Studies on the Synthesis of Linear Aliphatic Compounds. Part 2.[1] The Realisation of a Strategy for Repeated Molecular Doubling.

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Routes from C_{11} and C_{12} starting-materials, obtainable free from near homologues, to compounds of doubled chain length have been explored as approaches to the synthesis of n-paraffins and of terminally mono- or bi-functional derivatives. Acetylene alkylation routes lead to problems with protecting groups, but the use of the Wittig reaction provides a method of molecular doubling convenient for repeated use, with the formation of chain-lengths rising in a geometrical progression. The general problems inherent in the synthesis of very long-chain paraffins are discussed, earlier work is reviewed, and criteria for success are suggested. A useful protecting group for hydroxyl, the tri-*p*-tolylmethyl (trimtyl) ether, is described.

Linear polyethylene is a material of great industrial importance and, as the simplest organic polymer, the subject of much fundamental work in polymer physics.[2] Studies on *e.g.*, phase transitions in polyethylene would be facilitated by the availability in adequate quantity of model compounds (*i.e.* the n-paraffins) of known and sufficient molecular weight and high purity. The solid-state properties of paraffins of moderate length raise points of interest.[3] There have been surprisingly few examples of synthetic work on the higher ($>C_{70}$) n-paraffins, and conclusions of fundamental importance have emerged from specimens of (A) the C_{100} paraffin ($\sim$100 mg, m.p. 115—115.4 °C, made[4] in 1951) and (B) the C_{94} paraffin (16.9 g, m.p. 114.07—114.47 °C, made[5] in 1965). These preparative routes represent the approach of systematic synthetic organic chemistry to the problem and may be abbreviated to:

$$\text{(A) } 2EtO_2C(CH_2)_8CO_2^- \longrightarrow EtO_2C(CH_2)_{16}CO_2Et \longrightarrow EtO_2(CH_2)_{16}COCH_2CO_2Et;$$
$$\text{then } C_{12}H_{25}I \longrightarrow C_{12}H_{25}CH(CO_2Et)CO(CH_2)_{16}CO_2Et \longrightarrow C_{12}H_{25}CH_2CH_2(CH_2)_{16}CO_2Et$$
$$\longrightarrow C_{31}H_{63}I\text{; then by a similar addition of } (CH_2)_{19} \text{ to } C_{50}H_{101}I\text{; and finally Wurtz coupling;}$$

$$\begin{tikzcd}
\text{(B) } C_{21}H_{43}CO_2H \arrow[r] & C_{22}H_{45}ZnCl \arrow[dr] & & \\
 & & C_{22}H_{45}CO(CH_2)_{18}CO_2Me \arrow[r] & C_{42}H_{85}Br \\
HO_2C(CH_2)_{18}CO_2H \arrow[r] & MeOCO(CH_2)_{18}COCl \arrow[ur] & &
\end{tikzcd}$$
$$\longrightarrow [+ClCO(CH_2)_8COCl] \longrightarrow C_{94}\text{ diketone} \longrightarrow C_{94}\text{ paraffin.}$$

In order to assess the many experiments reported on these two specimens[6] it is necessary to consider probable degrees of purity. The Uppsala group[4] (route A) purified their starting materials carefully but could not (*ca.* 1950) detect, *e.g.*, 0.3% of a C_{12} compound in the half-ester of their C_{10} diacid, which would become 2.4% of a C_{102} homologue in the final product. Their C_{50} iodide, after 'molecular distillation,' should have been free from all but close homologues, but the Wurtz reaction must have produced $C_{50}H_{102}$ as well as $C_{100}H_{202}$ (the latter possibly[5] including branch-chained isomers). Our suspicions that the C_{50} paraffin could not have been removed by crystallisation were reinforced by our experience with C_{104} and C_{56} paraffins (see below); their products probably contained 0.5—5% of the C_{50} paraffin, as well as small amounts of C_{98} and/or C_{102} paraffins. From the m.p. range, a purity of 95% (molar) was deduced.[7] The Pennsylvania C_{94} paraffin[5] (route B) was probably free from compounds of considerably different chain-length. However, the use of 'Eastman Practical Grade' docosanoic acid, reduced to docosan-1-ol ('99.5% by g.l.c.') and of icosanedioic acid ('furnished by Shell Chemical Co'—no analysis) implies a percentage (> 1%) of near homologues in the final product.

An alternative approach to the problem is that of polymer chemistry; a bifunctional starting-material is oligomerised and the resultant low polymer is systematically fractionated. The problems are thus transferred from the synthesis itself to the complete separation of the successive members of the oligomeric series, a process which is, at best, very difficult. Thus, Carothers, Hill, Kirby and Jacobson[8] obtained the C_{20}—C_{70} paraffins by molecular distillation of the $H(CH_2)_{10n}H$ mixture which they prepared by a Wurtz synthesis from 1,10-dibromodecane. In addition to nx% of any near homologue related to the x% of a homologous dibromide in the starting material, the specimen of a given n-mer must have contained unknown amounts of the ($n - 1$) and ($n + 1$)mers. (Homologues above C_{70} proved to be undistillable and inseparable). This approach was later improved by Schill, Zurcher and Fritz,[9] who obtained C_{72} and C_{96} paraffins by oligomeric coupling of tetracosa-1,23-diyne (prepared by electrolysis of 11-bromoundecanoic acid and reaction of the C_{20} dibromide with lithium acetylide) followed by hydrogenation. While our own work was proceeding, Lee and Wegner[10] were improving Schill's method. After Eglinton-Galbraith coupling at high concentrations the mainly linear product was separated by adsorption chromatography into a series of compounds $HC{\equiv}C(CH_2)_{20}C{\equiv}C[C{\equiv}C(CH_2)_{20}C{\equiv}C]_nC{\equiv}C(CH_2)_{20}C{\equiv}CH$, where $n = 0$—6. Low oligomers *e.g.* with $n = 0$ or 1, were similarly coupled, and the polyacetylenic hydrocarbons obtained were then hydrogenated. Evidence of the extent to which it was possible to separate, *e.g.* the C_{168} compound (**1**) from analogues

$$HC{\equiv}C(CH_2)_{20}C{\equiv}C[C{\equiv}C(CH_2)_{20}C{\equiv}C]_5C{\equiv}C(CH_2)_{20}C{\equiv}CH$$

(**1**)

with 144 and 192 carbon atoms has not yet been published, but cross-contamination is so serious a problem that proof of homogeneity requires that the analytical method used is shown to distinguish between a "pure" compound and a known mixture with lower and higher components in, *e.g.*, a 2:96:2 ratio.

