

Studies on the Synthesis of Linear Aliphatic Compounds. Part. 3¹ The Synthesis of Paraffins with Very Long Chains

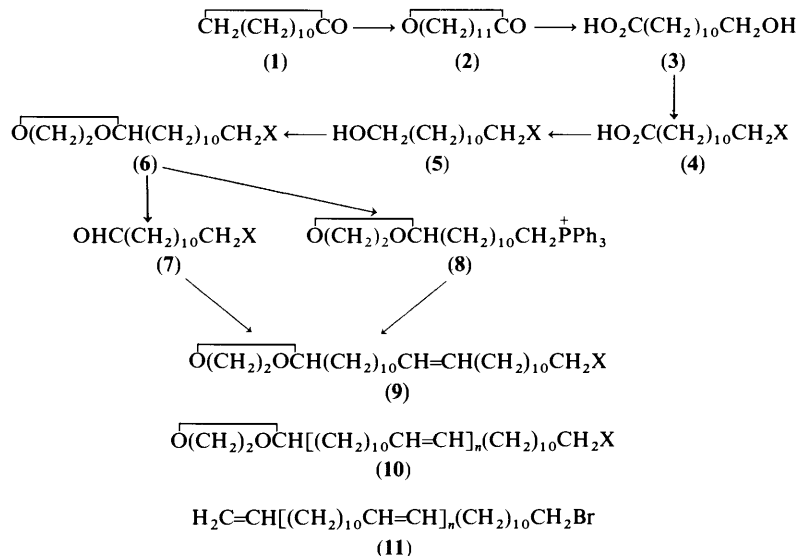
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The approach derived in Part 2 has been modified to increase the purity and yield of intermediates. The C_{12} starting materials have been doubled in chain length five times, and by using components of similar or different chain length in Wittig condensations ω -halogeno-acetals with $12n$ carbon atoms have been made up with n up to 32. They have been converted into paraffins with 102, 104, 150, 198, 246, 294, and 390 carbon atoms. Those paraffins with 150 or more carbon atoms show chain-folding in the crystalline state; this observation is contributing to the understanding of chain-folding behaviour long known in linear polyethylene but hitherto unknown in essentially pure paraffins.

The route to n -paraffins described in the previous paper (Scheme 1, $X = Br$) was intended to reach those compounds which, because they exceed in chain length the unit of folding in linear polyethylene (typically C_{70} — C_{150}), might throw light on this phenomenon. To achieve this, the yields in each doubling

distillation or chromatography on silica. Other minor impurities (<1%) in the bromo acetal (6) were the corresponding chloroacetal and the 12-bromododecanal and 12-bromododecan-1-ol from which it was prepared—these are relatively harmless.



Scheme 1.

operation required improvement; more important, the need for high purity (>90%, preferably *ca.* 99%) in the final product required less than 0.1% of those contaminants giving rise to paraffins of the wrong chain-length in early intermediates. To these ends our route has been re-examined, beginning with the development of efficient g.l.c. methods for C_{12} — C_{36} intermediates.

The starting material (1) proved to be free from contaminants in the C_8 — C_{16} range (<0.1%). The bromo acetal (6)² contained 0.2—2% of a contaminant found to be the bis acetal of dodecanedial, an undesirable impurity which would give a C_{36} diacetal in (9) and, ultimately, much longer paraffins in the final product, unlikely to be eliminated by crystallisation. It was traced to dodecane-1,12-diol in (5) and to dodecane-1,12-dioic acid in (3), and could be avoided by thorough washing of the dodecanolide with alkali [incomplete reaction (3)→(4) would also lead to this problem]. Neither at the stage of bromododecanol (as diol) nor at that of the bromo acetal (6) (as bis acetal) could it be removed by crystallisation, according to g.l.c. measurements, but at the latter stage it was readily removed by

in the conversion of the bromo acetal (6) into the corresponding aldehyde (7), residual C_{12} bromo acetal could be an undesirable impurity in the desired product (9). When the C_{12} bromo acetal was converted into the triphenylphosphonium salt (8), slight deprotection of the aldehyde function was detected in the crude product (band at 1730 cm^{-1})—another danger, since the Wittig reaction would then give a small amount of the C_{36} analogue (10; $n = 2$, $X = Br$). Thus, our synthesis would lead to products of n carbon atoms containing homologues with $(n + 12)$ and $(n - 12)$ atoms, *i.e.* would encounter the same problems as the oligomerisation methods discussed in the previous paper. G.l.c. analysis showed that the chromatographic separation of (6) and (9) was easy; even better, compound (6) was also easily removed by the crystallisation of the *cis-trans* mixture of (9), being much more soluble. On the contrary, crystallisation failed to separate the C_{36} dienal acetal (10; $n = 2$, $X = Br$), which concentrated in the solid phase, while in normal chromatography on silica it eluted ahead of the main fraction and was not separated efficiently. Medium-pressure chromatography at high resolution or short-path

distillation at low pressure was needed to remove it completely. As this was tedious, it was better to use the recrystallised C_{12} acetalphosphonium salt. In later chain-doubling sequences, where phosphonium salts were non-crystalline, it was necessary to re-protect the aldehyde group of the phosphonium salt. Surprisingly, ethylene glycol could be washed out of the salts by aqueous extraction, without loss.

The use of ether (12 + 12→24) or hexane (later stages) for Wittig reactions¹ gave good yields up to C_{48} , but proved to be a demanding and unreliable reaction, mainly because of the need to exclude air and water. Among other variants of the Wittig reaction, we tried that due to Boden,³ in which the phosphonium salt is stirred with the aldehyde, potassium carbonate and 18-crown-6 in tetrahydrofuran (THF), while being heated under nitrogen. This gave a good yield, with (despite the emphasis³ on *trans*-isomers when aryl-substituted olefins were involved) nearly as high a *cis/trans* ratio as in ether. This variant proved more reproducible and gave yields which declined with chain length less rapidly than was observed in our earlier work;¹ thus it became our method of choice. However, we at once encountered new nonpolar by-products which proved to be compounds (**11**; $n > 1$), derived from methyltriphenylphosphonium salts, formed when trimethyl orthoformate was added to reactions between bromoacetals and triphenylphosphine to retain anhydrous conditions, and not removed from the non-crystalline phosphonium salts. 2,2-Dimethyldioxolane served the same purpose without introducing any by-product.

When crude products from Wittig reactions carried out under Boden's conditions³ were chromatographed on silica-gel, it was difficult to separate unchanged aldehydes with 12, 24, or 48 carbon atoms from the bromo acetals having 24, 48, or 96 carbon atoms which were the main products. Sodium borohydride converted them into primary alcohols, and they were then easily removed (although it was then hard to separate them from the more polar by-products reported below). However, the chromatographically purified bromo acetals showed C=O stretching bonds (at 1740 cm^{-1} rather than at 1730 cm^{-1} for the aldehydes) and no absorption at 2700 cm^{-1} (HCO stretching). Reduction with lithium aluminium hydride removed the 1740 cm^{-1} absorption band, and on chromatography essentially pure bromo acetals were obtained, along with ω -hydroxy acetals (**10**; X = OH). Evidently some reaction of $BrCH_2$ compounds with potassium carbonate—18-crown-6 had taken place, giving carbonate esters (**10**; X = O-CO₂), which also co-chromatographed with bromo-acetals and co-crystallised with them. When this was known, lithium aluminium hydride reduction of crude Wittig products, from which most of the phosphine oxides had been removed by extraction from petroleum by acetonitrile or brief chromatography—otherwise these were reduced to phosphines and became hard to remove—became standard practice; although no signs of reduction of $BrCH_2$ groups were seen, we added bromoethane (6 ml) as a prophylactic measure.

