}{CH_3(CH_2)_{190}CO_2H}$$

Scheme 5



$$\underset{\substack{\mathbf{25}\ (n\,=\,3)\\ \mathbf{25}\ (n\,=\,15)}}{BrCH_2[(CH_2)_{10}CH{=}CH]_n(CH_2)_{10}CHO} \xrightarrow[\substack{\text{(iii) Mg, } CO_2\\ \text{(iv) } H_2/Pt}]{\substack{\text{(i) } LiAlH_4\\ \text{(ii) } Ph_3P/CBr_4 \longrightarrow \alpha,\omega\text{-di Br}}} \underset{\substack{\mathbf{57}\ (m\,=\,48)\\ \mathbf{58}\ (m\,=\,192)}}{HO_2C(CH_2)_mCO_2H}$$

Scheme 6

the unsaturated aldehyde was prepared serendipitously, this condensation reaction should be general for the synthesis of singly-branched long chain alkanes.

Finally, the versatility of the procedures described in this paper is illustrated by the possibility of being able to convert the α-bromine and the ω-acetal groups in the α,ω-bromoacetals **22** into other functionalities. Thus, we have synthesised the very long chain monocarboxylic acid $CH_3(CH_2)_{190}CO_2H$ **56** by the route shown in Scheme 5. Two dicarboxylic acids have also been prepared: $HO_2C(CH_2)_{48}CO_2H$ **57** and $HO_2C(CH_2)_{192}CO_2H$ **58** (Scheme 6).

Experimental

NMR spectra were recorded on the following instruments at the frequencies listed: a Varian VXR 400S [^1H (399.952 MHz), ^{13}C (100.582 MHz)], and a Bruker AMX 500 [^1H (500.139 MHz)]. Absorption multiplicities have been abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quintet) and m (multiplet). All chemical shifts are given in ppm with respect to TMS, present in $CDCl_3$ used as solvent. Silica refers to Merck silica gel F60 (230–400 mesh). 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. Melting points were determined on a Gallenkamp melting point apparatus, unless otherwise stated. Purification of C_{12} and C_{24} materials was carried out by short path distillation as described, using a short path distillation unit (KDL-1), manufactured by U.I.C. GmbH Alzenau, Germany. All reaction solvents were dried in the appropriate manner: acetonitrile and dichloromethane were freshly distilled from P_2O_5; THF was distilled from $LiAlH_4$ and NaH immediately prior to use. All light petroleum solvents were distilled on a rotary evaporator prior to use. The fraction distilling in the range 40–60 °C was used unless otherwise stated. 'Ether' refers to diethyl ether.

NMR analyses

^1H NMR was used in the identification of all compounds. After each chain doubling or chain extension reaction, the $-CH{=}CH-$ to $-CH(OCH_2)_2$ (ethylene acetal group) ratio increases. This ratio was used to identify a material's chain length, although accurate measurement became more difficult as the number of carbon–carbon double bonds increased. Due to the difficulty in removing the last traces of light petroleum from some products, measurement of the intensity of the $-CH_2-$ signal in the hydrocarbon chain proved less accurate. Integral measurements for the final alkanes also proved to be inaccurate, due to difficulties in shimming the spectrometer at 120 °C so no reliable ratio was achieved between the $-CH_3$ end groups and the internal $-CH_2-$ groups; the ^1H NMR could only be used to demonstrate the absence of carbon–carbon double bonds.

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. ^1H 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 and analysed by HPLC to determine the purity, since homologues of these were well separated.

The following method was used to prepare all DNP derivatives. The bromoacetal (0.1 g) was stirred with 2,4-dinitrophenylhydrazine (0.2 g) and concentrated sulfuric acid (0.5 ml) in butyl alcohol (10 ml) for 16 h at 45 °C. On cooling to room temperature, the orange DNP derivative precipitated, which was filtered, washed with methanol and dried.

Materials

12-Chlorododecanol (4 kg) was synthesised and supplied by High Force Research Ltd., Unit 1D, Mountjoy Research Centre, Stockton Road, Durham City, DH1 3SW, using the published route.[3,5] 12-Chlorododecanal ethylene acetal **2** was prepared in 83% overall yield by the Swern oxidation of the 12-chloro alcohol in 200 g batches followed by acetalisation and short path distillation at 85 °C and 4 × 10^{-2} mbar.[3] 12-Bromododecanal ethylene acetal **1** was prepared from the chloroacetal **2** by refluxing with tetrabutylammonium bromide in 1-bromopropane which had been dried beforehand by heating under reflux in a Soxhlet unit containing molecular sieves (4 Å).[4] After 42 h, ^1H NMR showed 9% of unreacted **2**, and 15% of aldehyde present. Reprotection of the aldehyde with ethylene glycol/toluene-*p*-sulfonic acid and a further transhalogenation reaction gave complete conversion of **2**, but again, reprotection of aldehyde had to be carried out (the addition of 2,2-dimethyl-1,3-dioxolane would prevent deprotection from occurring). Pure 12-bromododecanal ethylene acetal **1** was obtained by short path distillation at 80 °C and 6 × 10^{-3} mbar.

C_{12} Phosphonium salts

11-(Dioxolan-2-yl)undecyl(triphenyl)phosphonium chloride (the C_{12} acetal phosphonium chloride) 6. The 12-chloro acetal **2** (200 g) and triphenylphosphine (800 g) were heated at 102.5–103.5 °C and the melt stirred for 20 d. Acetonitrile (700 ml) was slowly added to the hot mixture, and when the solution had cooled to *ca.* 45 °C, light petroleum and acetonitrile were used to transfer the mixture to a separating funnel. The acetonitrile layer was washed with light petroleum (16 × 100 ml) and the combined petrol extracts were re-extracted with acetonitrile (4 × 50 ml). Removal of the solvent *in vacuo* from the combined acetonitrile extracts gave the crude phosphonium salt (456 g), the ^1H NMR of which showed the presence of deprotected acetal (13%). Reprotection of the aldehyde was carried out by heating a mixture of the crude salt, ethylene glycol (60 ml), toluene-*p*-sulfonic acid (3.1 g) and dichloromethane (600 ml) at reflux temperature overnight. The reaction mixture was cooled to room temperature, washed with dilute aqueous potassium carbonate (2 × 1 l containing 3 g of the base), followed by water (2 × 1.5 l); in the latter case, it was necessary to add a trace of potassium carbonate after each wash to break up the emulsion which formed. The organic phase was dried (Na_2SO_4), and the solvent removed *in vacuo*. Dry ether (1 l) was added to the viscous liquid which was stirred vigorously; the mixture was heated to boiling and left to cool overnight. The upper layer was decanted and replaced by more ether (1 l) and the procedure repeated again. This was carried out four more times. After the final decantation, there remained a white solid which was dried under high vacuum to give the *C_{12} acetal triphenylphosphonium chloride* **6** (351 g, 87%), a hygroscopic material, identified by comparison of its ^1H NMR spectrum with that of the authentic C_{12} acetal phosphonium bromide. Examination of the ether washings by ^1H NMR spectroscopy showed the presence of 12-diphenylphosphinoyldodecanal ethylene acetal. Evaporation of the petrol extracts, which removed the triphenylphosphine, and careful sublimation of the residue at 35 °C, gave 11-dodecenal ethylene acetal; δ_H 5.80 (m, H_a), 4.88 (d, H_c) and 4.87 (s, H_b) in $H_bH_{c,trans}$ C=$CH_{a,trans}$.

11-(Dioxolan-2-yl)undecyl(triphenyl)phosphonium bromide[3] (the C_{12} acetal phosphonium bromide) 5. Compound **5** was prepared from 12-bromododecanal ethylene acetal **1** triphenylphosphine (1.1 equiv.) and 2,2-dimethyl-1,3-dioxolane (0.1 equiv.) in anhydrous acetonitrile at reflux temperature for 72 h under nitrogen and worked up as before.

Wittig reactions using aldehydes, phosphonium salts and K_2CO_3/18-crown-6 *in situ*

24-Chlorotetracos-12-enal ethylene acetal[3] (the C_{24} chloro acetal) 9. This compound was prepared as before, using the C_{12} phosphonium chloride rather than the bromide salt. Purification of the C_{24} chloro acetal was accomplished by four passes through the short path distillation unit, two at 105 and one at 115 °C, 1 × 10^{-2} mbar, to remove C_{12} components, and once at 140 °C, at 1 × 10^{-2} mbar, to distil the C_{24} chloro acetal from longer chain compounds, principally the C_{36} chloro acetal. HPLC analysis of the product (70% THF, 30% water), showed that it was exclusively the C_{24} chloro acetal, the ^1H NMR spectrum of which was identical with that of an authentic sample.