We now describe a new approach to the preparation of pure n-paraffins of considerable chain length. The problems encountered by earlier workers led to the formulation of four principles for the choice of route. (i) Starting materials must be cheap, abundant, and free from near homologues. In particular, products ($>$ about C_{10}) derived from natural polyacetate condensation (*e.g.* stearic acid) or from ethylene oligomerisation are unsatisfactory. A specimen of Shell docos-1-ene (*ca.* 1975, '99%'), for example contained *ca.* 0.3% of other compounds $C_nH_{2n+1}CH{=}CH_2$ (*n* even), 0.3% of paraffins (both odd and even carbon numbers), and *ca.* 1.4% of *cis*- and *trans*-docos-2-enes, according to capillary gas chromatography–mass spectrometry.* No real success was achieved in attempts at purification.[11]

(ii) Differences in chemical or physical properties must allow the separation of products, by-products, and starting materials at each stage of the synthesis. Thus, the Wurtz coupling of RCH_2I (as in the Uppsala synthesis A) must give some RCH_3 as well RCH_2CH_2R.[8,12] These are unlikely to be separable on a large scale when R is large.

(iii) A route which converts an intermediate X–Y to a longer-chain intermediate X--Y should minimise the labour involved. Such schemes (*e.g.* scheme A above) are 'helical' (implying a cyclic sequence of reactions with progress in another dimension).

(iv) The helix, however, should be geometrical, rather than arithmetical as in route A;[4] at each turn the chain-length should be multiplied, in order to obtain significantly longer chain lengths than those of earlier workers.[4,5]

Principles (i) and (ii) show a distrust of crystallisation in this field which subsequent experience has reinforced. Chromatography can succeed only if the free energy of attachment to the stationary phase differs significantly, a given chemical difference therefore corresponding to progressively smaller differences in retention volume as chain-length increases. Thus, Reinhard and Dixon[5] were even unable to separate a saturated C_{94} hydrocarbon from a C_{94} ketone.

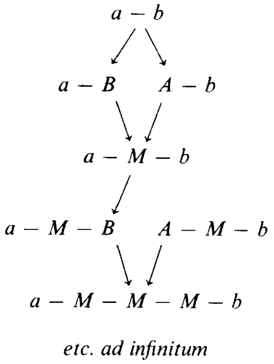
Principle (i) suggested two starting-materials: undec-10-enoic acid from ricinoleic acid, itself the product of an enzyme-catalysed oxidation to place the hydroxy group at a constant distance from $-CO_2H$ in a precursor of variable chain-length. C_{11} Derivatives of apparently good purity are available, and were used in preliminary work. The other is cyclododecanone, obtained *via* cyclododecene from a cyclic trimer of butadiene; ring-opening of the ketone and conversion into the desired unsymmetrical intermediates, as described in Part 1,[1] became the method of choice.

Alkylation of lithium acetylide–ethylenediamine with 1-bromoundecane in dimethyl sulphoxide (DMSO) gave tridec-1-yne,[13] which was converted into its lithium derivative with butyl-lithium in tetrahydrofuran (THF) and again alkylated[14] to give tetracos-12-yne. Potassium 3-aminoethylamide in propane-1,3-diamine[15] readily converted this into tetracos-1-yne, which was coupled oxidatively with cupric acetate in aqueous ethanolic pyridine[16] to octatetraconta-23,25-diyne. Alkylation of the lithium salt of tetracos-1-yne with 1-bromoundecane required the addition of hexamethylphosphoramide (HMPA),[17] and separation of the C_{35} acetylene from the C_{24} starting-material and succeeded only after fractional sublimation at 10^{-4} mmHg. Rearrangement gave n-$C_{33}H_{67}C{\equiv}CH$, which was oxidatively coupled to a C_{70} diyne; however it was considered unlikely that hydrocarbons of the desired chain-length would be reached by this procedure.

In a related approach, 12-bromododecan-1-ol was converted into its tetrahydropyranyl ether and this, with lithium acetylide, to tetradec-13-ynyl tetrahydropyranyl ether. A second alkylation with 1-bromoundecane gave pentacos-13-ynyl tetrahydropyranyl ether and, after deprotection, the alcohol. It was hoped to rearrange this to pentacos-24-yl-1-ol, but preliminary experiments were unsuccessful, no doubt because such migrations require very long reaction times.[18] Accumulating evidence of the carcinogenic properties of HMPA discouraged all further acetylene-alkylation routes requiring this co-solvent.

Hydrogenation of octatetraconta-23,25-diyne gave octatetracontane, m.p. 88.5—89 °C, which was studied as a model, and proved to be disconcertingly crystalline and insoluble. Its 0.1% solution in any solvent could be cooled to the point at which minute crystals separated with negligible super-saturation at a temperature defined to ±2 °C. Paraffins were the best solvents, with n-hexane and n-dodecane giving crystallisation temperatures of 41 °C and 43 °C respectively; however the limitations of work with such compounds at high temperature only would be a considerable handicap. To overcome this we added a fifth restriction to our choice of routes: intermediates having a prolonged sequence of methylene groups should be avoided. Instead, intermediates having unsaturated groups would be used and hydrogenated in the final stage, at a temperature high enough (m.p.s of X-$[CH_2]_n$-Y approach *ca.* 143 °C as $n \longrightarrow \infty$) to prevent the separation of partially hydrogenated products.

A general reaction scheme was now formulated:



Scheme 1.

Here, *A* represents an electrophilic group, and *B* a nucleophilic group, such that $—B + A— \longrightarrow —M—$, where *M* represents a medial grouping convertible into a C–C bond. Typically *M* would be $-C{\equiv}C-$ or $-CH{=}CH-$, preferably *cis* since in representative compounds, like stearic acid, introduction of *cis*-CH=CH lowers m.p.s more than the introduction of *trans*-CH=CH or $-C{\equiv}C-$; here *a* and *b* represent groups easily convertible into *A* and *B*, respectively, but completely unreactive towards *A* and *B*, and also towards each other, under the conditions of the reaction between *A* and *B*. Other conditions are that *a* must be stable during the deprotection $b \rightarrow B$, while *b* is stable during $a \rightarrow A$. Our first attempt to realise this scheme was based on $A = -CH_2Br$, $B = -C{\equiv}C^-$, so that *M* is $-C{\equiv}C-$. For group *a*, a derivative of $-CH_2OH$, the tri-*p*-tolylmethyl ether ('trimtyl' derivative—OTm) was selected; this was expected to be about as easily cleaved as the *p*-methoxy- or *p,p'*-dimethoxytrityl derivatives,[19] but with simplier n.m.r. spectra. (The trityl group itself required fairly drastic acid conditions for cleavage.) The other advantages of a group of this type were the certainty of easy location on phosphor-impregnated silica, and the hope of good crystallinity. The reagent, $(p\text{-}MeC_6H_4)_3C\text{-}Cl$, was readily prepared from *p*-tolylmagnesium bromide and methyl *p*-toluate, followed by acetyl chloride. Pent-4-ynyl and undec-10-ynyl ethers were prepared, but neither could be crystallised. Regeneration was straightforward. For group *b*, $Me_3SiC{\equiv}C-$ was chosen, following literature precedent.[20] Thus undec-10-yn-1-ol was converted into a C,O bistrimethylsilyl derivative, then the *O*-trimethylsilyl group was removed and –OH converted into –OTs,