All bromo compounds were frequently contaminated with the corresponding chloro compound, to an extent which varied unpredictably.⁴ Many hypotheses about the origin of these were tested before the culprit was shown to be the carefully purified solvent dichloromethane abetted by adventitious phase-transfer catalysts which resisted washing from glass surfaces and probably included the phosphonium salts used in the synthesis. This reaction was strongly retarded by hydroxylic solvents, carboxylic acid groups, and water, which presumably solvated the halide ions present. Once this was known $-CH_2Br$ was conserved by substituting bromoethane for dichloromethane in handling such compounds. However, before this point a Wittig reaction between two C_{48} components⁵ was saved from complete failure by just this process; the reaction of

$-CH_2Br$ with potassium carbonate-crown ether, allowed to proceed too long, converted to carbonate some 95% of the $BrCH_2-$ grouping present, but only some 20% of the substantial amount of chloride was lost, so that a reduced but not negligible yield of C_{96} halogenoacetal, mainly chloride, was obtained.

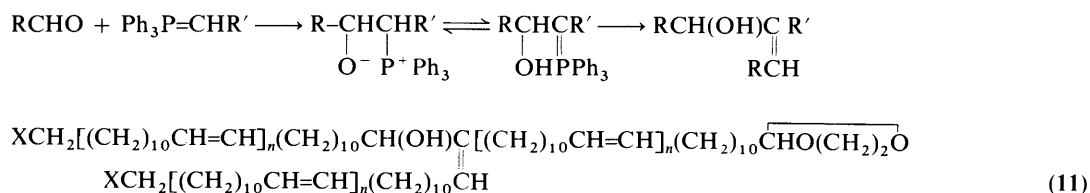
Plainly, the reactivity of $-CH_2Br$ toward nucleophiles imperilled our route, in which it should play the part of an unreactive form b of the nucleophile $B = \bar{C}H\bar{P}Ph_3$;¹ if we could use $-CH_2Cl$ instead, loss of yield through such processes would be diminished. Attempts to convert primary chlorides directly into alkyltriphenylphosphonium chlorides were unpromising, as the large molecular weights and low polarity of the media enforced inconveniently long reaction periods even with the bromides, some 250 times more reactive to triphenylphosphine. Addition of ionic bromides as catalysts proved ineffective and we turned to the method of Willy *et al.*⁶ for converting chlorides into bromides and *vice versa*, *i.e.* heating with a large excess of solvent containing the desired halogen, plus a salt as catalyst. They used *N*-methylpyrrolidone as solvent and alkali metal halides; these conditions are inapplicable to our long-chain compounds, which were immiscible with the solvent. The use of tetra-alkylammonium salts and neat 1-bromopropane or 1,2-dichloroethane gave better results, the chloride→bromide reaction proceeding in 97.5% yield in 42 h, and the reverse process in only 4h (*cf.* 3 d and 32 d, respectively⁶). The rationale and advantages of these and similar interconversions have been described.⁴

We therefore changed to the use of $ClCH_2-$ termini, beginning with 12-chlorododecanoic acid, obtained in good yield from the hydroxy acid by the use of thionyl chloride, with the addition of tetrabutylammonium chloride to encourage the known process (this needed to be >99.9% complete, see above):



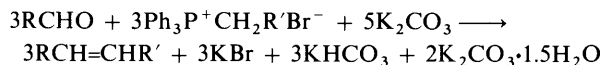
Conversion into the corresponding chlorododecanol and chlorododecanal and its acetal proceeded uneventfully. The chloro acetal was converted *via* 12-bromododecanal ethylene acetal into the phosphonium bromide, but the Wittig reaction between this and the C_{12} chloro acetal led to exchange of halogen, giving a mixture of C_{24} chloro- and bromo-acetals. Repeated shaking of a dichloromethane solution of the C_{12} phosphonium bromide with saturated aqueous potassium chloride (5 × 20 ml) led to a crystalline salt which was mainly the chloride, despite the adverse phase-transfer equilibrium constant; the C_{24} Wittig product then contained *ca.* 3% rather than *ca.* 30% of bromide. The phosphonium toluene-sulphonate was readily prepared, but gave a poor yield in the Wittig reaction. Thus the preparation of a mixed-halogen C_{24} Wittig product followed by two halide interconversions, using 1,2-dichloroethane and 1-bromopropane, was favoured. For the later stages, effect on a smaller scale, the ion-exchange process was preferred.

All our Wittig products appeared to contain two polar by-products [as well as the ω -hydroxy acetals (**10**; X = OH) also present when a lithium aluminium hydride reduction was added to our procedure], plus primary alcohols (**5**) from excess of ω -halogenoaldehyde. The alkyldiphenylphosphine oxides (**10**; X = Ph_2PO) were always present. These are derived from the action of base and adventitious water on alkyltriphenylphosphonium salts, and their presence may be responsible for the belief that triphenylphosphine oxide is hard to remove after Wittig reactions—in our experience, it is not. Typically yields were *ca.* 7%. Although the unsaturated alcohols (**11**) have been prepared before, they have not been reported as Wittig by-products; they probably result from the sequence:



We considered working with pure all-*cis* isomers, instead of statistical mixtures, and to that end subjected to (*cis* + *trans*) C₂₄ bromoacetal to urea clathration. A higher-melting *trans*-isomer was isolated without difficulty, free from absorption at 3 000 cm⁻¹ (*cis*-CH=CH-str.). It gave a crystalline triphenylphosphonium salt, and on hydrolysis a crystalline aldehyde; when these were coupled, a C₄₈ bromoacetal was obtained from which a small yield of all-*trans* C₄₈ triene acetal, m.p. 54–55 °C was obtained. The main fraction, *cis* C₂₄ bromo acetal, was free of absorption at 965 cm⁻¹ (*trans*-CH=CH out-of-plane bending) but neither it nor the derived phosphonium salt was much easier to purify than the *cis*-*trans* mixture, and we were unable to isolate an all-*cis* C₄₈ bromo-acetal. We concluded that there was no advantage in working with pure isomers. The *cis*/*trans* ratio was estimated at 4.

Although not all of the Wittig by-products at each stage of the synthesis were isolated, all appeared to be formed. The rates of reaction were variable, moreover, the successive chain-doubling sequences differed from case to case—as the molecular weight increased, molar concentrations inevitably fell, and ratios of first-order and second-order process therefore varied. Consideration of the stoichiometry of the reaction suggested that the formation of alkylidiphosphine oxide would be minimised if enough potassium carbonate were used to remove the water formed in its most stable hydrate, K₂CO₃·1.5H₂O—a large excess of carbonate would, of course, favour attack at -CH₂Br or -CH₂Cl:



A 1:1:2 ratio which allowed for a little initial water, and a little unwanted reaction with -CH₂X was adopted. Yields were improved over our initial 1:1:1.5 ratio. As attack on -CH₂Br was appreciable in most Wittig reactions, and even -CH₂Cl was not entirely unreactive, we preferred to remove halogen with lithium triethylborohydride before, rather than after, Wittig condensation whenever possible.

The final steps for converting bromo acetals into paraffin hydrocarbons in Part 2 required the replacement of Br by H, hydrolysis and Wittig condensation with a C₈ monofunctional phosphorane derived from 1-bromo-octane, and hydrogenation. When ClCH₂- was used instead of BrCH₂- the 'superhydride' reduction required a much longer reaction time but did go to completion, according to n.m.r.; however, further experience has shown this process to be unreliable. The 1-bromo-octane used was only *ca.* 97.5% pure, and neither it nor the derived triphenylphosphonium salt, m.p. *ca.* 40 °C, was easily purified. 1-Bromohexane, however, was obtained >99.9% pure by distillation through a spinning-band column, and its triphenylphosphonium salt had m.p. 200 °C and crystallised well; we used it in most of the present work.