23-(Dioxolan-2-yl)tricos-12-enyl(triphenyl)phosphonium chloride (the C_{24} acetal phosphonium chloride) 11. Compound **11** was prepared from the C_{24} chloro acetal **9** and triphenylphosphine as before over 28 d. Its ^1H NMR spectrum was identical with that of the authentic phosphonium bromide.[3] Once again there was NMR evidence of terminal CH_2=CH– and $Ph_2P(O)CH_2$– by-products being formed. The salt was very hygroscopic and was dissolved in anhydrous tetrahydrofuran as a standard solution for use in Wittig reactions.

36-Chlorohexatriaconta-12,24-dienal ethylene acetal (the C_{36} chloro acetal) 23 (n = 2). The C_{24} chloro aldehyde **13** was reacted as before with the C_{12} acetal phosphonium chloride **6** and to give the *product* **23** (n = 2), isolated by chromatography on silica using light petroleum–ether (85/15, v/v); δ_H($CDCl_3$) 5.36 [m, 2 × (CH=CH)], 4.84 [t, $CHO_2(CH_2)_2$], 3.9 [m, $O(CH_2)_2O$] and 3.5 (t, CH_2Cl), in the ratio 4.4:1.0:4.2:2.0. It formed a 2,4-*dinitrophenylhydrazone*, mp 44–48.5 °C (Found: C, 68.65; H, 9.85; N, 7.3. $C_{42}H_{71}ClN_4O_4$ requires C, 68.96; H, 9.78; N, 7.66%).

Wittig reactions using KH and phosphonium salts to pregenerate the ylide

48-Chlorooctatetraconta-12,24,36-trienal ethylene acetal (the C_{48} chloro acetal) 16. A solution of the C_{24} phosphonium chloride **11** (17.76 g) in tetrahydrofuran (40 ml), 18-crown-6 (0.805 g) and potassium hydride (1.198 g) was heated and stirred at 55 °C for 48 h. Examination of a small sample of the solution by ^{31}P NMR indicated 85% ylide (δ 12.6), 13% $Ph_2P(O)CH_2$–material (δ 27.2), 1% unreacted phosphonium chloride (δ 23.9) and 1% triphenylphosphine (δ –5.1). The C_{24} chloro aldehyde **13** (8.49 g) was added to the ylide and heating was continued for 2 h. The mixture was washed through a short column of silica using light petroleum–ether (the new work-up procedure) to give crude product which was chromatographed on silica, (loading *ca.* 10 g of the material onto 1 kg silica) using light petroleum–ether (90:10, v/v) as eluent to give pure *48-chlorooctatetraconta-*12,24,36-*trienal ethylene acetal* **16**, mp 41–43 °C (Found: C, 78.4; H, 12.8. $C_{50}H_{93}ClO_2$ requires C, 78.83; H, 12.31%); δ_H($CDCl_3$) 5.35 [m, 3 × (CH=CH)], 4.84 [t, $CHO_2(CH_2)_2$], 3.9 [m, $O(CH_2)_2O$] and 3.53 (t, CH_2Cl); signals were in the ratio 6.32:1:4.18:2.04. HPLC of the DNP derivative (70% THF, 30% water) indicated it was free from C_{24} and C_{72} materials. Fractions containing a slower eluting component were collected and heated *in vacuo* with stirring at 180 °C and 0.05 mmHg, volatile material being collected on a water-cooled finger. Examination of this crude sublimate by ^1H NMR showed the presence of only a very small proportion of – CH_2Cl (at *ca.* δ 3.5), but, significantly, a large CH_3– triplet at *ca.* δ 0.9, in proportion to the alkene and acetal features, which indicated the major presence of tetracos-12-enal ethylene acetal **35**.

48-Bromooctatetraconta-12,24,36-trienal ethylene acetal[3] (the C_{48} bromo acetal) 15. Compound **15** was prepared by a halogen exchange reaction on the chloro compound **16** using the method described above for 12-bromododecanal ethylene acetal **1**.

47-(Dioxolan-2-yl)heptatetraconta-12,24,36-trienyl(triphenyl)-phosphonium bromide[3] (the C_{48} acetal phosphonium bromide) 19. Compound **19** was prepared from the C_{48} bromo acetal **15**, triphenylphosphine and 2,2-dimethyl-1,3-dioxolane (5 ml) in acetonitrile at reflux temperature over 112 h and worked up as before. The product **19** (75%) was analysed by ^1H NMR and shown to be identical to an authentic sample.

72-Chlorodoheptaconta-12,24,36,48,60-pentaenal ethylene acetal (the C_{72} chloro acetal) 23 (n = 5). A crude sample was prepared using the C_{48} chloro aldehyde **18** and the C_{24} acetal phosphonium chloride **11**, and was converted into the DNP derivative for use as a standard for purity checks by HPLC.

Wittig reactions using lithium diisopropylamide (LDA) and phosphonium salts to pregenerate the ylide

24-Bromotetracos-12-enal ethylene acetal[3] (the C_{24} bromo-acetal) 8. The C_{12} acetal triphenylphosphonium bromide **5** (302 g, 0.530 mol, 1.1 equiv.) and THF (700 ml) were cooled to –10 °C whilst stirring under nitrogen. Lithium diisopropylamide (LDA) (1.5 mol l^{-1} in THF; 337 ml, 0.506 mol, 1.05 equiv.) was added, giving a deep orange–red colour, characteristic of the ylide **7**, and the mixture was stirred for 0.5 h at –10 °C. The temperature was held at –10 °C whilst a solution of the C_{12} bromo aldehyde **3** (127 g, 0.482 mol, 1 equiv.) in THF (10 ml) was added with stirring, causing the colour to fade, leaving a very pale cream–yellow mixture. This was allowed to reach room temperature over 16 h. Water

(20 ml) was added to the reaction mixture and the THF removed under vacuum leaving a slurry which was dissolved in acetonitrile (500 ml) and extracted with light petroleum (7 × 250 ml). The combined petrol layers were washed with water (3 × 250 ml), the aqueous layer being extracted with further light petroleum in each case. The petrol layers were combined, dried over sodium sulfate and the solvent was removed under vacuum, leaving an orange oil. This was passed through a short pad of silica (500 g) using light petroleum–diethyl ether (90:10, v/v) to remove any remaining phosphorus compounds and/or lithium salts. The resulting yellow oil (215 g) was purified by short path distillation to remove C_{12} impurities (3 distillations at 100 °C, 4×10^{-3} mbar, conditions under which the C_{12} chain lengths distilled, leaving C_{24} and C_{36} material) and C_{36} impurities (1 distillation at 155 °C, 4×10^{-3} mbar, conditions under which C_{24} compounds distilled, leaving C_{36} material in the residue). The resulting colourless oil **8** (138 g, 60%) formed a white crystalline solid at room temperature, the ^{1}H NMR of which was identical with that of an authentic sample. Analysis of the DNP derivative by HPLC (70% THF, 30% water) showed less than 0.2% of C_{12} material to be present and no C_{36} impurity.

23-(Dioxolan-2-yl)tricos-12-enyl(triphenyl)phosphonium bromide[3] (the C_{24} acetal phosphonium bromide) 10. The C_{24} bromo acetal **8**, triphenylphosphine, 2,2-dimethyl-1,3-dioxolane and acetonitrile were reacted over 66 h and worked-up as before to give the product **10**, the ^{1}H NMR of which was identical with that of an authentic sample.

36-Bromohexatriaconta-12,24-dienal ethylene acetal (the C_{36} bromo acetal) 22 ($n = 2$). The ylide **7** from the C_{12} triphenylphosphonium bromide **5** and LDA was treated with the C_{24} bromo aldehyde **12** as before, to give the *product* **22** ($n = 2$), isolated by chromatography on silica using light petroleum–diethyl ether (90:10, v/v); δ_H(CDCl$_3$) 5.35 [m, 2 × (CH=CH)], 4.85 [t, C*H*O$_2$(CH$_2$)$_2$], 3.9 [m, O(CH$_2$)$_2$O] and 3.4 (t, CH$_2$Br), in the ratio 4.19:1.02:4:2.00. The DNP derivative was prepared and used as a standard for HPLC analysis.

48-Bromooctatetraconta-12,24,36-trienal ethylene acetal[3] (the C_{48} bromo acetal) 15. The ylide **14** from the C_{24} triphenylphosphonium bromide **10** and LDA was treated with the C_{24} bromo aldehyde **12** as before to give the product **15** (58%), isolated by chromatography on silica using light petroleum–diethyl ether (90:10, v/v). The DNP derivative was prepared and analysed by HPLC which showed it was free from C_{24} and C_{72} materials.