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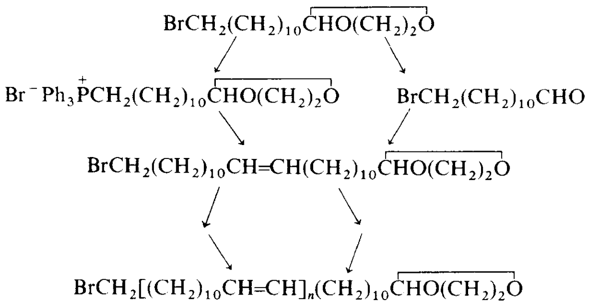
* We thank Professor G. Eglinton for this analysis.

giving (crystalline) $Me_3SiC{\equiv}C[CH_2]_8CH_2OTs$ from which the bromide was easily accessible. When this was treated with the lithium derivative of undec-10-ynyl trimtyl ether the product-mixture was complex, and left no doubt that rapid redistribution of the Me_3Si group had occurred between the two acetylenes, probably *via* an anion $RC{\equiv}C\overset{-}{Si}Me_3C{\equiv}CR'$. Similarly $Et_3SiC{\equiv}C[CH_2]_8CH_2Br$ and $LiC{\equiv}C[CH_2]_8CH_2OTm$ were brought together, but the products were again complex, and a crossover-product, $Et_3SiC{\equiv}C[CH_2]_8CH_2OTm$, rather than the desired alkylation product, was obtained when the main chromophoric fraction was isolated. Attempts to convert simple acetylenes into derivatives with more hindered silanes, Bu^tSiMe_2Cl and $Ph_2SiMeCl$, were unsuccessful. 1,2-Dibromohex-1-ene and 2-chlorohex-1-ene were obtained from hex-1-yne, but on treatment with lithiotridecyne both reverted to hex-1-yne. Indeed, the protection of $RC{\equiv}CH$ under the normal conditions of the ionic reaction $R'C{\equiv}C^- + BrCH_2R'' \rightarrow R'C{\equiv}CCH_2R''$ remained an unsolved problem when the success of an alternative approach led to a change in direction (Scheme 2).



Scheme 2.

The new scheme was based on –CHO as *A*, $-CH{=}PPh_3$ as *B*, and –CH=CH– as *M*. Hexanal was used as a model and the primary hydroxy group in $Br[CH_2]_{12}OH$[1] was protected as the tetrahydropyranyl rather than the trimtyl ether, since the latter can be conveniently prepared only in pyridine which is incompatible with $-CH_2Br$. It proved to be more convenient to treat the bromo alcohol with triphenylphosphine first, giving a crystalline salt, and then with dihydropyran and a trace of pyridinium toluenesulphonate. The syrupy phosphonium salt and dimsylsodium gave a Wittig reagent which reacted immediately with hexanal in dimethylsulphoxide (DMSO). The product isolated, however, was not octadec-12-enol, but rather the C_{18} β-hydroxyalkyldiphenylphosphine oxide, the elimination of Ph_3PO from the first-formed Wittig adduct evidently being slow in this polar solvent. Brief heating to 90 °C led to the apparent formation of the desired olefin, but under these conditions alkylation of the solvent by model primary bromides was appreciable. Although 1-bromotetracos-12-ene was obtained by a Wittig reaction in DMSO between dodecyltriphenylphosphonium bromide and 12-bromododecanal,[1] and 24-bromotetracos-12-enol from the aldehyde and the triphenylphosphonium salt of the C_{12} tetrahydropyranyl ether, yields were low. Extraction of the Wittig reagents derived from long-chain bromides with light petroleum, was therefore attempted and this gave deep-red solutions which were decolourised immediately on addition of aldehydes. As expected, the change to a less polar solvent accelerated the decomposition of the highly dipolar Wittig adducts, to give a fair yield of the tetrahydropyranyl ether of 24-bromotetracos-12-en-1-ol which was subsequently deprotected to the crystalline alkenol. This was oxidised by the Swern technique[21] to the C_{24} aldehyde, and also converted into a triphenylphosphonium salt. Repetition of the Wittig reaction gave a crude product which was essentially the desired C_{48} tetrahydropyranyl ether. Thus, the desired reaction scheme of sequential molecular doubling had been realised. However, the Swern oxidation at each doubling was undesirable, and when 12-bromododecanal ethylene acetal became available[1] it was treated with triphenylphosphine, to give a crystalline salt. This was converted into a Wittig reagent which was coupled with 12-bromododecanal, to give a C_{24} acetal; the exploration of routes for molecular doubling stopped here as a satisfactory method (Scheme 2) requiring further development had been identified.

The repeated extractions with hexane necessary to remove the Wittig reagent derived from the C_{12} acetal from dimethyl sulphoxide allowed aerial oxidation. Whereas the solubility of DMSO in hexane is only 0.06%, diethyl ether dissolves about 8% by weight at room temperature, and di-isopropyl ether about 4%; the latter however proved to be an inferior extractant for the Wittig reagent, and diethyl ether was chosen. The C_{24} bromo acetal could be crystallised, m.p. 23.5—24 °C, but only as a mixture of *cis* and *trans* isomers. The overall yield from the C_{12} acetal was *ca.* 40%. Deprotection of the C_{24} acetal under the conditions used for the C_{12} acetal (passage through silica gel impregnated with 25% toluene-*p*-sulphonic acid) was unsatisfactory, much unchanged acetal being eluted. Use of a 25:37.5:37.5 mixture of toluene-*p*-sulphonic acid–water–sulpholane (tetrahydrothiophene dioxide), chosen to maintain acidity while improving the solubility of the substrate in the aqueous phase, led to complete hydrolysis, as judged by the absence of C–O stretching bands in the product, formed in *ca.* 90% yield. The triphenyl C_{24}-phosphonium salt was non-crystalline; it gave a Wittig reagent which was readily extracted by hexane, and condensation with the C_{24} aldehyde gave a 30% yield (from the C_{24} bromo-acetal, in the best of several experiments) of a C_{48} trienal ethylene acetal as a mixture of eight isomers, m.p. 33—34 °C, distinctly less soluble in light petroleum than its C_{24} predecessor.

Deprotection to the C_{48} aldehyde appeared to be uncomplicated, as did the preparation of the C_{48} triphenylphosphonium salt. The Wittig reaction in hexane, however, gave a product containing aldehyde, not separated by chromatography on silica. Chromatography on alumina on an earlier occasion had hydrolysed a specimen of the bromo-C_{48}-acetal to the corresponding hydroxy acetal, but faster work led to a partial separation and gave, after crystallisation, the desired C_{96} bromo acetal (8% yield from the C_{48} bromo acetal), essentially pure by t.l.c. and i.r. analysis. One attempt to convert this into a C_{192} compound led to difficulties, *e.g.* in that the C_{96} bromo acetal proved to be immiscible with boiling acetonitrile, so that reaction with triphenylphosphine had to be effected in butyronitrile. Although a small amount of material was obtained with an n.m.r. spectrum similar to that expected, it was probably impure, and deteriorated on storage.