Application of the various improvements allowed the C₉₆ bromo acetal to be prepared pure, and in larger quantity than when Wittig reagents were prepared in DMSO and extracted;¹ hence two further doublings were achieved, to C₁₉₂ and C₃₈₄ acetals. Wittig reactions between components of different chain lengths also gave us C₁₄₄, C₂₄₀, and C₂₈₈ acetals. These remarkable compounds were all tractable, giving *ca.* 10%

solutions in deuteriochloroform in which single protons, and even the signals from impurities, *e.g.* -CH₂Cl compounds in bromo acetals, could be identified in 200 MHz n.m.r. spectra. The bromo acetals were converted by the methods of Part 2¹ into polyenes with 102, 150, 198, 246, 294, and 390 carbon atoms* which were hydrogenated in ethyl palmitate at 130 °C to n-paraffins⁵ which, with one exception, gave single sharp peaks at progressively shorter retention times in g.p.c. The *n* = 294 paraffin was accidentally contaminated with, presumably, the *n* = 198 paraffin, and gave a shoulder on the chromatogram corresponding to *ca.* 8% of the latter. The solid-state properties of these materials have already proved to be interesting⁷ and, indeed, important in the study of chain folding. This is most simply seen in m.p. behaviour, where the paraffins above C₁₉₈ are polymorphic, with the less stable polymorphs having folded chains. The m.p. of a paraffin with *n* carbon atoms crystallising with *x* parallel chains (*x* - 1 folds) approximates to that of an unfolded paraffin with *n/x* carbon atoms. Recrystallisation as a less folded polymorph can occur faster or slower than the process of melting, according to chain length and rate of heating. Differential scanning calorimetry revealed these effects, well seen in n-C₂₉₄H₅₉₀, m.p. 123 and 128 °C. The elucidation by Raman spectroscopy and low-angle X-ray diffraction of this phenomenon has been described,⁷ and work continues. Broadly similar results were announced⁸ (in a note received for publication on the same day as our own⁵) describing work on paraffins obtained by the oligomerisation route, but these gave less clear-cut results; interlaminal distances did not so exactly correspond to *n/x* carbon atoms, and the crystals showed some amorphous content. It seems possible that greater inhomogeneity in chain length *could* be responsible for such divergences, in that even in the most nearly idealised packing (A) of a once-folded polymorph a few longer or shorter chains will lead to residual disorder (B) and to less defined, broader interlaminal zones (see Figure). We would emphasise that our specimens also cannot be expected to be 100% homogeneous but it would not be surprising if, say, the 246-carbon paraffin contained only 0.5–5% of the (*n* + 12) homologue (the most probable impurity). The presence of the hexamer and octamer in the dehydroheptamer of the compound HC≡C(CH₂)₂₀C≡CH might give rise to more appreciable disorder in the crystals of the C₁₆₈ paraffin derived from it, than in paraffins formed *via* dimers and trimers,⁸ or in the present work.

Experimental

12-Chlorododecanoic Acid.—A mixture of 12-hydroxy-dodecanoic acid (27 g), tetrabutylammonium chloride (3.75 g) and thionyl chloride (25 cm³) was stirred until gas evolution

* The 12 mg specimen of the C₃₉₀ polyene hydrocarbon, molecular weight (for ¹²C and ¹H) 5 428, amounted to some 1.3 × 10¹⁸ molecules. It should be a mixture of 2³², *i.e.* 4 294, 967, 296 isomers, the all-*trans* form, on the basis that the Wittig reaction gives 80/20 mixtures of *cis* and *trans* isomers, being present to the extent of 1 in 5³² or about 4 × 10⁻²³; thus, this and indeed many of the other mainly *trans* isomers were probably absent from our product, as a consequence of the quantisation of matter! Such mixtures of 10³–10¹⁰ isomers 'crystallised' reasonably well and had fairly sharp m.p.s, all in the range 30–50 °C, despite the fact that the most abundant isomer (all-*cis*) amounted to as little as 0.08% of the product.

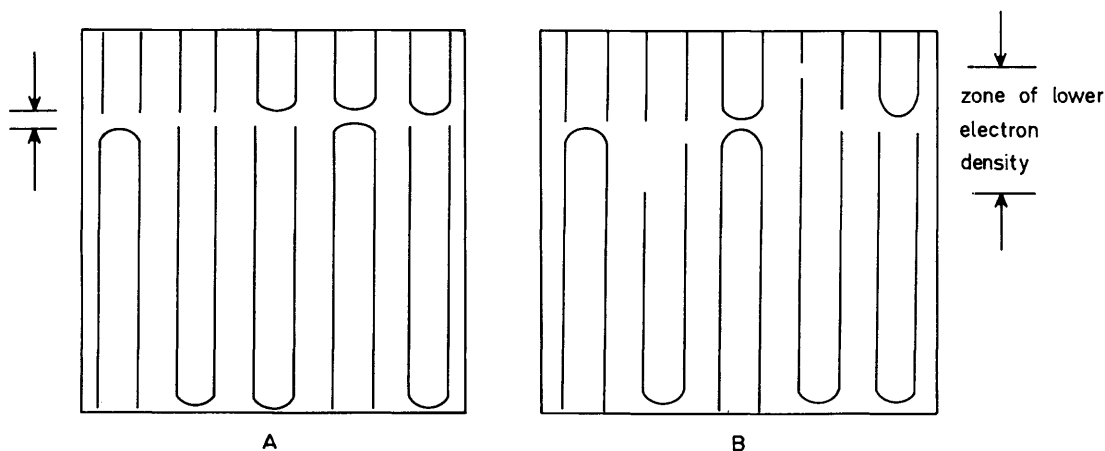


Figure.

Table 1. G.l.c. data

Compound	System A ^a 1m, 25% Embaphase		System B ^a 1m, 7% Dextsil	
	T (°C)	Retention time (min)	T (°C)	Retention time (min)
$\overbrace{\text{CH}_2(\text{CH}_2)_{10}}^{\text{CO}}$	200 (150)	3.5 (1.6)		
$\overbrace{\text{CO}(\text{CH}_2)_{11}}^{\text{O}}$	(150)	(17.5)		
$\text{HO}(\text{CH}_2)_{11}\text{CO}_2\text{Me}$	200 ^b	8 ^b		
$\text{Br}(\text{CH}_2)_{11}\text{CO}_2\text{Me}$	200	11.5		
$\text{Cl}(\text{CH}_2)_{11}\text{CO}_2\text{Me}$	200 ^b	8 ^b		
$\text{MeO}_2\text{C}(\text{CH}_2)_{10}\text{CO}_2\text{Me}$	200	9.5		
$\text{Br}(\text{CH}_2)_{11}\text{CH}_2\text{OH}$	200	10		
$\text{Cl}(\text{CH}_2)_{11}\text{CH}_2\text{OH}$	200	7		
$\text{HO}(\text{CH}_2)_{11}\text{CH}_2\text{OH}$	200	8		
$\text{Br}(\text{CH}_2)_{11}\text{CHO}$	200	8		
$\text{Cl}(\text{CH}_2)_{11}\text{CHO}$	200	5.5		
$\text{Br}(\text{CH}_2)_{11}\text{CH}(\text{OMe})_2$	200	14		
$\text{Br}(\text{CH}_2)_{11}\text{CHO}_2\text{C}_2\text{H}_4$	200 (220)	20 (10)	200	8
$\text{Cl}(\text{CH}_2)_{11}\text{CHO}_2\text{C}_2\text{H}_4$	200	14.5	200	6
$\text{Br}(\text{CH}_2)_{11}\text{CH}=\text{CH}(\text{CH}_2)_{10}\text{CHO}$			280	9
$\text{Cl}(\text{CH}_2)_{11}\text{CH}=\text{CH}(\text{CH}_2)_{10}\text{CHO}$			280	7
$\text{Br}(\text{CH}_2)_{11}\text{CH}=\text{CH}(\text{CH}_2)_{10}\text{CHO}_2\text{C}_2\text{H}_4$			280	15.5
$\text{Cl}(\text{CH}_2)_{11}\text{CH}=\text{CH}(\text{CH}_2)_{10}\text{CHO}_2\text{C}_2\text{H}_4$			280	12
$\text{Cl}(\text{CH}_2)_{11}[\text{CH}=\text{CH}(\text{CH}_2)_{10}]_2\text{CHO}_2\text{C}_2\text{H}_4$			330	13.5
$\text{Br}(\text{CH}_2)_{11}[\text{CH}=\text{CH}(\text{CH}_2)_{10}]_2\text{CHO}_2\text{C}_2\text{H}_4$			330	17.5
$\text{C}_2\text{H}_4\text{O}_2\text{CH}(\text{CH}_2)_{10}\text{CHO}_2\text{C}_2\text{H}_4$	200	28.5		
$n\text{-C}_{16}\text{H}_{34}$	200	4.5		
$n\text{-C}_{16}\text{H}_{33}\text{Br}$	200	17		
$n\text{-C}_{16}\text{H}_{33}\text{OH}$	200	13		
18-Crown-6	200	11		
Ph_3PO			280	3