72-Bromodopheptaconta-12,24,36,48,60-pentaenal ethylene acetal (the C_{72} bromo acetal) 22 ($n = 5$). The ylide **14** from the C_{24} triphenylphosphonium bromide **10** and LDA was reacted with the C_{48} bromo aldehyde **17** as before to give the product, separated by chromatography on silica using light petroleum–diethyl ether (90:10, v/v); δ_H(CDCl$_3$) 5.35 [m, 5 × (CH=CH)], 4.85 [t, C*H*O$_2$(CH$_2$)$_2$], 3.9 [m, O(CH$_2$)$_2$O] and 3.4 (t, CH$_2$Br), in the ratio 9.05:1.05:4:1.91. The DNP derivative was prepared and used as a standard for HPLC analysis.

96-Chlorohexanonaconta-12,24,36,48,60,72,84-heptaenal ethylene acetal (the C_{96} chloro acetal) 23 ($n = 7$). The ylide **21** from the C_{48} triphenylphosphonium bromide **19** and LDA was treated with the C_{48} chloro aldehyde **18**. The work-up procedure was modified by filtering the products from the Wittig reaction through a short column of silica using light petroleum–diethyl ether (90:10, v/v), followed by loading *ca.* 10 g of the C_{96} chloro acetal onto 1 kg silica, and chromatography using light petroleum–ether (90:10, v/v) as eluent, to give 96-*chlorohexanonaconta*-12,24,36,48,60,72,84-*heptaenal ethylene acetal* **23** ($n = 7$) (76%), mp 41–43 °C (Found: C, 82.6; H, 13.1. $C_{98}H_{181}ClO_2$ requires C, 82.49; H, 12.78%); δ_H(CDCl$_3$) 5.36 [m, 7 × (CH=CH)], 4.84 [t, C*H*O$_2$(CH$_2$)$_2$], 3.9 [m, O(CH$_2$)$_2$O] and 3.53 (t, CH$_2$Cl), in the ratio 14.29:1:4.03:1.95. HPLC analysis of the DNP derivative indicated the presence of *ca.* 0.7% C_{48} contamination and no C_{144} impurities.

96-Bromohexanonaconta-12,24,36,48,60,72,84-heptaenal ethylene acetal[3] (the C_{96} bromo acetal) 22 ($n = 7$). *Via Wittig reaction.* This compound was prepared as in the previous experiment only using the C_{48} bromo aldehyde **17** instead of **18**, and was identified by ^{1}H NMR. HPLC analysis of the DNP derivative showed no C_{48} or C_{144} materials present.

Via halogen exchange. The C_{96} chloro acetal **23** ($n = 7$) (67 g) was reacted with tetrabutylammonium bromide in 1-bromopropane as described above for the reaction with the C_{12} chloro acetal **2**. After 120 h, 10% –CH$_2$Cl remained, and deprotected acetal (*i.e.* aldehyde) was present. Further treatment with tetrabutylammonium bromide in 1-bromopropane gave a product which mainly consisted of two components: the C_{96} bromo aldehyde **25** ($n = 7$) [*i.e.* deprotected C_{96} bromo acetal **22** ($n = 7$)] and 2-(94-bromotetranonaconta-10,22,34,46,58,70,82-heptaenyl)-98-bromooctanonaconta-2,14,26,38,50,62,74,86-octaenal (the C_{192} dibromo-α,β-unsaturated aldehyde) **36**, readily identified from its ^{1}H NMR spectrum. The mixture was treated with ethylene glycol and toluene-*p*-sulfonic acid monohydrate in refluxing bromoethane: only the C_{96} bromo aldehyde underwent conversion to acetal. The two components were separated by chromatography on silica (1 kg) with a loading of *ca.* 4 g of mixture, using light petroleum–ether (90:10, v/v) as eluent. The ^{1}H NMR of the slower moving component was identical with that of an authentic sample of the C_{96} bromo acetal **22** ($n = 7$), but with an additional bromomethylene signal; δ_H(CDCl$_3$) 5.36 [m, 7 × (CH=CH)], 4.84 [t, C*H*O$_2$(CH$_2$)$_2$], 4.02 (tt, CHBr), 3.9 [m, O(CH$_2$)$_2$O] and 3.4 (t, CH$_2$Br) were in the ratio 14.6:1.06:4.16:2.0, after making the allowance for the loss of one –CH=CH– for each –CHBr–. The secondary bromide functionality was identified by comparison of a model bromide made by reacting the C_{24} bromo acetal **8** with hydrobromic acid (48%) in a sealed tube at 105 °C.

The faster moving component, 2-(94-*bromotetranonaconta*-10,22,34,46,58,70,82-*heptaenyl*)-98-*bromooctanonaconta*-2,14,26,38,50,62,74,86-*octaenal* (*the branched* C_{192} *dibromo*-α,β-*unsaturated aldehyde*) **36a** had the characteristic features of –CH$_2$CH=C(CHO)– group; δ_H(CDCl$_3$) 9.37 (CHO), 6.45 [t, –CH$_2$C*H*=C(CHO)], 5.36 [m, 14 × (CH=CH)] and 3.4 (t, CH$_2$Br), in the ratio 14.8:2.0, after correcting for the secondary –CHBr– (at δ 4.02).

95-(Dioxolan-2-yl)pentacontanona-12,24,36,48,60,72,84-heptaenyl(triphenyl)phosphonium bromide[3] (the C_{96} acetal phosphonuium bromide) 27 ($n = 7$). This compound, completely free from secondary bromide (see below), was prepared by the previously described method using a C_{96} bromo acetal **22** ($n = 7$):triphenylphosphine:2,2-dimethyl-1,3-dioxolane ratio of 1:4:0.1, respectively. The excess triphenylphosphine was separated from the product by chromatography on silica using dichloromethane–methanol (98:2, v/v) as eluent, and the salt was eluted with dichloromethane–methanol (95:5, v/v); δ_H(CDCl$_3$) 7.75 (m, 3 × C$_6$H$_5$), 5.35 [m, 7 × (CH=CH)], 4.85 [t, C*H*O$_2$(CH$_2$)$_2$], 3.9 [m, O(CH$_2$)$_2$O] and 3.7 (m, C*H*$_2$P$^+$Ph$_3$) in the ratio 15.2:14.7:0.95:4:1.75.

The C_{96} bromo acetal **22** ($n = 7$) described above, which contained secondary bromide functionality, reacted with triphenylphosphine exactly as in the previous experiment, exclusively at the primary alkyl bromide site even though excess triphenylphosphine was used. The ^{1}H NMR was identical with that of **27** ($n = 7$), apart from the additional signal at δ 4.02 (tt, CHBr). There were no signals in the region δ 4.2–4.6 [expected for –CH(P$^+$Ph$_3$)–, which were found in a sample obtained by the reaction of 6-bromododecane with triphenylphosphine in acetonitrile and isolated by chromatography on silica using dichloromethane–methanol (80:20, v/v) as eluent].

120-Bromocoshecta-12,24,36,48,60,72,84,96,108-nonaenal ethylene acetal (the C_{120} bromo acetal) 22 ($n = 9$). Treatment of the C_{96} bromo aldehyde **25** (n = 7) with the ylide **14** from the C_{24} phosphonium bromide **10** gave the *C_{120} bromo acetal* **22** (n = 9), mp 41–42 °C (Found: C, 81.2; H, 12.7. $C_{122}H_{225}BrO_2$ requires C, 81.23; H, 12.57%); $\delta_H(CDCl_3)$ 5.36 [m, 9 × (CH=CH)], 4.84 [t, C*H*$O_2(CH_2)_2$], 3.9 [m, $O(CH_2)_2O$] and 3.53 (t, CH_2Br) in ratio 18.8:1.0:4.1:2.0.

144-Chlorotetratetracontahecta-12,24,36,48,60,72,84,96,108,120,132-undecaenal ethylene acetal (the C_{144} chloro acetal) 23 (n = 11). A sample of this compound was prepared as in the previous synthesis using the C_{96} chloro aldehyde obtained from the C_{96} chloro acetal **23** (n = 7) and the C_{48} phosphonium bromide **19**; $\delta_H(CDCl_3)$ 5.36 [m, 11 × (CH=CH)], 4.84 [t, C*H*$O_2(CH_2)_2$], 3.9 [m, $O(CH_2)_2O$] and 3.53 (t, CH_2Cl), in the ratio 22.8:1.0:4.0:2.0. It was converted into the DNP derivative for use as a standard for purity checks by HPLC.