The aldehyde and the phosphonium salt need not have the same number of carbon atoms. A Wittig reaction between C_{48} aldehyde and C_{12} phosphonium salt readily gave a C_{60} bromo-acetal. Thus our methods are general for the preparation of compounds having 12*n* carbon atoms, with the termini, bromine and aldehyde, suitable for conversion into other functional groups. As many other ω-bromoaldehydes are readily available, a good general synthesis of terminally mono- or bi-functional aliphatic compounds is implied. Mass spectra provided direct evidence of the chain-length of the bromo acetals. The C_{12}, C_{24}, C_{48}, and C_{60} compounds all gave complex isotopic multiplets for the M^+ and $(M-1)^+$ ions, the latter presumably being derived from loss of H^- from the cyclic acetal, under electron-impact conditions. For the C_{96} acetal this method failed, but a spectrum with maxima in the 1 457 region in agreement with the composition $C_{98}H_{181}O_2Br$ was obtained by the FAB technique.

The synthesis of n-paraffins required the removal of the terminal halogen atom and and aldehyde function, then hydrogenation. A Wittig reaction in hexane with the reagent derived from n-octyltriphenylphosphonium bromide converted the C_{48} bromoaldehyde into a C_{56} bromo tetraene, which underwent hydrogenation at 150 °C in ethyl palmitate with only slight loss of bromine to a C_{56} saturated bromide, which was reduced by lithium triethylborohydride to hexapentacosane. More conveniently the bromo tetraene was treated first with lithium triethylborohydride, then hydrogenated. The m.p. of the C_{56} paraffin, 95.5—96 °C, agreed well with interpolated values. The C_{96} acetal was similarly deprotected, debrominated, and hydrogenated, but the m.p. of the C_{104} paraffin was initially unsharp and was raised with difficulty on recrystallisation to 114.5—115 °C (*cf.* 115.1—115.4 °C for n-hectane,[4] which itself may have contained some pentacontane). Gel-permeation chromatographic analysis by Dr. J. Stejny showed that, whereas the C_{56} paraffin gave a single sharp peak at the expected elution volume, the C_{104} paraffin gave a sharp peak at the expected position with a second peak at about the position expected for hexapentacontane—thus, the C_{48} aldehyde initially present in the C_{96} acetal had resisted complete removal, and had been converted into the expected product, present in *ca.* 7% of our final product.

In summary, a practicable method of synthesizing long-chain unbranched aliphatic compounds, including the n-paraffins, by repeated molecular doubling has been demonstrated,[22] but the preparation of compounds of the greater chain-length that might be expected to reveal chain-folding in the solid state must await further improvements. These are described in the following paper.

Experimental

Tetracos-1-*yne*.—To a stirred solution of tridec-1-yne[13,14] (3.6 g) in THF butyl-lithium (1.1 mol) was added dropwise at 20 °C. The mixture was cooled to below 10 °C while 1-bromoundecane (5.6 g) was added; after 30 min at 10—15 °C water was added and the neutral product was isolated with hexane, giving the desired hydrocarbon (7.25 g), 89% pure by g.l.c., the remainder being mainly tridec-1-yne. After fractional distillation tetracos-12-yne had b.p. 148—151 °C/0.05 mmHg, m.p. 33—34 °C, *m/z* 334 (Calc. for $C_{24}H_{46}$, 334). Addition of this hydrocarbon (2.55 g) to a solution prepared[15] from potassium hydride (1 g) and 1,3-diaminopropane (25 cm^3) followed, after 4 min, by addition of water and isolation with pentane gave a mixture of tetracos-1-yne and (apparently) tetracos-12-yne, analysed by g.l.c. (1 m packed column, 7% Dexsil, oven temperature 220 °C, R_t 25 and 22.2 min; the latter peak was as sharp as that of the starting material, so it is unlikely to represent a statistical mixture of internal acetylenes). Chromatography on alumina followed by recrystallisation of fractions absorbing at 3 300 and 2 120 cm^{-1} gave tetracos-1-yne, m.p. 47.5—49 °C.

Pentatriacont-12-*yne and Pentatriacont*-1-*yne*.—The foregoing hydrocarbon (500 mg) was dissolved in THF (2 cm^3) and cooled to below 10 °C. Butyl-lithium solution (1 equiv., 1.6 cm^3) was added followed by 1-bromoundecane (500 mg) in HMPA (4 cm^3). After 24 h at 20 °C water was added and the product was isolated, to give a 63:37 mixture (800 mg) of the product C_{35} hydrocarbon with tetracos-1-yne. Fractional sublimation gave the C_{35} *acetylene* (99.8% pure by g.l.c.), subl. 140 °C (bath temp.)/10^{-4} mmHg, m.p. 55.5—56 °C, free from absorption at 3 300 cm^{-1} (Found: C, 85.35; H, 14.4. $C_{35}H_{68}$ requires C, 86.05; H, 13.95%). Rearrangement as described above furnished the mono-substitued *acetylene*, m.p. 72.5—73.5 °C, $\nu_{max.}$ 3 300 cm^{-1}, in small yield after purification (Found: C, 85.75; H, 14.05). Pentatriacont-12-yne and tetracos-1-yne had R_t 32.5 and 2.05 min at 280 °C on the Dexsil column at 60 cm^3 min^{-1}.

Octatetraconta-23,25-*diyne and Octatetracontane*.—Tetracos-1-yne (700 mg), methanol (15 cm^3), pyridine (25 cm^3), and cupric acetate (7 g) were heated under reflux for 7 h and allowed to stand for 45 h.[16] The mixture was extracted with warm cyclohexane, washed with dilute hydrochloric acid and aqueous sodium hydrogen carbonate, and dried. Evaporation of the solvent and crystallisation gave the diacetylene, m.p. 74—75.5 °C, $\lambda_{max.}$ 215, 226, 240, and 254 nm (relative intensities 1.5:1.8:1.7:1);[23] $\nu_{max.}$(Raman, solid) 2 073 and 2 252 cm^{-1}. Hydrogenation over platinic oxide in cyclohexane gave the C_{48} paraffin, m.p. 88.5—89 °C (Lit.,[24] m.p. 88—88.5 °C), *m/z* 674 (Calc. for $C_{48}H_{98}$, 674). On a 30 cm Dexsil column (2.3% loading) at 50 cm^3 min^{-1} at 330 °C it gave a single peak with R_t 10.2 min.

11-*Trimethylsilylundec*-10-*yn*-1-*ol and its Toluene*-p-*sulphonate*.—Butyl-lithium in hexane (21.2 cm^3, 3 equiv. by double titration) was added to undec-10-yn-1-ol (1.9 g) and chlorotrimethylsilane (4.1 cm^3, 3 equiv.) in THF (20 cm^3) at −70 °C, under nitrogen. The mixture was left to warm to room temperature and then stirred for 18 h, after which aqueous hydrochloric acid (2M, 10 cm^3) was added; the mixture was then stirred for a further 2 h to hydrolyse the $-OSiMe_3$ group. Isolation of the neutral fraction gave the alcohol (2.6 g) with spectroscopic properties as expected. Addition to a suspension of toluene-*p*-sulphonyl chloride (1.1 equiv.) in pyridine (1.2 equiv.) led to an exothermic reaction; after 1 h water (a few drops) was added, and the mixture was set aside for 10 min. Isolation of the neutral fraction now gave the *toluene*-p-*sulphonate* (3.95 g), m.p. 50—52 °C (Found: C, 63.95; H, 8.75. $C_{21}H_{34}O_3SiS$ requires C, 63.95; H, 8.65%).