^a In all cases the carrier gas was nitrogen, flow rate ($5\text{ cm}^3\text{ min}^{-1}$) (column A) or $30\text{ cm}^3\text{ min}^{-1}$ (column B). ^b In view of this coincidence, we used 10% Carbowax at 200°C , on which the chloro and hydroxy esters had R_t of 7 and 24 min, respectively. ^c $\text{CHO}_2\text{C}_2\text{H}_4$ implies the 1-dioxolan-2-yl group.

was moderated, and then heated under reflux with continued stirring. The excess of thionyl chloride was removed under reduced pressure leaving the acid chloride, which when added to a mixture of methanol and pyridine gave a specimen of the methyl ester, 99.9% of which formed a single g.l.c. peak. Addition to potassium hydroxide solution (200 cm^3 , 5%) with stirring, followed by potassium carbonate until just alkaline gave a solution which was acidified and extracted with ether. The extract was washed with water, dried, and evaporated, leaving an oil (28.5 g, 97%) which was recrystallised from light petroleum (b.p. $30\text{--}40^\circ\text{C}$) after treatment with charcoal, to

give the acid (24.4 g, 83.5%), m.p. $43\text{--}44^\circ\text{C}$ (lit.,⁹ m.p. $42.5\text{--}43.5^\circ\text{C}$).

12-Chlorododecan-1-ol. This was prepared from the foregoing acid (23.4 g) and borane-dimethyl sulphide (12.8 g) in ether (128 cm^3) by the method used² for the bromine analogue. The alcohol (20.2 g, 91.5%) had m.p. $27\text{--}28^\circ\text{C}$ (lit.,¹⁰ 28°C), and a dodecane-1,12-diol content of ca. 0.06% by g.l.c.

12-Chlorododecanal Ethylene Acetal.—This was prepared from the acid (95 g) in dichloromethane (284 cm^3) using oxalyl chloride (80 g), DMSO (96.5 cm^3) and triethylamine (320.5

Table 2. ^{13}C and ^1H n.m.r. of unperturbed terminal groups, $\text{XCH}_2\text{CH}_2\text{CH}_2-$

X	δ_{C}				δ_{H}			
	<i>ipso</i>	$\alpha(o)$	$\beta(m)$	$\gamma(p)$	<i>ipso</i>	$\alpha(o)$	$\beta(m)$	(<i>p</i>)
Cl		45.2	32.7	26.9		3.53	1.76	
<i>cis</i> CH=CH-	129.9	27.2			5.34	2.02		
<i>trans</i> CH=CH-	130.3	32.6			5.38	1.85		
POPh ₂		29.7	21.4	30.95		2.25	1.61	
$\ddot{\text{P}}\text{Ph}_3$		22.8	22.6	30.45		3.71	1.61	
POPh ₂ (Ar)	133.2	130.7	128.5	131.5		7.75	<i>ca.</i> 7.5	<i>ca.</i> 7.5
$\overset{\dagger}{\text{P}}\text{Ph}_3$ (Ar)	118.5	133.7	130.5	135.5		<i>ca.</i> 7.8	<i>ca.</i> 7.8	<i>ca.</i> 7.8
		$J(^{31}\text{P}-^{13}\text{C}, \text{Hz})$						
POPh ₂		70.3	3.9	14.65				
$\ddot{\text{P}}\text{Ph}_3$		49.6	4.6	15.6				
POPh ₂ (Ar)	97.7	9.8	11.7	1.95				
$\overset{\dagger}{\text{P}}\text{Ph}_3$ (Ar)	85.9	9.8	12.7	2.9				

cm^{-1}), as described² for the bromine analogue. The *acetal* (105.5 g, 93.5%) had m.p. 22–23 °C (Found: C, 63.9; H, 10.45. $\text{C}_{14}\text{H}_{27}\text{O}_2\text{Cl}$ requires C, 64.0; H, 10.35%). G.l.c. showed 99.2% purity, and no detectable chloroalcohol or dodecanedial diacetal.

24-Bromotetracos-12-enal Ethylene Acetal (cis and trans-Isomers).—A solution of 12-bromododecanal (44 g, containing 1.4% of its ethylene acetal) in THF (50 cm^3) was added to 11-(dioxolan-2-yl)undecyltriphenylphosphonium bromide (114.5 g, m.p. 138–140 °C, recrystallised), anhydrous potassium carbonate (55.6 g), 18-crown-6 (1.0 g) and THF (150 cm^3) with stirring. Stirring and heating under reflux were continued for 157 h, under a very slow stream of nitrogen. (Reaction times varied, the precipitation of triphenylphosphine oxide at the liquid/nitrogen interface giving some guidance, with g.l.c. analysis best for the 12 + 12→24 step.) The solvent was removed using a rotary evaporator and slightly reduced pressure, light petroleum (600 cm^3) was added, and the solid was filtered off and washed with more light petroleum. The combined light petroleum layers were washed with acetonitrile (3 × 100 cm^3), and then evaporated to give the crude product (71.2 g) (ν_{max} , 1 730–1 740 cm^{-1}) which was dissolved in ether (150 cm^3) and bromoethane (56 cm^3) and treated with lithium aluminium hydride (1.0 g). After 25 min at 20 °C hydrochloric acid (2M) was slowly added, followed by water (100 cm^3), and the aqueous layer was washed with ether (2 × 100 cm^3). The combined ether layer and washings were washed with 10% potassium carbonate and then brine, dried (Na_2SO_4), and evaporated. The residue, now free from absorption at *ca.* 1 740 cm^{-1} , was dissolved in 10% ether–light petroleum and chromatographed on silica gel (600 g) which had been stirred with the same solvent plus bromoethane (56 cm^3). The fractions essentially pure by g.l.c. and t.l.c. were combined and crystallised from light petroleum at –45 °C (CO_2 – CCl_4 – CHCl_3), giving (*cis* + *trans*) C_{24} bromodioxolane (55.8 g), m.p. 23–24 °C, ν_{max} (CS_2) 3 000 (*cis*-CH=CH str.), 1 145, 1 135, and 1 040 (C–O str.), 970 (*trans*-CH=CH out-of-plane bend), 725 (*cis*-CH=CH out-of-plane bend plus CH_2 rock), and 650 cm^{-1} (CBr str.); δ_{H} values as expected.¹ The C_{12} bromoacetal was found to be absent (<0.05%) by g.l.c., but 1.7% of the corresponding chloroacetal was present, plus 0.6% of minor unidentified impurities. The ether eluate from the column left a residue (6.0 g) which is discussed below. The following by-products were obtained:

12-Diphenylphosphinoxyldodecanal ethylene acetal, m.p. 91–93 °C, isolated after recrystallising the residue (3.9 g) from the acetonitrile layer (Found: C, 72.5; H, 9.0. $\text{C}_{26}\text{H}_{37}\text{O}_3\text{P}$ requires C, 72.9; H, 8.7%); ν_{max} , 1 200 (P=O str.), and 1 120 cm^{-1} (P–Ar str.); (*cis* + *trans*) 24-Hydroxytetracos-12-enal ethylene acetal, m.p. 48–50 °C, separated from the polar fraction by repeated chromatography and crystallisation (Found: C, 75.95; H, 12.2. $\text{C}_{26}\text{H}_{50}\text{O}_3$ requires C, 76.0; H, 12.3%); ν_{max} , 3 650 (OH str.), 3 000, 1 145, 1 135, 1 040, 970, and 750 cm^{-1} ; δ_{H} as expected; 13-(12'-Bromohydroxydodecyl)-24-bromotetracos-12-enal ethylene acetal (**11**; *n* = 0), m.p. 56–58 °C (Found: C, 62.1; H, 9.7; Br, 21.5. $\text{C}_{38}\text{H}_{72}\text{Br}_2\text{O}_3$ requires C, 61.95; H, 9.85; Br, 21.7%), its structure being confirmed by its i.r. and n.m.r. spectra.