192-Bromodononacontahecta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180-pentadecaenal ethylene acetal[3] (the C_{192} bromo acetal) 22 (n = 15). The ylide prepared from C_{96} acetal triphenylphosphonium bromide **27** (n = 7) and LDA was treated with the C_{96} bromo aldehyde **25** (n = 7), worked-up as before and the product separated by chromatography on silica using light petroleum–ether (96:4, v/v) as eluent to give the pure product (80%), identified by ^1H NMR spectroscopy. Analysis of the DNP derivative showed the absence of both C_{96} homologues and any material at longer retention times.

The C_{192} bromo acetal **22** (n = 15) containing secondary alkyl bromide was obtained in similar yield from secondary alkyl bromide-containing moieties, the ^1H NMR spectrum showing this functionality at δ 4.02 (tt, CHBr).

191-(Dioxolan-2-yl)hennonacontahecta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180-pentadecaenyl(triphenyl)phosphonium bromide[3] (the C_{192} acetal phosphonium bromide) 27 (n = 15). This compound was prepared as for the C_{96} acetal phosphonium bromide **27** (n = 7); $\delta_H(CDCl_3)$ 5.36 [m, 15 × (CH=CH)], 3.9 [m, $O(CH_2)_2O$] and 3.82 (m, $CH_2P^+Ph_3$). The integral ratio for the alkene protons and the combined aliphatic protons was 29.6:6.

240-Bromotetracontadicta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192,204,216,228-nonadecaenal ethylene acetal (the C_{240} bromo acetal) 22 (n = 19). Reaction of the C_{192} bromo aldehyde **25** (n = 15) (containing secondary bromide) and the ylide **21** from C_{48} phosphonium bromide **19** and LDA gave the C_{240} bromo acetal **22** (n = 19) which was purified by chromatography on silica (1 kg) with a loading of *ca.* 4 g using light petroleum–ether (95:5, v/v) as eluent (81% yield), the ^1H NMR spectrum of which was exactly as expected, but with an additional bromomethylene signal; $\delta_H(CDCl_3)$ 5.36 [m, 19 × (CH=CH)], 4.84 [t, C*H*$O_2(CH_2)_2$], 4.02 (tt, CHBr), 3.9 [m, $O(CH_2)_2O$] and 3.4 (t, CH_2Br), in the ratio 38.5:1.04:4.21:2 after making the allowance for the loss of one –CH=CH– for each –CHBr–.

288-Bromooctaoctacontadicta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192,204,216,228,240,252,264,276-tricosaenal ethylene acetal[3] (the C_{288} bromo acetal) 22 (n = 23). Treatment of the C_{192} bromo aldehyde **25** (n = 15) with the ylide from C_{96} phosphonium bromide **27** (n = 7) and LDA (both moieties containing secondary bromine) gave the C_{288} bromo acetal **22** (n = 23) which was purified by chromatography on silica (1 kg) with a loading of *ca.* 4 g using light petroleum–ether (97.5:2.5, v/v) as eluent (57% yield), the ^1H NMR spectrum of which was exactly as expected, but with an additional bromomethylene signal; $\delta_H(CDCl_3)$ 5.36 [m, 23 × (CH=CH)], 4.84 [t, C*H*$O_2(CH_2)_2$], 4.02 (tt, CHBr), 3.9 [m, $O(CH_2)_2O$] and 3.4 (t, CH_2Br), in the ratio 45.9:0.91:3.86:2.0, after making the allowance for the loss of one –CH=CH– for each –CHBr–.

384-Bromotetraoctacontatricta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192,204,216,228,240,252,264,276,288,300,312,324,336,348,360,372-hentriacontaenal ethylene acetal (the C_{384} bromo acetal) 22 (n = 31). Treatment of the C_{192} bromo aldehyde **25** (n = 15) with the ylide from C_{192} phosphonium bromide **27** (n = 15) and LDA gave the *C_{384} bromo acetal* **22** (n = 31) which was partially purified by chromatography on silica (see later); $\delta_H(CDCl_3)$ 5.36 [m, 31 × (CH=CH)], 4.84 [t, C*H*$O_2(CH_2)_2$], 3.9 [m, $O(CH_2)_2O$] and 3.4 (t, CH_2Br), in the ratio 63.0:0.95:3.89:2.0.

Syntheses of long chain primary bromides and their phosphonium salts for 'capping' reactions

(i) Octadec-12-enyl bromide 37. The ylide from hexyl(triphenyl)phosphonium bromide and LDA was treated with 12-bromododecanal **3** and then filtered through a short column of silica using light petroleum. The solvent was evaporated to give a viscous liquid **37** (Found: C, 65.6; H, 11.0. $C_{18}H_{35}Br$ requires C, 65.24; H, 10.64%); $\delta_H(CDCl_3)$ 5.36 [m, 1 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 2.0:2.10.

(ii) Octadec-12-enyl(triphenyl)phosphonium bromide 38. The bromide **37** was treated with triphenylphosphine (1.2 equiv.) in acetonitrile at reflux temperature for 5 d. The solvent was removed *in vacuo* at 40 °C to give a highly viscous oil from which the excess triphenylphosphine was removed by stirring with light petroleum and decanting the supernatant liquid. Removal of traces of solvent gave a viscous liquid **38** which was used without further treatment in subsequent Wittig reactions; $\delta_H(CDCl_3)$ 5.36 [m, 1 × (CH=CH)] and 3.65 (t, $CH_2P^+Ph_3$), in the ratio 2.0:2.06.

(iii) Pentaconta-12,24,36,48-tetraenyl bromide 39. The ylide from ethyl(triphenyl)phosphonium bromide and LDA was treated with the C_{48} bromo aldehyde **25** (n = 3) and the crude product was isolated as in (i), above. Chromatography on silica using light petroleum gave the pure *C_{50} tetraenyl bromide* **39** (82%) as a glass (Found: C, 77.45; H, 12.2. $C_{50}H_{93}Br$ requires C, 77.57; H, 12.10%); $\delta_H(CDCl_3)$ 5.36 [m, 4 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 7.96:2.0.

(iv) Pentaconta-12,24,36,48-tetraenyltriphenylphosphonium bromide 40. The C_{50} tetraenyl bromide **39** was treated as in (ii), and the crude product was chromatographed on silica using dichloromethane–methanol (98:2, v/v) to give the pure salt **40** as a glass (Found: C, 78.45; H, 10.9. $C_{68}H_{108}BrP$ requires C, 78.80; H, 10.50%); $\delta_H(CDCl_3)$ 5.36 [m, 4 × (CH=CH)] and 3.78 (m, $CH_2P^+Ph_3$), in the ratio 8.18:2.0.

(v) Hexahexaconta-12,24,36,48,60-pentaenyl bromide 41. The ylide **43** from octadec-12-enyl(triphenyl)phosphonium bromide **38** and LDA was treated with the C_{48} bromo aldehyde **17**, and the crude product, isolated as in (i), was chromatographed on silica using light petroleum to give the pure *C_{66} pentaenyl bromide* **41** (82%), mp 27–28 °C (Found: C, 80.0; H, 12.9. $C_{66}H_{123}Br$ requires C, 79.54; H, 12.44%); $\delta_H(CDCl_3)$ 5.36 [m, 5 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 10.4:2.0.

(vi) Hexahexaconta-12,24,36,48,60-pentaenyl(triphenyl)phosphonium bromide 42. The C_{66} pentaenyl bromide **41** was treated as in (ii), and the crude product was chromatographed on silica using dichloromethane–methanol (95:5, v/v) to give the pure salt **42** as a glass (Found: C, 80.2; H, 11.0. $C_{84}H_{138}BrP$ requires C, 79.19; H, 11.12%); $\delta_H(CDCl_3)$ 5.36 [m, 5 × (CH=CH)] and 3.78 (m, $-CH_2P^+Ph_3$), in the ratio 5.6:1.

Capping reactions

(i) C_{96} + C_2 $\longrightarrow$ C_{98}. A mixture of ethyl(triphenyl)phosphonium bromide (4.41 g, 11.9 mmol) and anhydrous THF (43.7 ml) was cooled to −20 °C under argon and treated with LDA (1.5 mol l^{-1} in THF, 6.3 ml, 9.4 mmol). A proportion of this solution (12.5 ml, 2.38 mmol) was added under argon to a suspension of the C_{96} bromo aldehyde **25** (n = 7) (3.2 g, 1.16 mmol) in anhydrous THF (5 ml) at −20 °C followed by further ylide (3.5 ml, 0.66 mmol). The mixture was allowed to warm to room temperature overnight and washed through a short silica column with light petroleum and the solvent evaporated. Chromatography on silica using light petroleum gave *octa-*

nonaconta-12,24,36,48,60,72,84,96-*octaenyl bromide* (*the* C_{98} *bromo polyene*) **46** (≡ **30**, $n = 7$, R = CH_3), mp 37–38 °C (Found: C, 81.7; H, 12.8. $C_{98}H_{181}Br$ requires C, 81.77; H, 12.67%); $\delta_H(CDCl_3)$ 5.35 [m, 8 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 16.6:2.