In the same way, pent-4-yn-1-ol (2.0 g) gave 5-trimethylsilylpent-4-yn-1-ol (3.2 g) and its toluene-*p*-sulphonate (4.3 g, after recrystallisation, as a low-melting solid) with i.r. spectra very similar to those of their higher homologues. 1-Trimethylsilylhex-1-yne, b.p. 91 °C, was also prepared. In all cases the absence of absorption at 3 300 cm^{-1} and the presence of a strong band at 2 160 cm^{-1} characterised the grouping $Me_3SiC{\equiv}C-$. In the derivative of hex-1-yne the $SiMe_3$ group was stable to LiBr (conditions comparable with those for preparing $-CH_2Br$ from $-CH_2OTs$) but was removed by treatment with the lithium salt of tridec-1-yne[18] in THF (2 cm^3) under the conditions of the reaction, $RCH_2Br + {}^-C{\equiv}CR' \rightarrow RCH_2C{\equiv}CR'$, as shown by g.l.c. analysis. We therefore sought a more bulky protecting group. Reactions between 1-lithiohex-1-yne and chlorodimethyl-t-butylsilane, and between lithiohexyne and chloromethyldiphenylsilane were unsuccessful, but chloro- and bromo-triethylsilanes reacted with the lithium derivatives of undec-10-yn-1-ol to give good yields of the silylated compound, which appeared to be more stable to $R'C{\equiv}C^-$, and was used in coupling experiments. To this end, 11-triethylsilylundec-10-yn-1-ol was converted into its toluene-*p*-sulphonate, which was purified by preparative t.l.c. to give a product with an i.r. spectrum in agreement with the trimethylsilyl derivative.

The trimethylsilyl derivative of undec-10-yn-1-yl toluene-*p*-sulphonate (0.5 g) reacted with tetrabutylammonium bromide (0.82 g) in THF (6 h under reflux), giving the corresponding bromide with an i.r. spectrum as expected and R_t (50′ SCOT at 170 °C) of 26 min; absence of the starting tosylate was verified by t.l.c. The corresponding iodide was obtained from the tosylate (1.97 g) and sodium iodide (1.55 g) in acetone after 2.5 h under reflux, and was obtained homogeneous to t.l.c. and g.l.c. in 84% yield after chromatography on alumina. The triethylsilyl derivative of undec-10-ynyl tosylate (243 mg) and tetrabutylammonium bromide (200 mg) similarly gave the corresponding bromide (159 mg) after preparative t.l.c.

*Undec-*10-*ynyl Tri-*p-*tolylmethyl* (*'Trimtyl'*) *Ether.*—Chlorotri-*p*-tolylmethane (10.7 g),[25] undec-10-yn-1-ol (5.1 g), triethylamine (6.35 cm^3), and 4-(*N,N*-dimethylamino)pyridine (0.15 g) in dichloromethane (50 cm^3) were stirred at 25 °C for 72 h, after which t.l.c. showed the alcohol to be absent. Water (30 cm^3) was added, and the aqueous solution was extracted with dichloromethane. The combined organic layers were washed with water (60 cm^3), HCl (2M, 2 × 60 cm^3), water, and saturated brine, then dried and evaporated. The residue (15.84 g) was chromatographed on alumina (800 g), giving a heart fraction (9.44 g), plus early and late fractions which were rechromatographed to give a further 3.00 g of ether, pure to t.l.c. (12.44 g, 91%), the i.r. spectrum of which was unchanged after distillation at 160—167 °C/3 × 10^{-4} mmHg. The *ether* (Found: C, 87.6; H, 9.15. $C_{33}H_{40}O$ requires C, 87.55; H, 8.9%), $\nu_{max.}$ 3 320 (HC≡C str), was an extremely viscous liquid.

This ether (3.77 g) was used to explore conversion into the triethylsilyl derivative *via* the bromomagnesium derivative, obtained from magnesium (219 mg) and ethyl bromide (1 g) in THF (3 cm^3), after heating under reflux for 30 min. Addition of bromotriethylsilane (1.63 g) gave a mixture of silylated and unchanged material, rather inefficiently separated by chromatography on alumina (400 g) to give nearly pure silylated ether (0.4 g). The other fractions (1.2 g) were re-silylated using butyl-lithium, as described above, to give the triethylsilyl trimtyl ether (1.6 g), $\nu_{max.}$ 2 170 cm^{-1}; strong molecular ion at 560, base peak $[(C_7H_7)_3C^+]$ 285. The ether (1.9 g) was added to methanol (3.1 cm^3) and concentrated sulphuric acid (1 drop). After 10 min the mixture became homogeneous, but t.l.c. showed deprotection to be incomplete. After treatment with more methanol (5 cm^3) and conc. H_2SO_4 (4 drops), isolation gave the pure 11-triethylsilylundec-10-yn-1-ol (237 mg) having an i.r. spectrum identical with that of the starting material. More conveniently, the ether (3.01 g) was treated with acetic acid (80 cm^3) and water (10 cm^3) and stirred for 16 h at 20 °C when a homogeneous solution which contained, according to t.l.c., very little ether was obtained. The chromatographic separation of the silyl-acetylenic alcohol and tri-*p*-tolylmethanol was difficult, and the mixture was converted *via* the toluenesulphonate into the bromide (56% overall), without loss of the triethylsilyl group.

Alkylation of undec-10-ynyl trimtyl ether with 11-bromo-1-triethylsilylundec-1-yne was attempted by treating the former (1.2 g) in dry THF (3 cm^3) with n-butyl-lithium (1.57M, by double titration) in hexane (1.9 cm^3) at 0 °C. Ice-cooling was discontinued and the solution, initially wine-red, was stirred for 40 min, after which it became colourless. The bromide (1.0 g) in dry HMPA (4.5 cm^3) was added after again cooling the mixture to 0 °C. Isolation of the fraction absorbing strongly at 254 nm, using phosphor-impregnated silica t.l.c. plates, gave the triethylsilylated undec-10-ynyl trimtyl ether, identical with a specimen prepared as above; there was no sign of the desired coupling product.

Because of the failure of the coupling attempt, a result unaltered by variations in temperature or the use of the corresponding iodide, desilylation received only preliminary investigation. However, heating the solution of the 11-triethylsilylundec-10-ynyl trimtyl ether (560 mg) with a saturated solution of caesium fluoride in ethanol (3 cm^3) gave the deprotected ether, according to t.l.c.