The main component in this fraction was 12-bromododecan-1-ol, derived from unchanged bromododecanal.

Separation of Stereoisomers.—A solution of the (*cis* + *trans*) C_{24} bromodioxolane (28.2 g) in *n*-hexane (25 cm^3) was added to a saturated solution of urea (37.75 g) in ethanol, and the mixture cooled to 0 °C. The solid was collected and treated with water and then extracted with hexane; evaporation left *trans*-rich dioxolane (12 g). The filtrate was saturated with urea, cooled again, and filtered, the solid giving a mixed fraction (8.7 g), of predominantly *cis* isomer. The final filtrate was diluted with water and extracted with hexane and then ether, giving a further 7.2 g of *cis*-rich material. The latter two crops were recrystallised at –70 °C from light petroleum (3 × 200 cm^3), giving pure *cis*-24-bromotetracos-12-enal ethylene acetal (14.7 g), m.p. 23–24 °C (Found: C, 65.9; H, 10.7; Br, 17.0. $\text{C}_{26}\text{H}_{49}\text{BrO}_2$ requires C, 65.9; H, 10.4; Br, 16.9%); ν_{max} (CS_2) 3 000, 2 925, 2 850, 1 145, 1 135, 1 040, 940, 725, and 625 cm^{-1} , but no band at 970 cm^{-1} .

A solution of the *trans*-enriched acetal (12.0 g) in hexane (10 cm^3) was added to urea (15.2 g) in ethanol and cooled. When treated as before, virtually pure *trans* material (4.95 g) was obtained, which on crystallisation from light petroleum gave *trans*-24-bromotetracos-12-enal ethylene acetal, m.p. 48.5–50 °C (Found: C, 66.0; H, 10.5; Br, 17.0%); ν_{max} (CS_2) 2 925, 2 850, 1 145, 1 135, 1 040, 940, 970, 725, and 650 cm^{-1} , but no absorption at 3 000 cm^{-1} [note that the out-of-plane bending mode of *cis*-CH=CH– and rocking mode of ($-\text{CH}_2-$)_{*n*} coincide, but that as the intensity of the CH stretching band of *trans*-CH=CH– is negligible, the absorbance at 3 000 cm^{-1} is a measure of *cis*-content].

Triphenylphosphonium Salts.—These were obtained from the pure isomers by the method of Part 2¹ (using trimethyl orthoformate, which would be better omitted). The *cis* isomer was obtained in crystalline form, m.p. 40–43 °C, but could not be obtained analytically pure; however pure *cis*-23-(dioxolan-2-yl)tricos-12-enyltriphenylphosphonium iodide was obtained, m.p. 58–60 °C (Found: C, 67.3; H, 8.3; I, 16.3. C₄₄H₆₄IO₂P requires C, 67.5; H, 8.2; I, 16.2%). The *trans*-23-(dioxolan-2-yl)tricos-12-enyltriphenylphosphonium bromide, m.p. 93.5–95 °C, was easily purified (Found: C, 71.9; H, 8.9; Br, 11.0. C₄₄H₆₄BrO₂P requires C, 71.8; H, 8.8; Br, 10.9%). Despite aromatic C–H stretching bands at 3 030 cm⁻¹ in both isomers, the *cis* compound showed absorption at 3 000 cm⁻¹ absent in the *trans*-isomer, and the 970 cm⁻¹ band of the *trans*-bond could be seen in the latter; n.m.r. data on the salts were also as expected.

Deprotection¹ of the *trans*-acetal afforded *trans*-24-bromotetracos-12-enal, m.p. 32.5–35.5 °C (Found: C, 66.9; H, 10.8; Br, 18.6. C₂₄H₄₄BrO requires C, 67.1; H, 10.6; Br, 18.6%); ν_{\max} (CS₂) 2 925, 2 850, 2 820, 2 720, 1 730, 970, 725, and 650 cm⁻¹, and n.m.r. spectra as expected. The *cis* aldehyde did not crystallise.

24-Chlorotetracos-12-enal Ethylene Acetal.—12-Chlorododecanal (15.0 g) was prepared as described² for 12-bromododecanal and added to a mixture of 11-(dioxolan-2-yl)undecyltriphenylphosphonium bromide (42.8 g), potassium carbonate (20.8 g), and 18-crown-6 (1.0 g) in THF (150 cm³). After reaction for 158 h, treatment with lithium aluminium hydride and chromatography gave the C₂₄ halogeno acetal (21.8 g) which consisted of 71.1% chloro acetal and 26.6% bromo acetal, plus 2.3% of minor impurities by g.l.c. Such mixed halogeno acetals were converted into pure compounds as follows. (a) The foregoing mixture (11.1 g), tetrabutylammonium bromide (0.2 g) and 1,2-dichloroethane (50 cm³) were heated under reflux for 20 h (much longer than needed), when g.l.c. indicated the C₂₄ acetal to be 99% chloride. After isolation (yield almost quantitative) the (*cis* + *trans*) 24-chlorotetracos-12-enal ethylene acetal had m.p. 23–24 °C.

(b) A similar mixture of halogeno acetals (20.0 g), tetrabutylammonium bromide (30.1 g), 1-bromopropane (424 cm³), and 2,2-dimethyldioxolane (0.5 g) was heated under reflux for 46 h, cooled, and evaporated under reduced pressure. Light petroleum, b.p. 30–40 °C (150 cm³) and water (200 cm³) were added; the light petroleum layer was washed with water (2 × 200 cm³), dried, and evaporated. Analysis (g.l.c.) showed the presence of bromo aldehyde (*ca.* 2%) and chloro acetal (1%) in the residue (21.7 g), which was reprotected using ethanediol (0.36 g), toluene-*p*-sulphonic acid (12 mg), and bromoethane (150 cm³), the mixture being heated in a Soxhlet apparatus with 3 Å molecular sieve in the thimble. After isolation the neutral fraction (21.3 g) showed no absorption at 1 730 cm⁻¹; the only impurity was chloro acetal (*ca.* 1%) by g.l.c. It gave an almost quantitative yield of phosphonium salt.