(ii) $C_{120} + C_2 \longrightarrow C_{122}$. The C_{120} bromo aldehyde **25** ($n = 9$) was reacted with the ylide from ethyl (triphenyl)phosphonium bromide as in (i) to give *docosahecta*-12,24,36,48,60,72,84,96,108,120-*decaenyl bromide* **47** (≡ **30**, n = 9, R = CH_3) (64%), mp 37–38 °C (from light petroleum) (Found: C, 82.6; H, 12.6. $C_{122}H_{225}Br$ requires C, 82.69; H, 12.79%); $\delta_H(CDCl_3)$ 5.35 [m, 10 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 20.6:2.0.

(iii) $C_{96} + C_{66} \longrightarrow C_{162}$. The C_{96} bromo aldehyde **25** ($n = 7$) was added to the ylide **45** from the C_{66} triphenylphosphonium bromide **42**, as in (i), to give *dohexacontahecta*-12,24,36,48,60,72,84,96,108,120,132,144,156-*triadecaenyl bromide* **48** {≡ **30**, $n = 7$, R = $C_5H_{11}[CH{=}CH(CH_2)_{10}]_5$} (65%), mp 30–31 °C (Found: C, 83.5; H, 13.0. $C_{162}H_{289}Br$ requires C, 83.62; H, 12.95%); $\delta_H(CDCl_3)$ 5.35 [m, 13 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 27.2:2.0.

(iv) $C_{192} + C_2 \longrightarrow C_{194}$. The C_{192} bromo aldehyde **25** ($n = 15$) was treated with the ylide from ethyl(triphenyl)phosphonium bromide as in (i), to give *tetranonacontahecta*-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192-*hexadecaenyl bromide* **49** (≡ **30**, $n = 15$, R = CH_3) (64%), mp 37–38 °C (from light petroleum) (Found: C, 84.1; H, 13.0. $C_{194}H_{357}Br$ requires C, 84.12; H, 12.99%); $\delta_H(CDCl_3)$ 5.35 [m, 16 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 33.6:2.0.

(v) $C_{192} + C_6 \longrightarrow C_{198}$. The C_{192} bromo aldehyde **25** ($n = 15$), containing the CHBr feature, was treated with the ylide from hexyl(triphenyl)phosphonium bromide as in (i), to give *octanonacontahecta*-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192-*hexadecaenyl bromide*[3] **30** ($n = 15$, R = C_5H_{11}) (75%). The ^1H NMR spectrum was identical with that of an authentic sample, but with an additional bromomethylene signal; $\delta_H(CDCl_3)$ 5.36 [m, 16 × (CH=CH)], 4.02 (tt, CHBr) and 3.4 (t, CH_2Br). The ratio of alkene to bromomethyl protons was 16.5:1, after making the allowance for the loss of one –CH=CH– for each –CHBr–.

(vi) $C_{192} + C_{18} \longrightarrow C_{210}$. The C_{192} bromo aldehyde **25** ($n = 15$) was added to the ylide **43** from the C_{18} triphenylphosphonium bromide **38**, as in (i), to give *decadicta*-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192,204-*heptadecaenyl bromide* **50** {≡ **30**, $n = 15$, R = C_5H_{11} $[CH{=}CH(CH_2)_{10}]$} (60%), mp 31–32 °C (Found: C, 84.05; H, 13.0. $C_{210}H_{384}Br$ requires C, 84.29; H, 13.03%); $\delta_H(CDCl_3)$ 5.35 [m, 17 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 35.0:2.0.

(vii) $C_{192} + C_{50} \longrightarrow C_{242}$. The C_{192} aldehyde **26** ($n = 15$) was added to the ylide **44** from the C_{50} phosphonium bromide **40**, as in (i), to give *dotetracontadicta*-2,14,26,38,50,62,74,86,98,110,122,134,146,158,170,182,194,206,218,230-*cosaene* **51** {≡ **31**, $n = 15$, R = $CH_3[CH{=}CH(CH_2)_{10}]_4$} (60%), mp 32–33 °C (Found: C, 86.9; H, 13.5. $C_{242}H_{446}$ requires C, 86.71; H, 13.24%); $\delta_H(CDCl_3)$ 5.35 [m, 17 × $CH_2CH{=}CHCH_2$] and 2.0 [m, $CH_2CH{=}CHCH_2$], in the ratio 2.0:3.8.

(viii) $C_{240} + C_6 \longrightarrow C_{246}$. The C_{240} bromo aldehyde **25** ($n = 19$), containing the –CHBr– feature, was treated with the ylide from hexyl(triphenyl)phosphonium bromide as in (i) to give *hexatetracontadicta*-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192,204,216,228,240-*cosaenyl bromide*[3] **30** ($n = 19$, R = C_5H_{11}). The ^1H NMR spectrum was identical with that of an authentic sample, but with an additional bromomethylene signal; $\delta_H(CDCl_3)$ 5.36 [m, 20 × (CH=CH)], 4.02 (tt, CHBr) and 3.4 (t, CH_2Br). The alkene and bromomethyl integrals were in the ratio 20.8:1, after making the allowance for the loss of one – CH=CH– for each –CHBr–.

(ix) $C_{192} + C_{66} \longrightarrow C_{258}$. The C_{192} bromo aldehyde **25** ($n = 15$) was added to the ylide **45** from C_{66} triphenylphosphonium bromide **42**, as in (i) to give *octapentacontadicta*-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192,204,216,228,240,252-*hencosaenyl bromide* **52** {≡ **30**, $n = 15$, R = $C_5H_{11}[CH{=}CH(CH_2)_{10}]_5$} (36%), mp 36–37 °C (Found: C, 84.3; H, 13.2. $C_{258}H_{475}Br$ requires C, 84.72; H, 13.08%); $\delta_H(CDCl_3)$ 5.35 [m, 21 × (CH=CH)] and 3.4 (t, CH_2Br), in the ratio 44.3:2.0.

(x) $C_{288} + C_6 \longrightarrow C_{294}$. The C_{288} bromo aldehyde **25** ($n = 23$), containing the –CHBr– feature, was treated with the ylide from hexyl(triphenyl)phosphonium bromide as in (i) to give *tetranonacontadicta*-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180,192,204,216,228,240,252,264,276,288-*tetracosaenyl bromide*[3] **30** ($n = 23$, R = C_5H_{11}). The ^1H NMR spectrum was identical with that of an authentic sample, but with an additional bromomethylene signal; $\delta_H(CDCl_3)$ 5.36 [m, 24 × (CH=CH)], 4.02 (tt, CHBr) and 3.4 (t, CH_2Br). The alkene and bromomethyl integrals were in the ratio 24.7:1, after making the allowance for the loss of one –CH=CH– for each –CHBr–.

(xi) $C_{384} + C_6 \longrightarrow C_{390}$. The C_{384} aldehyde[3] **26** ($n = 31$) (see below) was treated with the ylide from hexyl(triphenyl)phosphonium bromide as in (i) to give *nonacontatricta*-6,18,30,42,54,66,78,90,102,114,126,138,150,162,174,186,198,210,222,234,246,258,270,282,294,306,318,330,342,354,366,378-*dotriacontaene*[3] **53** (≡ **31**, $n = 31$, R = C_5H_{11})[3], mp 37–38 °C (Found: C, 86.5; H, 13.5. $C_{390}H_{718}$ requires C, 86.62; H, 13.38%); $\delta_H(CDCl_3)$ 5.35 [m, 32 × (CH=CH)], 1.95 (m, 64 × $CH_2CH{=}$), 1.3 [m, 260 × (CH_2), *i.e.* 520 protons] and 0.88 (2 × CH_3), in the ratio 64.0:128.5:520:5.9.