Pentacos-13-*yn*-1-*ol.*—Tetradec-13-ynyl tetrahydropyran-2-yl ether (7.5 g) (from 12-bromododecanyl tetrahydropyran-2-yl ether and lithium acetylide[26]) in THF (30 cm^3) was added to 1.3M butyl-lithium (20 cm^3) in light petroleum at 0 °C. After 60 min at 25 °C, the mixture was cooled to 0 °C and HMPA (9.1 cm^3) was added, followed after 5 min by 1-bromoundecane (6.0 g) in THF (20 cm^3). The mixture was heated under reflux for 1 h, cooled, and treated cautiously with water. Isolation of the neutral fraction gave the crude C_{25}-tetrahydropyranyl ether (10.1 g, 88%). A portion (3.87 g) was dissolved in a mixture of THF (150 cm^3) and sulphuric acid (10%, 30 cm^3) and heated under reflux for 5 h. Isolation of the neutral fraction gave *pentacos*-13-*yn*-1-*ol* (3.0 g, 84% overall), m.p. 57.5—58.5 °C (Found: C, 82.55; H, 13.35. $C_{25}H_{48}O$ requires C, 82.4; H, 13.2%).

Treatment of this alcohol with potassium 3-aminopropylamide in propane-1,3-diamine for 5 min at 20 °C failed, as expected,[18] to rearrange it to a terminal acetylene.

Preparation of Dimsylsodium Solution.—This reagent was best prepared as follows.[27] A suspension (50—80%) of sodium hydride in paraffin oil was freed from the latter by stirring with diethyl ether, allowing the suspension to settle, and removing the supernatant liquid. Dry DMSO (at least 12 times the weight of sodium hydride) was added, and the flask containing the mixture was connected to a water pump and a reservoir large enough to accommodate the calculated volume of evolved hydrogen at n.t.p., *via* a silica-gel trap. After evacuation to *ca.* 15 mmHg, the sodium hydride and DMSO were isolated, and the suspension was stirred magnetically at room temperature for *ca.* 48 h (or at *ca.* 35 °C for 18 h), when a clear black, virtually odourless solution of dimsylsodium was obtained. This was standardised by adding an aliquot to water and titrating with dilute hydrochloric acid. Solutions were typically 1—2.5M, and could be completely freed from black insoluble matter by centrifugation in stoppered tubes.

General Methods for Wittig Reactions.—(*a*) The phosphonium salt (1 mol) was dissolved in dry DMSO and *ca.* three-quarters of the solvent was evaporated at *ca.* 1 mmHg using a rotary evaporator. Dimsylsodium solution (1.25 mols), withdrawn by syringe from the nearly clear liquid overlying a black precipitate and standardised, was added under nitrogen with stirring. The Wittig reagent sometimes separated as an upper layer. After 10 min the aldehyde (1 mol, in ether or DMSO) was added, and the stirring was continued, typically for 3 h. Addition of water and isolation of the neutral product with light petroleum was usually followed by shaking with dry acetonitrile, which removed triphenylphosphine oxide.

In this way dodecyltriphenylphosphonium bromide (5.6 g) and 12-bromododecanal (2.4 g) in DMSO (*ca.* 7 cm^3, reaction time 10 min) gave, after chromatography on silica (100 g), 1-*bromotetracos*-13-*ene* (1.5 g, 34%), as a liquid, homogeneous to t.l.c., with an i.r. spectrum as expected (Found: C, 68.95; H, 11.3; Br, 18.9. $C_{24}H_{47}Br$ requires C, 69.35; H, 11.4; Br, 19.2%). Similarly, 12-bromododecan-1-ol was converted into the crude triphenylphosphonium salt by heating with triphenylphosphine in acetonitrile under reflux for 64 h, and then isolating and removing petroleum-soluble material. The salt (9.7 g) was converted into the tetrahydropyranyl ether by treatment with dihydropyran (2.3 g) and pyridinium toluene-*p*-sulphonate (0.5 g) in dichloromethane (50 cm^3). Conversion into the Wittig reagent and addition of 12-bromododecanal (4 g) gave a crude product of which 3.2 g was isolated from the petroleum layer of an acetonitrile–petroleum partition. Deprotection of 3.1 g with methanol and conc. hydrochloric acid gave a product (2.26 g) which was extracted with light petroleum and again distributed between petroleum and acetonitrile; the petroleum layer gave (*cis* and *trans*) 24-bromotetracos-12-en-1-ol (765 mg), m.p. 34—35 °C, identical with that prepared by the better method below.

Method (*b*). The Wittig reagent was prepared as above, then extracted into light petroleum (b.p. 40—60 °C), hexane, or ether.

Care was taken to minimise contact with air; on a large scale it was convenient to use a specially-made double separating funnel, the two cylindrical bodies being connected *via* a tap near the top, and at the bottom by a three-way tap which alternatively allowed one phase in either to be drained into an external receiver, or transferred to the other funnel. This allowed the DMSO solution to be extracted repeatedly under nitrogen, after each extraction the lower layer being transferred to the other funnel, and the upper layer removed for reaction with the aldehyde, until a nearly colourless upper layer was obtained. On a smaller scale, transfers could be made by syringe under nitrogen. It was necessary to avoid the precipitation of sodium or potassium bromide, thus dimsylsodium solutions were *ca.* 1M rather than *ca.* 2M when the phosphonium salt solution was concentrated.

12-*Hydroxydodecyltriphenylphosphonium Bromide*.—12-Bromododecan-1-ol (4.165 g), triphenylphosphine (5 g), and acetonitrile (dried over 3 Å molecular sieve; 15 cm^3) were heated under reflux for 48 h. The excess of solvent was evaporated at 20 mmHg and the viscous product was heated with light petroleum (b.p. 40—60 °C) repeatedly, the mobile upper phase being discarded. The residue crystallised and was triturated with diethyl ether giving the *salt* (8.11 g, 98%; but probably a hemihydrate, so 96%), m.p. 92—94 °C (Found: C, 67.15; H, 7.4; Br, 15.05. $C_{30}H_{40}BrOP$ requires C, 68.3; H, 7.65; Br, 15.15%. $C_{30}H_{48}Br{\cdot}OP\ 0.5H_2O$ requires C, 67.15; H, 7.65; Br, 14.9%).

24-*Bromotetracos*-12-*en*-1-*ol*.—The foregoing salt was converted into its tetrahydropyran-2-yl ether by reaction with dihydropyran (1.5 mol) in dry dichloromethane in the presence of pyridinium toluene-*p*-sulphonate (0.1 g); after brief heating under reflux, evaporation left a residue showing the expected i.r. spectrum. This syrup (15.4 g) was dissolved in DMSO (dried by stirring with 3 Å molecular sieve, 30 cm^3), and most of the solvent was evaporated in a rotary evaporator at 1 mmHg to ensure complete drying. More DMSO (80 cm^3) was added, and the solution was mixed under nitrogen with a solution (0.68M, 43 cm^3) of dimsylsodium in DMSO in a pressure-compensated dropping funnel, as described above (Method *b*). Hexane (100 cm^3) was added, the mixture was shaken, then the phases were allowed to settle, and the lower layer was re-extracted with hexane. To the hexane solution was added 12-bromododecanal (5.26 g) in hexane (50 cm^3) under nitrogen, upon which the colour was discharged. The mixture was stirred at 20 °C for 16 h, after which triphenylphosphine oxide was precipitated. The solution was filtered and extracted three times with acetonitrile, then evaporated, to give the tetrahydropyranyl ether (8.4 g, 82%). The crude ether (7.0 g) was added to methanol (100 cm^3) and concentrated hydrochloric acid (3 cm^3) and stirred for 16 h at 20 °C, when it became homogeneous. Water (400 cm^3) was added and the mixture was extracted with light petroleum (5 × 100 cm^3) and then with ether (150 cm^3). Evaporation of these extracts gave 24-*bromotetracos*-12-*en*-1-*ol* (4.1 g and 1.6 g, respectively), m.p. 37.5—39 °C (Found: C, 66.6; H, 11.0; Br, 18.7. $C_{24}H_{47}\ BrO$ requires C, 66.8; H, 10.9; Br, 18.55%). The alcohol had the expected ^{1}H and ^{13}C n.m.r. spectra, the latter giving a *cis*/*trans* ratio of *ca.* 6.