48-Bromo-octatetraconta-12,24,36-trienal Ethylene Acetal.—A solution of the C₂₄ acetal phosphonium bromide (30.0 g, *cis/trans* mixture, non-crystalline) in toluene (50 cm³) was evaporated to small volume to remove water, and potassium carbonate (8.5 g), 18-crown-6 (0.3 g), and 24-bromotetracos-12-enal (17.4 g, *cis* + *trans*) in THF (50 cm³) were added. The mixture was heated under reflux and stirred under nitrogen for 136 h. The solvent was evaporated in a rotary evaporator, warm light petroleum (b.p. 40–60 °C; 200 cm³), was added, and the mixture was filtered. The filtrate was evaporated to a volume of 125 cm³, washed with acetonitrile (3 × 100 cm³) and then evaporated again, to leave a residue (29.75 g, 90% yield); the purity at this stage may be comparable with the final product from the method of Part 2¹), which showed some C=O

absorption. Reduction with lithium aluminium hydride, chromatography on bromoethane-impregnated silica gel, and recrystallisation from light petroleum gave the C₄₈ bromo acetal (17.25 g, 47.5% overall from 24-bromotetracosenyl acetal) as a mixture of eight isomers, m.p. 36–40 °C (Found: C, 74.5; H, 11.9; Br, 9.8. C₅₀H₉₃BrO₂ requires C, 74.5; H, 11.6; Br, 9.8%), with i.r. and n.m.r. spectra as expected, and essentially similar to those of specimens prepared by the earlier method.¹ From the polar fractions (5.4 g) repeated chromatography and crystallisation allowed the recognition of 24-bromotetracos-12-enol (*cis* + *trans*), 48-hydroxyoctatetraconta-12,24,36-trienal ethylene acetal (*cis/trans* mixture, m.p. 58–60 °C), and 25-(24-bromo-1-hydroxytetracos-12-enyl)-48-bromo-octatetraconta-12,24,36-trienal ethylene acetal (not obtained crystalline). All were identified by i.r. and n.m.r. spectra.

When the C₂₄ acetal triphenylphosphonium bromide was prepared in the presence of triethyl orthoformate,¹ 1-bromopentacos-12,24-diene was obtained in the least polar fractions, identified by its i.r. bands at 3 075, 990, and 910 cm⁻¹.

When the C₂₄ components contained *ca.* 2% of C₃₆ analogues, the C₄₈ bromo-acetal (8.5 g) contained a corresponding amount (*ca.* 4%) of its C₆₀ analogue. This was removed by careful flash chromatography on silica gel using 5 and 10% ether in light petroleum. Thus 4.4 g gave 3.25 g of pure C₄₈ acetal, plus 0.76 g of mixed fractions which were added to the remaining 4.1 g and gave a further 3.0 g of pure material. A third chromatogram on the mixed fractions gave a further 0.9 g of pure C₄₈ compound, the C₆₀ compound being concentrated in the remaining mixed fractions. Analysis was by t.l.c.; R_F values, C₄₈, 0.42; C₆₀, 0.45 (using 10% ether in light petroleum). The purified product had the correct ratio of n.m.r. signal intensities at δ 5.34 (olefin C–H) to δ 3.9 (acetal CH₂): required 1.5, found 1.5. When pure C₂₄ components were used, a minute amount (*ca.* 0.1%) of the C₇₂ bromo acetal, R_F value *ca.* 0.48, was found to be present in the early fractions of the preparative chromatogram and was efficiently removed by flash chromatography.

When pure *trans* C₂₄ components were used in a similar Wittig reaction, the all *trans*-48-octatetraconta-12,24,36-trienal ethylene acetal, m.p. 54–55 °C, was obtained on recrystallising the mixture. It resembled the mixed isomers spectroscopically except for the absence of bands attributable to *cis*-CH=CH- and higher intensities for *trans*-CH=CH-. The mixture of *cis*, *trans*, *cis*, and *all-cis*-trienals obtained when pure *cis*-C₂₄ components were used, m.p. 37.5–38.5 °C, could not be separated by clathration or crystallisation.

47-(Dioxolan-2-yl)heptatetraconta-12,24,36-trienyl-triphenylphosphonium Bromide.—The C₄₈ bromo acetal (8.5 g; mixture of isomers), triphenylphosphine (3 g), and butyronitrile (32 cm³) were heated under reflux for 41 h under nitrogen. After evaporation of the solvent the residue was heated with light petroleum (8 × 25 cm³), each portion being poured off; however, t.l.c. showed traces of triphenylphosphine to be still present. The gum was therefore dissolved in ether (10 cm³), light petroleum (50 cm³) was added, and the mixture was cooled to 0 °C. The amorphous material which separated was again precipitated in the same way, giving (after drying *in vacuo*) the salt (10.56 g, 94%) free from its covalent precursors according to t.l.c. (R_F , SiO₂, 10% methanol-dichloromethane 0.3, *cf.* triphenylphosphine 0.78, C₄₈ acetal 0.83).

96-Bromohexanonaconta-12,24,36,48,60,72,84-heptaenal Ethylene Acetal.—A mixture of the C₄₈ acetal triphenylphosphonium bromide (10.56 g), the C₄₈ bromo aldehyde (7.53 g), potassium carbonate (2.05 g), 18-crown-6 (72 mg), and THF (25 cm³) was heated under reflux and stirred for 232 h. The product was isolated with light petroleum (100 cm³) and the

extract was washed with acetonitrile ($2 \times 100 \text{ cm}^3$) and evaporated. The residue (15.2 g) showed carbonyl absorption and was treated with lithium aluminium hydride (150 mg), as described for lower analogues. Chromatography of the residue (14.6 g) on silica gel (600 g) previously treated with bromoethane (25 cm^3) using 10% ether–light petroleum gave some early fractions containing the C_{96} acetal (1.66 g) free from polar materials, but the main fraction (6.97 g) was mixed; pure ether eluted polar by-products (5.1 g), which appeared to be similar to those obtained in Wittig syntheses of lower analogues. The mixed fractions were re-chromatographed on silica gel (800 g), which removed *ca.* 1 g of polar material but gave no acceptable C_{96} bromo acetal. Flash chromatography (4 cm column, 10% ether–light petroleum) in three batches largely resolved the mixture, a fourth chromatogram being needed for mixed fractions. When all material homogeneous to t.l.c. was combined and recrystallised, the C_{96} bromo acetal (5.76 g, 38% based on C_{48} bromo acetal) was obtained as a mixture of 128 isomers, m.p. 45–51 °C (Found: C, 80.1; H, 12.2; Br, 5.2. $\text{C}_{98}\text{H}_{181}\text{BrO}_2$ requires C, 80.0; H, 12.4; Br, 5.4%). I.r. and n.m.r. spectra were as expected; the ^1H n.m.r. spectrum was checked quantitatively, intensities for types of proton being, within experimental error, as calculated.

This compound was best purified by normal column chromatography of the initial Wittig product to remove alkyl-diphenylphosphine oxide, then reduction, then flash chromatography.

95-(*Dioxolan-2-yl*)pentanonaconta-12,24,36,48,60,72,84-heptaenyltriphenylphosphonium bromide was prepared from the foregoing bromo acetal (517 mg) and triphenylphosphine (120 mg) in butyronitrile (2.5 cm^3) which were heated under reflux for 69 h in nitrogen. The crude product (650 mg) was soluble in light petroleum, but was purified by flash chromatography on a 3 cm column using 5% methanol–dichloromethane. Fractions were analysed by t.l.c. using 5% methanol–dichloromethane; triphenylphosphine had R_F 0.90, the C_{96} bromo acetal 0.95, and the salt 0.30. Early fractions yielded the precursors (120 mg), and later fractions the salt (510 mg, 84%), which had partly deprotected and was reprotected by the method used for the C_{48} analogue, giving a glassy solid with i.r. and n.m.r. spectra as expected.

When a sample of C_{96} halogenoacetal (3.5 g) containing *ca.* 20% of chloride was treated in this way, the covalent fraction, after separation of the triphenylphosphine, was practically pure C_{96} chloro acetal. When heated with the same weight of tetrabutylammonium bromide (5 mol) in bromobutane for 45 h at 80 °C (unnecessarily vigorous conditions) and re-protected, it gave a quantitative yield of *ca.* 99% pure C_{96} bromo acetal (analysed by ^1H spectrum in the XCH_2 region), R_F (SiO_2 , 10% ether–light petroleum) 0.62.