Replacement of bromine by hydrogen

(i) C_{98} bromo polyene $\longrightarrow$ C_{98} polyene. The C_{98} bromo polyene **46** (2.41 g, 1.67 mmol) and 'Superhydride' (lithium triethylborohydride; 1.0 mol l^{-1} solution in THF; 10 ml, 0.1 mol), were stirred together at room temperature under argon for 4 h. The product was dissolved in light petroleum and washed with dilute sulfuric acid (0.5 mol l^{-1}; 200 ml) and water (200 ml). In each case the aqueous layers were extracted with light petroleum, and the organic layers combined and dried over sodium sulfate. The solvent was removed under vacuum, leaving a colourless oil, which was chromatographed on silica using light petroleum, to give *octanonaconta*-2,14,26,38,50,62,74,86-*octaene* (*the* C_{98} *polyene*) **59** (≡ **31**, $n = 7$, R = CH_3), (2.14 g, 94%), mp 37.5–38 °C (Found: C, 86.6; H, 13.6. $C_{98}H_{182}$ requires C, 86.52; H, 13.48%); $\delta_H(CDCl_3)$ 5.35 [m, 8 × (CH=CH)], 1.95 (m, 15 × $CH_2CH{=}$), 1.3 [m, $(CH_2)_9$ and 7 × $(CH_2)_8$, *i.e.* 130 protons], with intensities in the ratio 16.0:29.1:126; and 1.6 (dd, $=CHCH_3$) and 0.87 (t, CH_2CH_3).

(ii) C_{122} bromo polyene $\longrightarrow$ C_{122} polyene. The C_{122} bromo polyene **47** was treated as in (i) to give *docosahecta*-2,14,26,38,50,62,74,86,98,110-*decaene* **60** (≡ **31**, $n = 9$, R = CH_3) (98%), mp 31–32 °C (Found: C, 86.5; H, 13.6. $C_{122}H_{226}$ requires C, 86.54; H, 13.45%); $\delta_H(CDCl_3)$ 5.35 [m, 10 × (CH=CH)], 1.95 (m, 19 × $CH_2CH{=}$), 1.3 [m, CH_2 and 10 × $(CH_2)_8$, *i.e.* 162 protons], with intensities in the ratio 20.0:37.9:162.0; and 1.60 and 1.64 (both d, $=CHCH_3$) and 0.87 [t, CH_2CH_3].

(iii) C_{162} bromo polyene $\longrightarrow$ C_{162} polyene. The C_{162} bromo polyene **48** was treated as in (i) to give *dohexacontahecta*-6,18,30,42,54,66,78,90,102,114,126,138,150-*triadecaene* **61** {≡ **31**, $n = 7$, R = C_5H_{11} $[CH{=}CH(CH_2)_{10}]_5$} (84%), mp 36–37 °C (Found: C, 86.5; H, 13.5. $C_{162}H_{300}$ requires C, 86.55; H, 13.45%); $\delta_H(CDCl_3)$ 5.35 [m, 13 × (CH=CH)], 2.0 (m, 26 × $CH_2CH{=}$) and 1.3 [m, 108 × (CH_2), *i.e.* 216 protons], in the ratio 26.0:53.9:215.

(iv) C_{192} bromo acetal $\longrightarrow$ C_{192} acetal. The C_{192} bromo acetal **22** ($n = 15$) was treated as in (i) to give dononacontahecta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180-pentadecaenal acetal[3] **24** ($n = 15$); $\delta_H(CDCl_3)$ 5.36 [m, 15 × (CH=CH)] and 4.84 [t, $CHO_2(CH_2)_2$], in the ratio 31.2:4.

(v) C_{194} bromo polyene $\longrightarrow$ C_{194} polyene. The C_{194} bromo polyene **49** was treated as in (i) to give *tetranonacontahecta*-2,14,26,38,50,62,74,86,98,110,122,134,146,158,170,182-*hexadecaene* **62** (≡ **31**, $n = 15$, R = CH_3), mp 35–36 °C (Found: C, 86.35; H, 13.5. $C_{194}H_{358}$ requires C, 86.59; H, 13.41%); $\delta_H(CDCl_3)$ 5.35 [m, 16 × (CH=CH)], 2.0 [m, 31 × $CH_2CH=$] and 1.3 [m, 129 × (CH_2), *i.e.* 258 protons], in the ratio 32.0:61.4:272.

(vi) C_{198} bromo polyene ⟶ C_{198} polyene. The C_{198} bromo polyene **30** ($n = 15$, R = C_5H_{11}) containing the CHBr feature was treated as in (i) to give octanonacontahecta-6,18,30,42,54,66,78,90,102,114,126,138,150,162,174,186-hexadecaene[3] **31** ($n = 15$, R = C_5H_{11}). The ^1H NMR spectrum was identical with that of an authentic sample, but with an additional bromomethylene signal; $\delta_H(CDCl_3)$ 5.35 [m, (CH=CH)], 4.02 (tt, CHBr), 2.0 (m, 31 × $CH_2CH=$) and 1.3 [m, (CH_2)]. The residual CHBr was removed by heating the polyene (1.53 g) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.32 g) under argon at 150 °C for 4 h. The mixture was cooled, shaken with sulfuric acid (4 mol l^{-1}) and ether–light petroleum, and the organic solvents removed *in vacuo* at 20 °C to avoid the formation of an emulsion. The solid which separated was filtered and washed with water, dissolved in ether–light petroleum, dried (Na_2SO_4) and the solvent evaporated. The product was chromatographed on silica using light petroleum–ether (98.5:1.5, v/v) as eluent, to give the halogen-free polyene **31** ($n = 15$, R = C_5H_{11}).

(vii) C_{210} bromo polyene ⟶ C_{210} polyene. The C_{210} bromo polyene **50** was treated as in (i) to give *decadicta*-6,18,30,42,54,66,78,90,102,114,126,138,150,162,174,186,198-*heptadecaene* **63** [≡ **31**, $n = 15$, R = $C_5H_{11}CH{=}CH(CH_2)_{10}$] (87%), mp 31–32 °C (Found: C, 86.5; H, 13.0. $C_{210}H_{388}$ requires C, 86.57; H, 13.42%); $\delta_H(CDCl_3)$ 5.35 [m, 17 × (CH=CH)], 1.95 (m, 34 × $CH_2CH=$) and 1.3 [m, 140 × (CH_2), *i.e.* 280 protons], in the ratio 34.0:68.8:299.

(viii) C_{246} bromo acetal ⟶ C_{246} acetal. The C_{246} bromo polyene **30** ($n = 19$, R = C_5H_{11}) containing the –CHBr– feature was reacted as in (i) and dehydrobrominated as in (vi) to give isomers of hexatetracontadicta-6,18,30,42,54,66,78,90,102,114,126,138,150,162,174,186,198,210,222,234-cosaene[3] **31** ($n = 19$, R = C_5H_{11}); $\delta_H(CDCl_3)$ 5.35 [m, 20 × (CH=CH)], 1.95 (m, 40 × $CH_2CH=$), 1.3 [m, 164 × (CH_2), *i.e.* 328 protons] and 0.92 (2 × CH_3), in the ratio 40.0:81:337:6.1.

(ix) C_{258} bromo polyene ⟶ C_{258} polyene. The C_{258} bromo polyene **52** {≡ **30**, $n = 15$, R = $C_5H_{11}[CH{=}CH(CH_2)_{10}]_5$} was reacted as in (i) to give *octapentadicta*-6,18,30,42,54,66,78,90,102,114,126,138,150,162,174,186,198,210,222,234,246-*hencosaene* **64** {≡ **31**, $n = 15$, R = $C_5H_{11}[CH{=}CH(CH_2)_{10}]_5$} (43%), mp 38–39 °C (Found: C, 86.4; H, 13.5. $C_{258}H_{476}$ requires C, 86.59; H, 13.40%); $\delta_H(CDCl_3)$ 5.35 [m, 21 × (CH=CH)], 1.95 (m, 42 × $CH_2CH=$) and 1.3 [m, 172 × (CH_2), *i.e.* 344 protons], in the ratio 42.0:82.1:349.

(x) C_{294} bromo polyene ⟶ C_{294} polyene. The C_{294} bromo polyene **30** ($n = 23$, R = C_5H_{11}) containing the –CHBr– feature was reacted as in (i) and dehydrobrominated as in (vi) to give isomers of tetranonacontadicta-6,18,30,42,54,66,78,90,102,114,126,138,150,162,174,186,198,210,222,234,246,258,270,282-tetracosaene[3] **31** ($n = 23$, R = C_5H_{11}); $\delta_H(CDCl_3)$ 5.35 [m, 24 × (CH=CH)], 1.95 (m, 48 × $CH_2CH=$), 1.3 [m, 196 × (CH_2), *i.e.* 392 protons] and 0.92 (2 × CH_3), in the ratio 48.0:92.6:394.