Diphenyl-[12-(*tetrahydropyran*-2-*yl*)*oxydodecyl*]*phosphine oxide* was obtained when, in a similar experiment, the phosphonium salt (17.7 g) and dimsylsodium (1.14M, 32 cm^3) were mixed in inadequately dried DMSO. No red colour was observed, and no aldehyde was added. The *oxide* (5.3 g, 39%) had m.p. 64—66 °C (Found: C, 74.2; H, 9.1. $C_{29}H_{43}O_3P$ requires C, 74.0; H, 9.2%) and i.r. and n.m.r. spectra as expected.

11-(*Dioxolan*-2-*yl*)*undecyltriphenylphosphonium Bromide*.—12-Bromododecanal ethylene acetal (23 g), triphenylphosphine (24 g), trimethyl orthoformate (1.6 cm^3), and dry acetonitrile (100 cm^3) were heated under reflux for 60 h. The solvent was evaporated and the residue was warmed with light petroleum (15 × 100 cm^3), which was then decanted off. The residue crystallised and was triturated with diethyl ether (3 × 100 cm^3) and dried to 10 mmHg, to give the *salt* (40.0 g, 94%), m.p. 130—131 °C (Found: C, 67.5; H, 7.25; Br, 13.85. $C_{32}H_{42}BrO_2P$ requires C, 67.5; H, 7.45; Br, 14.05%). This specimen had ^{1}H and ^{13}C n.m.r. spectra as expected, but probably contained *ca.* 2% of methyltriphenylphosphonium bromide, unimportant for present purposes; it showed no CHO absorption at 1 730 and 2 700 cm^{-1}.

24-*Bromotetracos*-12-*enal Ethylene Acetal*.—The foregoing salt (73.1 g) in DMSO (180 cm^3) was converted into the phosphorane by adding a solution of dimsylsodium in DMSO (2.6M; 62 cm^3) and extracting with diethyl ether (3 × 150 cm^3), under nitrogen, using a double separating funnel (Method *b*). 12-Bromododecanal was prepared[1] from its acetal (23 g), silica gel (600 g), and a 25% solution of toluene-*p*-sulphonic acid monohydrate (60 cm^3) in light petroleum–dichloromethane (3:1). After evaporation of most of the solvent, the aldehyde was added to the phosphorane solution, and the mixture was stirred for 16 h. The ether was evaporated under reduced pressure, light petroleum was added, and the solution was filtered, then washed with acetonitrile. Evaporation of the solvent and recrystallisation from light petroleum at *ca.* 40 °C gave the (cis and trans) *acetal* (41.3 g, 81%), m.p. 23.5—24 °C (Found: C, 65.5; H, 10.6; Br, 17.5. $C_{26}H_{51}BrO_2$ requires C, 65.9; H, 10.4; Br, 16.9%).

48-*Bromo-octatetraconta*-12,24,36-*trienal Ethylene Acetal*.—The foregoing C_{24} bromo acetal was converted (76% yield) into the related triphenylphosphonium salt, isolated as a syrup in the same way as the C_{12} analogue (22.4 g), which when treated with dimsylsodium (1.14M, 35.5 cm^3) gave, after extraction (Method *b*), a solution of the phosphorane in light petroleum (b.p. 60—80 °C). A further portion was deprotected by the same method as its C_{12} analogue, except that the 25% toluene-*p*-sulphonic acid was prepared in a 1:1 mixture of water and sulpholane (tetramethylenesulphone). The aldehyde was eluted with 3:1 light petroleum–dichloromethane, as pure dichloromethane dissolves much sulpholane. Fractions were checked for the absence of acetal C–O stretching bands at 1 140 and 1 125 cm^{-1}. The C_{24} aldehyde (8.8 g) in light petroleum (50 cm^3) was added to the phosphorane solution, which it decolourised. After isolation, the crude C_{48} bromo acetal was crystallised three times from light petroleum, and had m.p. 33—34 °C (14.9 g) (Found: C, 74.35; H, 11.85; Br, 10.85. $C_{50}H_{91}BrO_2$ requires C, 74.45; H, 11.65; Br, 9.9%). Although its i.r. spectrum and low concentration ^{1}H n.m.r. spectra agreed well with expectations, and analyses were near theoretical values, it was probably impure, as well as being a statistical mixture of geometrical isomers.

48-*Bromo-octatetraconta*-12,24,36-*trienal*, m.p. 28 °C, was obtained by deprotection (as for the C_{24} analogue) in 97% yield (Found: C, 76.35; 75.15, 74.75; H, 12.15, 12.3, 11.8; Br, 10.45, 10.4, 9.75. $C_{48}H_{89}BrO$ requires C, 75.65; H, 11.75; Br, 10.5%), with i.r. and n.m.r. spectra as expected.

1-*Bromohexapentaconta*-12,24,36,48-*tetraene* was obtained from the foregoing aldehyde (2.4 g) and an ether solution of the phosphorane derived from the non-crystalline octyltriphenylphosphonium bromide (3 g). After 60 h the crude product was separated from triphenylphosphine oxide and chromatographed on silica gel (100 g) using 1% ether in light petroleum (b.p. 30—40 °C). The least polar fraction was hexadec-8-ene; the desired bromide was separated from more polar materials, probably impurities in the aldehyde used, and after crystallisation from light petroleum the bromide (850 mg) had m.p. 32.5—35.5 °C, and i.r., ^1H and ^{13}C n.m.r. spectra as expected.

Hexapentacontane.—(*a*) The foregoing compound (588 mg) in THF (10 cm^3) was treated with lithium triethylborohydride (1M, 2 cm^3). After 15 min at 20 °C the product was isolated and chromatographed on silica gel, giving hexapentaconta-8,20,32,44-tetraene (340 mg, 64%), m.p. 37—38.5 °C. This compound (265 mg), platinum oxide (40 mg) and ethyl palmitate (redistilled) were heated to 150 °C in hydrogen for 18 h. The mixture was cooled, light petroleum was added, and the black residue (paraffin plus catalyst) was collected. This was extracted by refluxing with light petroleum, b.p. 80—100 °C, which dissolved the hydrocarbon; on cooling the *paraffin* separated (164 mg, 61%) m.p. 95.5—96 °C (Found: C, 85.5; H, 14.5. $C_{56}H_{110}$ requires C, 85.4; H, 14.6%). A gel permeation chromatogram in *o*-dichlorobenzene, carried out by Dr. J. Stejny, showed a single narrow peak, separated from the n-decane internal standard by *ca.* the expected difference in retention volume.