96-Bromohexanonaconta-12,24,36,48,60,72,84-heptaenal.—The C_{96} bromo acetal (1.0 g) was hydrolysed on silica gel impregnated with 25% toluenesulphonic acid in 1:1 sulpholane–water, giving the aldehyde, m.p. 44–48 °C (Found: C, 80.8; H, 12.3; Br, 5.5. $\text{C}_{96}\text{H}_{177}\text{BrO}$ requires C, 80.8; H, 12.5; Br, 5.6%), with i.r. and n.m.r. spectra as expected.

192-Bromodononacontahecta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180-pentadecaenal Ethylene Acetal.—A mixture of the C_{96} halogeno acetal (1.5 g, bromo:chloro 4:1), the C_{96} acetal phosphonium bromide (2.0 g), potassium carbonate (320 mg), 18-crown-6 (20 mg) and THF (15 cm^3) was heated under reflux in nitrogen for 140 h. Isolation of the Wittig product and lithium aluminium hydride reduction gave a crude product (3.2 g) free from carbonyl absorption but unexpectedly dark and malodorous. Flash chromatography on a 6 cm

column with 2.5% ether–light petroleum gave homogeneous fractions (600 mg) which were crystallised, giving the C_{192} halogeno acetal (0.49 g), m.p. 41–45 °C, with i.r. and n.m.r. spectra as expected, bromide–chloride ratio *ca.* 1:4, R_F 0.57 using 5% ether–light petroleum as eluant. When this product (200 mg) was heated under reflux in 1-bromobutane (3 cm^3) with tetrabutylammonium bromide (117 mg) for 48 h and the neutral product was isolated (179 mg), flash chromatography gave the bromo acetal (170 mg), showing a triplet centred at δ 3.40 (BrCH_2) but no absorption at δ 3.53 (ClCH_2), and having the expected ratio of the signals at δ 5.34 (HC=) to δ 3.90 ($\text{C}_2\text{H}_4\text{O}_2$ of acetal) (Found: 7.3, required 30/4 = 7.5).

191-(*Dioxolan-2-yl*)hennonacontahecta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180-pentadecaenyltriphenylphosphonium Bromide.—The C_{192} bromo acetal (160 mg), triphenylphosphine (22 mg), butyronitrile (3 cm^3), and toluene (1 cm^3 —the long-chain compound was immiscible with boiling butyronitrile) were heated under reflux in nitrogen for 65 h. Isolation of the product by flash chromatography on a 2 cm column using 5%, then 10% methanol–dichloromethane gave starting materials (107 mg) followed by the salt (64.5 mg). The starting materials plus more triphenylphosphine (100 mg) were heated in butyronitrile (3 cm^3) and toluene (1 cm^3) for a further 114 h, when isolation gave a second batch of salt (59.8 mg). The two crops were reprotected, using ethanedilol (100 mg) and toluene-*p*-sulphonic acid (10 mg) as described for lower analogues. The C_{192} salt was obtained as a brown glass with the n.m.r. and the ratio of olefinic to ethylene acetal protons as expected; R_F (SiO_2 , 10% $\text{MeOH-CH}_2\text{Cl}_2$, I_2 , 0.4). The use of a large excess of triphenylphosphine is clearly desirable for the preparation of such long-chain salts in good yield.

Wittig reactions were more successful when the terminal halogen atoms were replaced by hydrogen. Thus hexanonaconta-12,24,36,48,60,72,84-heptaenal ethylene acetal was prepared from its bromo analogue (510 mg), in THF (1 cm^3) and lithium triethylborohydride (1.4 cm^3 , 1M, in THF), stirred at 25–30 °C for 4 h. After addition of water, isolation of the product gave the acetal (460 mg, 96%), m.p. 42–47 °C (Found: C, 84.7; H, 12.9. $\text{C}_{98}\text{H}_{182}\text{O}_2$ requires C, 84.5; H, 13.2%), its i.r. spectrum resembling that of the starting material save for the band at 650 cm^{-1} ; in its n.m.r. spectrum a triplet at δ 0.88 (CH_3CH_2) replaced one at δ 3.40 (BrCH_2CH_2); R_F (10% ether–light petroleum on silica) 0.65, *cf.* 0.61 for the bromodioxolane. Hydrolysis on silica gel gave hexanonaconta-12,24,36,48,60,72,84-heptaenal, m.p. 42–46 °C (Found: C, 85.4; H, 13.1. $\text{C}_{96}\text{H}_{178}\text{O}$ requires C, 85.5; H, 13.3%), with i.r. and n.m.r. spectra as expected. Similarly, the C_{192} bromo and chloro acetal was reduced for 4 h, but some 22% of ClCH_2 remained; two further reductions were needed before the halogen-free C_{192} acetal (98% yield) was obtained; evidently chlorides are reduced much more slowly than bromides. Hydrolysis gave dononacontahecta-12,24,36,48,60,72,84,96,108,120,132,144,156,168,180-pentadecaenal (95%), m.p. 43–47 °C (Found: C, 86.1; H, 13.2. $\text{C}_{192}\text{H}_{334}\text{O}$ requires C, 86.1; H, 13.3). Its i.r. and n.m.r. spectra were as expected; R_F (SiO_2 , light petroleum–dichloromethane 3:1, I_2) 0.57, *cf.* 0.42 for the acetal.

Wittig reactions of halogen-free aldehydes with acetal phosphonium salts proceeded as follows (*i*) tetratetracontahecta-12,24,36,48,60,72,84,96,108,120,132-undecaenal ethylene acetal (138 mg, 34%), from the C_{96} aldehyde (270 mg) and C_{48} phosphonium salt (330 mg), reaction time 104 h, m.p. 40–44 °C (Found: C, 85.6; H, 13.1. $\text{C}_{144}\text{H}_{270}\text{O}_2$ requires C, 85.2; H, 13.2%); ratio of δ 5.34: δ 3.90, found 5.4, expected 22/4 = 5.5; hydrolysed to the C_{144} aldehyde, m.p. 40–44 °C (Found: C, 85.8; H, 13.3. $\text{C}_{144}\text{H}_{260}\text{O}$ requires C, 85.9; H, 13.3); R_F (SiO_2 , light petroleum–dichloromethane 3:1, I_2) 0.49, *cf.* 0.32 for the acetal.

(ii) *Dononacontahecta*-12,24,36,48,60,72,84,96,108,120,132,-144,156,168,180-pentadecaenal ethylene acetal (291 mg, 31%) from the C_{96} aldehyde (388 mg) and C_{96} phosphonium salt (50.9 mg), reaction time 140 h, m.p. 44–47 °C (Found: C, 85.6; H, 13.2. $C_{194}H_{358}O_2$ requires C, 85.6; H, 13.25%); ratio of δ 5.34: δ 3.90, found 7.7, expected $30/4 = 7.5$; R_F (SiO_2 , 5% ether-light petroleum, I_2 , 0.65).

(iii) *Tetracontadicta*-12,24,36,48,60,72,84,96,108,120,132,-144,156,168,180,192,204,216,228-nonadecaenal ethylene acetal (44 mg, 26%), from the C_{192} aldehyde (134 mg) and the C_{48} phosphonium salt (80 mg), reaction time 144 h. Ratio of δ 5.34: δ 3.90, found 11.8, expected $38/4 = 9.5$ —poor agreement, probably because of a weak solution rather than a wrong structure or serious impurity. The *aldehyde* was prepared by hydrolysis, with the expected i.r. spectrum.

(iv) *Octacontadicta*-12,24,36,48,60,72,84,96,108,120,-132,144,156,168,180,192,204,216,228,240,252,264,276-tricoenaal ethylene acetate (46 mg, 29%) from the C_{192} aldehyde (106 mg) and the C_{96} phosphonium salt (103 mg), reaction time 136 h. Ratio of δ 5.34: δ 3.90, found 11.2, expected $46/4 = 11.5$; R_F (SiO_2 , 5% ether-light petroleum, I_2 , 0.76). The hydrolysis to the aldehyde left some 18% of acetal unchanged according to n.m.r. measurements, insufficient silica having been used.