(xi) C_{384} bromo acetal ⟶ C_{384} acetal. The C_{384} bromo acetal **22** ($n = 31$) was reacted as in (i) and purified by chromatography on silica using light petroleum–ether (96:4, v/v) to give the C_{384} acetal[3] **24** ($n = 31$); $\delta_H(CDCl_3)$ 5.36 [m, 31 × (CH=CH)], 4.82 [t, $CHO_2(CH_2)_2$] and 3.9 [m, $O(CH_2)_2O$], in the ratio 63.2:0.9:4.

Hydrogenation of straight chain polyenes

(i) $C_{98}H_{198}$ formation. The C_{98} polyene **59** (2.01 g), 5% Pt on activated carbon (1 g) and ethyl palmitate (10 ml) were stirred together and heated at 130 °C in an atmosphere of hydrogen for 14 h. Light petroleum (bp 100–120 °C) (10 ml) was added to the mixture at 110 °C which was then allowed to cool slowly to room temperature. Solid material was filtered and washed with light petroleum, placed in a cellulose extraction thimble and extracted for 16 h with boiling light petroleum (bp 100–120 °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, and finally heated at 110 °C and 0.01 mmHg for 48 h to remove traces of dibutyl and dioctyl phthalate to give *octanonacontane* (1.84 g, 90%), mp 113–114 °C (Found: C, 85.4; H, 14.5. $C_{98}H_{198}$ requires C, 85.50; H, 14.49%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(ii) $C_{122}H_{246}$ formation. The C_{122} polyene **60** was hydrogenated as in (i) to give *docosahectane* (1.62 g, 97%), mp 116–117 °C (Found: C, 85.6; H, 14.7. $C_{122}H_{246}$ requires C, 85.53; H, 14.47%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(iii) $C_{162}H_{326}$ formation. The C_{162} polyene **61** was hydrogenated as in (i) to give *dohexacontahectane* (2.74 g, 97%), mp 121–121.5° (Found: C, 85.4; H, 14.5. $C_{162}H_{326}$ requires C, 85.55; H, 14.44%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(iv) $C_{194}H_{390}$ formation. The C_{194} polyene **62** was hydrogenated as in (i) to give *tetranonacontahectane* (1.41 g, 90%), mp 122–123 °C (Found: C, 85.6; H, 14.2. $C_{194}H_{390}$ requires C, 85.56; H, 14.43%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(v) $C_{198}H_{398}$ formation. The C_{198} polyene **31** ($n = 15$, R = C_5H_{11}) was hydrogenated as in (i) to give octanonacontahectane[3] (1.46 g); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(vi) $C_{210}H_{422}$ formation. The C_{210} polyene **63** was hydrogenated as in (i) to give *decadictane* (1.23 g, 93%), mp 125–126 °C (Found: C, 85.6; H, 14.4. $C_{210}H_{422}$ requires C, 85.58; H, 14.42%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(vii) $C_{242}H_{486}$ formation. The C_{242} polyene **51** was hydrogenated as in (i) to give *dotetracontadictane* (1.41 g, 91%), mp 120–121 °C (Found: C, 85.7; H, 14.6. $C_{242}H_{486}$ requires C, 85.58; H, 14.42%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(viii) $C_{246}H_{494}$ formation. The C_{246} polyene **31** ($n = 19$, R = C_5H_{11}) was hydrogenated as in (i) to give hexatetracontadictane (3.38 g);[3] the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(ix) $C_{258}H_{518}$ formation. The C_{258} polyene **64** was hydrogenated as in (i) to give *octapentacontadictane* (0.3 g, 61%), mp 125–126 °C (Found: C, 85.65; H, 14.4. $C_{258}H_{518}$ requires C, 85.58; H, 14.41%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(x) $C_{294}H_{590}$ formation. The C_{294} polyene **31** ($n = 23$, R = C_5H_{11}) was hydrogenated as in (i) to give tetranonacontadictane[3] (2.57 g); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

(xi) $C_{390}H_{782}$ formation. The C_{390} polyene **53** was hydrogenated as in (i) to give nonacontatrictane[3] (0.83 g, 96%), mp 125–126 °C (Found: C, 85.8; H, 14.5. $C_{390}H_{782}$ requires C, 85.60; H, 14.40%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of alkenic absorptions at δ 5.36.

Syntheses of branched chain alkanes

(a) $C_{96}H_{193}CH(CH_3)C_{94}H_{189}$. (i) The branched C_{192} dibromo-α,β-unsaturated aldehyde containing –CHBr– **36** (4.97 g) in anhydrous THF (20 ml) was added to a stirred suspension of lithium aluminium hydride (1.75 g) in anhydrous THF (35 ml) at −40 °C over 5 min. The excess hydride was destroyed with ethyl acetate, the mixture acidified (4 mol l^{-1} H_2SO_4), extracted with light petroleum–ether, the extracts dried (Na_2SO_4) and solvent evaporated. Chromatography of the crude product on silica using light petroleum–ether (90:10, v/v) gave the branched *C_{192} dibromo unsaturated alcohol*, the ^{1}H NMR of which showed 16% conversion of –CH_2Br to –CH_3; $\delta_H(CDCl_3)$ 5.36 (m, 29 × C*H*=C), 4.02 (s, C*H*$_2$OH) (masking the CHBr) and 3.4 (t, C*H*$_2$Br) in the ratio 29.0:2.16:3.9.

(ii) The branched C_{192} dibromo unsaturated alcohol from (i) (3.06 g) in dry light petroleum (6 ml) was treated at 15 °C with PBr_3 (0.168 g) in dry light petroleum (2.5 ml). After 1 h, the mixture was added to water, extracted with ether, the extracts dried (Na_2SO_4) and solvent evaporated. The crude product was purified by chromatography on silica using light petroleum–ether (98:2, v/v) to give the branched *C_{192} dibromo unsaturated bromide*; $\delta_H(CDCl_3)$ 5.62 [t, C*H*=C(CH_2-Br)], 5.26 [m, 14 × (CH=CH)], 4.0 [s, CH=C(C*H*$_2$Br), overlapping the CHBr at δ 4.02] and 3.4 (t, CH_2Br); also $\delta_H(CDCl_3)$ 5.15 and 4.9 (both s, CHBrC=C*H*$_2$) and 4.5 (t, CH_2C*H*BrC=CH_2), the result of *ca.* 4% S_N2' displacement of OH.

(iii) The branched C_{192} dibromo unsaturated bromide from (ii) was reacted with 'Superhydride' (lithium triethylborohydride) as described before. The ^{1}H NMR of the C_{192}–C_1 branched product showed the –CHBr– at δ 4.02 and also evidence of S_N2' displacement of Br; $\delta_H(CDCl_3)$ 5.12 [t, CH_2C*H*=C(CH_3)] and 4.7 [s, CH_2C(=C*H*$_2$)CH_2], in the ratio 90:10; and 1.56 and 1.67 [both s, due to geometrical isomers of CH=C(C*H*$_3$)]. The bromine from the –CHBr– was removed with DBU as described before.

(iv) The C_{191}–CH_3 branched polyene from (iii) (1.72 g) was hydrogenated as described before to give 95-*methylhennonacontahectane* **54** (1.57 g), mp 116 °C (DSC) (Found: C, 86.5; H, 13.7. $C_{192}H_{386}$ requires C, 86.53; H, 13.47%); the ^{1}H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of any alkenic absorptions.

(b) $C_{96}H_{193}CH(CH_2CH_2CH_2CH_3)C_{94}H_{189}$. (i) The branched C_{192} dibromo α,β-unsaturated aldehyde containing –CHBr– **36** (2.66 g), was treated under argon at room temperature with the ylide from propyl(triphenyl)phosphonium bromide and LDA in anhydrous THF (0.035 mol l^{-1}) until the orange–yellow colour persisted. The mixture was washed through a short column of silica with light petroleum–ether (90:10, v/v) and the solvent evaporated. The crude product (2.88 g) was chromatographed on silica to give the 95-(*but*-1-*enyl*) *C_{191} dibromo polyene*; $\delta_H(CDCl_3)$ 5.58, 5.72 and 5.93 (associated with CH_3CH_2C*H*=C*H*C*H*=C*H*) and 0.98 and 1.01 (both t, geometrical isomers of C*H*$_3$$CH_2$CH=CH).