(*b*) When the order of the above reactions was interchanged, 1-bromohexapentacontane, m.p. 94—95 °C, was obtained, contaminated with about 12% of the paraffin, as judged by elementary analyses. Reduction with lithium triethylborohydride (heating under reflux, 3 h) gave material identical with the specimen obtained by method (*a*), in 34% yield from the bromotetraene.

60-*Bromohexaconta*-12,24,36,48-*tetraenal Ethylene Acetal.*—The C_{12} acetal triphenylphosphonium salt (670 mg) was converted into a solution of the phosphorane in light petroleum (3 cm^3), using Method b with syringe transference; extraction was incomplete. A solution of the C_{48} trienal (740 mg) was prepared as above from the corresponding acetal (970 mg) and added; after 16 h the crude C_{60} acetal was isolated (630 mg) and purified by flash chromatography using silica-gel and a 5% solution of ethyl acetate in light petroleum. After crystallisation the C_{60} *bromo acetal* (183 mg) had m.p. 48—49 °C (Found: C, 76.9; H, 12.65; Br, 7.75. $C_{62}H_{115}BrO_2$ requires C, 76.55; H, 11.9; Br, 8.2%). Some 5% of the chlorine analogue was present according to n.m.r. data, hence the analytical data.

Tetrahectane.—48-Bromo-octatetraconta-12,24,36-trienal ethylene acetal (8.17 g), triphenylphosphine (2.3 g), trimethyl orthoformate (0.16 cm^3) and butyronitrile (30 cm^3) were heated under reflux for 60 h. The excess of solvent was evaporated in a rotary evaporator under reduced pressure, and the residue was extracted with warm light petroleum (3 × 30 cm^3); evaporation of the extracts left 1.73 g, thus the residual gum (10.27 g) must have retained some 1.53 g of butyronitrile. It was dissolved in DMSO (34 cm^3) and treated with dimsylsodium solution (1.9M, 7 cm^3), giving the coloured phosphorane which was extracted with hexane (3 × 50 cm^3). 48-Bromo-octatetraconta-12,24,36-trienal (5.76 g, prepared as above) in dry hexane (50 cm^3) was added. After 16 h the triphenylphosphine oxide was removed and the crude product was isolated (5.22 g showing a band at 1 725 cm^{-1} indicating an excess of aldehyde). This was chromatographed on alumina (600 g, deactivated with 60 cm^3 of 10% acetic acid), giving a main fraction (4.64 g) which still contained aldehyde and was rechromatographed on alumina (750 g, deactivated with 62 cm^3 of 10% acetic acid), using light petroleum as eluant. Early fractions containing acetal peaks (1 120 and 1 040 cm^{-1}) (1.96 g) were followed by nearly pure C_{48} bromo aldehyde (1.76 g). The former were chromatographed on silica gel (100 cm^3) and after separation of an unidentified non-polar contaminant, fractions essentially free from absorption at 1 725 cm^{-1} were combined and recrystallised at −15 °C, giving essentially pure 96-bromohexanonaconta-12,24,36,48,60,72,84-heptaenal ethylene acetal (600 mg, m.p. 46—47 °C). This acetal was deprotected by passing a 3:1 light petroleum–dichloromethane solution down a column of silica-gel impregnated with a 25:37.5:37.5 mixture of toluene-*p*-sulphonic acid, water and sulpholane, giving the C_{96} heptaenal (480 mg), m.p. 47—48 °C, free from absorption at 1 120 and 1 040 cm^{-1}. Its solution in hexane (20 cm^3) was added to a solution of the phosphorane prepared from n-octyltriphenylphosphonium bromide (1.6 g) and dimsylsodium (1.5M, 4 cm^3) and extracted into hexane (80 cm^3). After 16 h, isolation gave a crude product (564 mg) which was chromatographed on silica gel. Elution with light petroleum gave crystalline fractions (220 mg); ether gave a further 70 mg of apparently identical material. It was deduced that part of the C_{104} bromide had crystallised on the adsorbent, and indeed the continuous hot extraction of the silica gave a further 180 mg of apparently identical material, (total yield 470 mg, 92%), m.p. 42—43 °C (Found: C, 80.65; H, 12.65; Br, 5.65. $C_{104}H_{193}Br$ requires C, 82.0; H, 12.75; Br, 5.25%). We comment on its purity below; its i.r. ^1H and ^{13}C n.m.r. spectra (low concentration) were as expected.

(ii) The bromide (430 mg) was added to dry THF (15 cm^3), and lithium triethylborohydride (1M; 1 cm^3) was added. On being heated under reflux the mixture became homogeneous. After 1 h the mixture was cooled, an excess of water was added and the product was isolated with light petroleum; evaporation of the extract left the C_{104} octaene (280 mg, 69%), which lacked the C–Br stretching band at 640 cm^{-1}. This was added to ethyl palmitate (2.5 cm^3) and heated to 150 °C in hydrogen in the presence of platinic oxide (15 mg) with stirring for 20 h and then cooled. The separated solid was collected by filtration and washed with light petroleum. After hot extraction with light petroleum, b.p. 100—120 °C, the crude paraffin (242 mg) separated and had m.p. 107—108 °C, lower than expected. In the belief that residual unsaturation was present, it was hydrogenated at 150 °C successively over platinic oxide (35 mg), 5% rhodium on carbon (304 mg), and the same catalyst (597 mg), and then had m.p. 114—115 °C. A third Rh–C hydrogenation, and a final attempt with Wilkinson's catalyst (50 mg) effected no improvement, the essentially pure *tetrahectane* (56 mg) having m.p. 114.5—115 °C (Found: C, 85.7; H, 14.85. $C_{104}H_{210}$ requires C, 85.5; H, 14.5%). Gel permeation chromatography by Dr. J. Stejny in *o*-dichlorobenzene gave a narrow peak corresponding to a calculated molecular weight of 1 513 (Calc. 1 458), plus a small peak, *ca.* 7%, corresponding to *M*, 813 (Calc. for $C_{56}H_{114}$, 786).

In retrospect, the crude paraffin probably contained a little n-$C_{104}H_{209}$ Cl, which would be hard to remove by super-hydride reduction but would not survive drastic hydrogenation. The C_{104} bromo-octaene probably contained some of the chlorine analogue, and *ca.* 7% of C_{56} bromo tetraene.

Acknowledgements

We thank I.C.I. Ltd. for a postdoctoral fellowship held by D. J. S., and the S.E.R.C. for a C.A.S.E. studentship held by O. I. P. One of us thanks Prof. Sir E. R. H. Jones, F. R. S., Prof. R. A. Raphael, F. R. S., and Dr. A. H. Willbourn, for helpful discussions before the beginning of this project.

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Received 16*th July* 1986; *Paper* 6/1410