(v) *Tetracontatricia*-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 (54 mg, 25%) was obtained from the C_{192} aldehyde (119 mg) and the C_{192} phosphonium salt (124 mg). Ratio of δ 5.34: δ 3.90, found 14.7, expected $62/4 = 15.5$. Hydrolysis gave the C_{384} *aldehyde*, with the i.r. spectrum as expected.

1-Bromo-octane (commercial), 97.5% by g.l.c., resisted purification by fractional distillation and gave a syrupy triphenylphosphonium salt which slowly crystallised, m.p. ca. 40 °C, but could not be recrystallised. 1-Bromohexane (99%, commercial, 98.4% by g.l.c.) however, was successfully fractionated at atmospheric pressure, the heart-cut being >99.9% single peak on a 1m 25% Embaphase column at 55 °C. It gave a triphenylphosphonium salt, m.p. 200–202 °C (lit., 198–200 °C) after recrystallisation.

Tetradecahecta-8,20,32,44,56,68,80,92-*octaene*. The volume of a solution of octyltriphenylammonium bromide (1.7 g) in DMSO (15 cm³) was reduced by about one third by evaporation under reduced pressure in a rotary evaporator. Dimethylsodium (1M; 5 cm³) was added and the orange ylide was extracted with hexane (3 × 10 cm³). The extract was added to a solution of dononacontaheptaenal (157 mg) in hexane (10 cm³), and the mixture was stirred for 18 h, during which the triphenylphosphine oxide was precipitated and the colour faded. A few drops of acetic acid were added, giving a colourless solution which was decanted and washed with acetonitrile (3 × 20 cm³). Evaporation left a residue (300 mg) which was chromatographed on silica gel (100 g). Light petroleum eluted hexadec-8-ene (90 mg), then 5% ether eluted the C_{104} octaene (84 mg), m.p. 43–50 °C.

Dohecta-6,18,30,42,54,66,78,90-*octaene*, prepared similarly from hexyltriphenylphosphonium bromide (770 mg, a large excess) in DMSO (3 cm³) and dimethylsodium (0.44M; 4 cm³), was extracted into hexane (4 × 1 cm³) to give an orange solution to which the C_{96} aldehyde (66 mg) was added. Isolation by flash chromatography (2 cm column) gave the C_{102} octaene (53 mg, 76%), easily separated from the dodec-6-ene (Found: C, 86.6; H, 13.7. $C_{102}H_{190}$ requires C, 86.5; H, 13.5%).

1-Bromodohecta-12,24,36,48,60,72,84,96-*octaene* was similarly prepared from the bromo C_{96} aldehyde (496 mg) and hexyltriphenylphosphonium bromide (750 mg). The crude bromide (480 mg), free from aldehyde by i.r., was flash chromatographed (4 cm column) using light petroleum, then

ether, to give the *bromide* (366 mg, 70%), m.p. 41–46 °C (Found: C, 82.0; H, 12.8; Br, 5.4. $C_{102}H_{189}Br$ requires C, 81.9; H, 12.75; Br, 5.35%), with i.r. and n.m.r. spectra as expected. Reduction with lithium triethylborohydride gave the C_{102} hydrocarbon, identical with the specimen prepared as above, m.p. 43–47 °C.

Pentacontahecta-6,18,30,42,54,66,78,90,102,114,126,138-*dodecaene* (104 mg, 86%), m.p. 40–43 °C, was prepared from the reduced C_{144} aldehyde (117 mg) (Found: C, 86.45; H, 13.3. $C_{150}H_{278}$ requires C, 86.5; H, 13.5%); ratio of δ 5.34: δ 0.88 (terminal methyl), found 3.8, expected $12/3 = 4.0$; n.m.r. and i.r. spectra similar to analogues.

Octanonacontahecta-6,18,30,42,54,66,78,90,102,114,126,138,-150,162,174,186-*hexadecaene* (112 mg), m.p. 42–46 °C was similarly prepared from the C_{192} reduced aldehyde (Found: C, 86.2; H, 13.2. $C_{198}H_{366}$ requires C, 86.6; H, 13.4%); ratios δ 5.34: δ 0.88, found 5.25; expected $16/3 = 5.33$.

Hexatetracontadicta-6,18,30,42,54,66,78,90,102,114,126,138,-150,162,174,186,198,210,222,234-*icosae*ne (20 mg) was similarly obtained from the C_{240} reduced aldehyde. It had i.r. and (albeit determined on a reduced concentration) n.m.r. spectra as expected, with the ratio of δ 5.34: δ 0.88, found 6.0, expected $20/3 = 6.67$.

Tetranonacontadicta-6,18,30,42,54,66,78,90,102,114,138,-150,162,174,186,198,210,222,234,246,258,270,282-*tetracosae*ne (18 mg) was similarly obtained from the C_{288} reduced aldehyde (32 mg). It had i.r. and n.m.r. spectra as expected, with the ratio of δ 5.34: δ 0.88, found 8.1, expected $24/3 = 8.0$.

Nonaccontatricia-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* (12 mg, 23%) was obtained similarly from the reduced C_{384} aldehyde (50 mg). It had i.r. and n.m.r. spectra as expected, with the ratio of δ 5.34: δ 0.88, found 9.7, expected $32/3 = 10.7$.

Long-chain paraffins were prepared by the method of Part 2,¹ from the corresponding polyenes in ethyl palmitate at 130 °C. The following compounds were produced.

Tetrahectane, m.p. 115–115.5 °C (Kofler), 114.1 (DSC). Gel-permeation chromatography (g.p.c.) gave a single peak in contrast to the specimen of Part 2.¹ The sample contained ca. 2% of near homologues derived from the 1-bromo-octane.

Dohectane, m.p. 115.5–116.5 °C (Kofler), 115.1 (DSC); single peak by g.p.c., retention volume (R_v) 77.8 relative to n-decane = 100, in g.p.c. system A (Found: C, 85.35; H, 14.7. $C_{102}H_{206}$ requires C, 85.5; H, 14.5%).

Pentacontahectane, m.p. 123–123.5 °C (Kofler), 121.9 (DSC); single peak in g.p.c. system B, R_v 59.6 (Found: C, 85.8; H, 14.75. $C_{150}H_{302}$ requires C, 85.55; H, 14.45%).

Octanonacontahectane, m.p. 127.5–128 °C (Kofler), 126.1 (DSC); rapid heating showed a small endotherm followed by an exotherm at ca. 120 °C before the 126 °C endotherm; single peak in g.p.c. system A, relative R_v 72.1 (Found: C, 85.8; H, 14.5. $C_{198}H_{398}$ requires C, 85.6; H, 14.4%).

Hexatetracontadictane, m.p. 128–130 °C (Kofler), endotherms at 117.5 and 126.9 °C with a strong intermediate exotherm (DSC); single peak, R_v 56.9, in g.p.c. system B.

Tetranonacontadictane, m.p. 125–128 °C (Kofler), 123 and 128.1 °C (DSC); two peaks; (i) R_v 56.3, in g.p.c. system B, (ii) smaller peak (ca. 8%) at R_v 58.5, probably due to accidental contamination with n- $C_{198}H_{398}$.

Nonaccontatriciaene, m.p. 129–130 °C (Kofler), 119.8, 126.8, and 130.9 °C (DSC); single peak, retention volume 54.5, in g.p.c. system B.

Systems A (4 columns) and B (5 columns) in g.p.c. gave retention times which are not easily compared but which are consistent within themselves; system A was used with n-decane for calibration. The peak widths at half height for the long-chain compounds were 117–125% of those observed for n-decane,

and were around 2.6% of retention times. Measurements were made by Dr. J. Stejny using a Waters GPC 200 apparatus using *o*-dichlorobenzene solutions at 130 °C, with a refractive index detector.

Acknowledgements

We thank the S.E.R.C. for a Studentship to I. B.

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Received 16th July 1986; Paper 6/1411