(ii) The 95-(but-1-enyl) C_{191} dibromo polyene from (i) was reacted with 'Superhydride' (lithium triethylborohydride) as described before. The ^{1}H NMR of the 95-(but-1-enyl) C_{191} polyene showed the –CHBr– group at δ 4.02 ($CDCl_3$); careful removal of all traces of light petroleum by co-distillation with chloroform revealed three clean triplets, at 0.89 (2 × CH_3 at the end of chain), and 0.98 and 1.01 (geometrical isomers of C*H*$_3$$CH_2$CH=CH) in the ratio 2:1. The bromine from the – CHBr– group was removed with DBU as described before.

(iii) The 95-(but-1-enyl) C_{191} polyene from (ii) was hydrogenated as described before to give 95-*butylhennonacontahectane* **55** (1.84 g), mp 116 °C (DSC) (Found: C, 85.5; H, 14.8. $C_{195}H_{392}$ requires C, 85.56; H, 14.44%); the ^{1}H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of any alkenic absorptions.

Syntheses of long chain carboxylic acids

(a) $CH_3(CH_2)_{190}CO_2H$. (i) The C_{192} acetal **24** (*n* = 15) (0.84 g) was deprotected on silica (73 g) impregnated with toluene-*p*-sulfonic acid monohydrate (1.83 g) and water (5.4 ml), with light petroleum–dichloromethane (3:1, v/v) as eluent. The resulting aldehyde **26** (*n* = 15) was dissolved in a mixture of THF (6 ml) and ethanol (3 ml) and $AgNO_3$ (1.27 g), and sodium hydroxide (0.35 g) in water (2.5 ml) was added. After stirring for 2 h at room temperature, the mixture was acidified with sulfuric acid (4 mol l^{-1}), extracted with light petroleum–ether, the extracts dried (Na_2SO_4) and the solvent evaporated. The crude product (0.96 g) was purified by chromatography on silica using light petroleum–ether (85:15, v/v) as eluent to give *dononacontahecta*-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180-*pentadecaenoic acid*, mp 44.5–47 °C (Found: C, 85.8, H, 13.3. $C_{192}H_{354}O_2$ requires C, 85.57; H, 13.24%); $\delta_H(CDCl_3)$ 5.35 [m, 15 × (CH=CH)], 2.36 (t, CH_2C*H*$_2$$CO_2$H), 1.95 (m, 30 × C*H*$_2$CH=) and 1.65 (q, C*H*$_2$$CH_2CO_2$H), in the ratio 30.2:2.0:62:1.94.

(ii) The C_{192} carboxylic acid from (i) was hydrogenated as described before, but extracted with octane, to give *dononacontahectanoic acid* **56** (0.60 g), 127.5–130.5 °C (Found: C, 84.6; H, 14.4. $C_{192}H_{384}O_2$ requires C, 84.62; H, 14.20%); the ^{1}H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of any alkenic absorptions.

(b) $HO_2C(CH_2)_{192}CO_2H$. (i) The C_{192} bromo aldehyde **25** (*n* = 15) (3.29 g) in bromoethane (5 ml) was added to lithium aluminium hydride (0.26 g) in anhydrous ether (10 ml) at 0 to −5 °C. After 30 min, ether (30 ml) was added and the mixture was added to light petroleum–ether over sulfuric acid (4 mol l^{-1}). The organic layer was separated, dried (Na_2SO_4), the solvent evaporated and the crude product chromatographed on silica using light petroleum–ether (90:10, v/v) as eluent to give 192-*bromodononacontahecta*-12,24,36,48,60,72,84,96,108,120,132,-144,156,168,180-*pentadecaenol*, mp 44–45 °C (Found: C, 84.0; H, 13.0. $C_{192}H_{355}BrO$ requires C, 83.56; H, 12.96%); $\delta_H(CDCl_3)$ 5.35 [m, 15 × (CH=CH)], 1.95 (m, 30 × C*H*$_2$-CH=), 3.65 (t, CH_2OH) and 3.4 (t, CH_2Br), in the ratio 30:60.7:1.73:1.70.

(ii) A mixture of the C_{192} bromo alcohol from (i) (2.03 g), carbon tetrabromide (0.327 g) suspended in anhydrous dichloromethane (30 ml) at −5 °C was treated with triphenylphosphine (0.318 g) in dry dichloromethane (5 ml) and the temperature allowed to rise to room temperature. After 3 h the mixture was washed through a short silica column using ether, the solvents were evaporated and the crude product (2.22 g) chromatographed on silica using light petroleum–ether (90:10, v/v) to give 1,192-*dibromodononacontahecta*-12,24,-36,48,60,72,84,96,108,120,132,144,156,168,180-*pentadecaene*, mp 37.5–39 °C (Found: C, 82.1; H, 12.7. $C_{192}H_{354}Br_2$ requires C, 81.70; H, 12.64%); $\delta_H(CDCl_3)$ 5.35 [m, 15 × (CH=CH)] and 3.4 (t, 2 × CH_2Br), in the ratio 30:3.87.

(iii) The C_{192} dibromo compound from (ii) (2.02 g), magnesium powder (1.00 g) and ether (12 ml) freshly distilled from $LiAlH_4$, were heated together under reflux with anhydrous 1,2-dibromoethane being added (two drops at a time) to the mixture every 30 min over 2 h. Carbon dioxide, dried by passage through conc. sulfuric acid then through molecular sieves, (4 Å) was bubbled through the mixture for 20 min, which was then acidified (4 mol l^{-1} H_2SO_4), extracted with ether, the extracts dried and the solvent evaporated. The crude residue was chromatographed on silica using light petroleum–ether (90:10, v/v) as eluent. The slowest moving component was *tetranonacontahecta*-13,25,37,49,61,73,85,97,109,121,133,145,157,169,181-*pentadecaen*-1,194-*dioic acid*, mp 43–44.5 °C (Found: C, 84.3; H, 12.8. $C_{194}H_{356}O_4$ requires C, 84.64; H, 13.03%); $\delta_H(CDCl_3)$ 5.35 [m, 15 × (CH=CH)], 2.36 (t, 2 × CH_2C*H*$_2$$CO_2$H), 1.95 (m, 30 × C*H*$_2$CH=), 1.65 (q, 2 × C*H*$_2$$CH_2CO_2$H) and 1.3 [128 × ($CH_2$), *i.e.* 256 protons], in the ratio 30.0:3.92:59:3.75:252.

(iv) The C_{194} dicarboxylic acid from (iii) was hydrogenated as described before, but extracted for 7 days to give *tetranonacontahectane*-1,194-*dioic acid* **58** (0.59 g), mp 131–133 °C (Koffler block) (Found: C, 83.6; H, 14.0. $C_{194}H_{386}O_4$ requires C, 83.72; H, 13.98%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of any alkenic absorptions; δ_H 2.4 (t, 2 × $CH_2CH_2CO_2H$), 1.7 (q, 2 × $CH_2CH_2CO_2H$) and 1.4 (m, 188 × CH_2, *i.e.* 376 protons), in the ratio 4.0:4.17:371.

(c) $HO_2(CH_2)_{48}CO_2H$. (i) The C_{48} bromo aldehyde **17** was converted, by the method described before, into 48-*bromooctatetraconta*-12,24,36-*trienol*, mp 45.5–48 °C (Found: C, 75.9; H, 12.1. $C_{48}H_{91}BrO$ requires C, 75.45; H, 12.00%).

(ii) The C_{48} bromo alcohol from (i) was reacted with PBr_3 as described before, to give the C_{48} *dibromo compound*, which in turn reacted with magnesium–carbon dioxide to give *pentaconta*-13,25,37-*trien*-1,50-*dioic acid*; $\delta_H(CDCl_3)$ 5.35 [m, 3 × (CH=CH)], 2.36 (t, 2 × $CH_2CH_2CO_2H$), 1.95 (m, 6 × $CH_2CH=$), 1.65 (q, 2 × $CH_2CH_2CO_2$) and 1.3 [32 × (CH_2), *i.e.* 64 protons], in the ratio 6.0:3.95:12.0:3.97:68.7.

(iii) The C_{50} dicarboxylic acid was hydrogenated as described before, to give *pentacontane*-1,50-*dioic acid* **57** (0.46 g), mp 127.5–130 °C (Koffler block, but two peak maxima on DSC) (Found: C, 79.0; H, 13.1. $C_{50}H_{98}O_4$ requires C, 78.68; H, 12.94%); the ^1H NMR in 1,1,2,2-tetrachloro[$^2H_2$]ethane at 120 °C showed the absence of any alkenic absorptions; δ_H 2.4 (t, 2 × $CH_2CH_2CO_2H$), 1.7 (q, 2 × $CH_2CH_2CO_2H$) and 1.4 (m, 44 × CH_2, *i.e.* 88 protons), in the ratio 4.0:3.87:91.

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