The Synthesis of Pure n-Paraffins with Chain-lengths between One and Four Hundred

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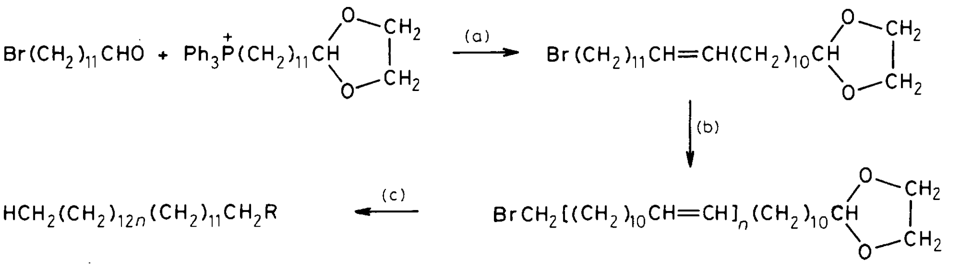
Syntheses are described for pure paraffins having 102, 150, 198, 246, and 390 carbon atoms; unlike lower homologues, all but the first show interesting properties in the solid state, bridging the gap between the chain-extended and the chain-folded modes of crystallisation typical of the lower n-paraffins and the linear polyethylenes, respectively.

Linear polyethylene crystallises in laminae in which the long chains wind backwards and forwards repeatedly, the parallel straight segments having, typically, 100—200 methylene groups.[1] Essentially pure synthetic n-paraffins of up to one hundred carbon atoms synthesised by earlier workers,[2] and approximately pure C_{120}—C_{160} paraffins obtained (in minute quantities) by the fractionation of oligomeric mixtures,[3] do not show this behaviour, but crystallise as extended chains. The question clearly arises as to the chain length at which the transition between extended-chain 'paraffinic' and chain-folded 'polymeric' crystallisation occurs. The present synthetic work was undertaken in order to locate this region.

We recently described[4] an approach to the synthesis of essentially pure n-paraffins, applicable in principle to any desired chain-length, which is based on the repeated doubling of the chain of a completely homogeneous building-block obtained from cyclododecanone, and therefore ascends the homologous series by a geometrical, rather than an arithmetical progression (Scheme 1). In practice, the extent to which this is possible depends on the yields obtained in the Wittig



Scheme 1. (a) Base, (b) hydrolysis (half material); reaction with Ph_3P (half material); repetition, (c) hydrolysis, reaction with $R\overset{+}{P}Ph_3Br$ and base, $LiBHEt_3$, hydrogenation at 130 °C.

reactions used. In the version described[4] these were moderate and somewhat inconsistent, and diminished with increasing molecular weight. Use of the Wittig variant described by Boden[5] gave better and more reliable yields, the ethylenic bonds formed remaining *ca.* 90% *Z*. It was thus possible to obtain C_{192} and C_{384} bromo-acetals by doubling the C_{96} intermediate described, and C_{144}, C_{240}, and C_{288} analogues when components of dissimilar length were employed. The C_{192} compound defeated mass spectrometry even when fast-atom bombardment was used, but elemental analysis plus measurements of ^1H n.m.r. signal intensities observed at 200 MHz for $-CH_2Br$, $-CH(O_2C_2H_4)$, $-CH{=}CH-$, $CH_2-C{=}$, and $CH_2CH_2CH_2$ assured constitution and purity (these compounds are freely soluble at room temperatures). Removal of bromine, hydrolysis, and reaction with n-hexyltriphenylphosphonium bromide (available in 99.97% purity, *cf.* 98% for the octyl analogue[4]), followed by hydrogenation has given a range of paraffins with 102, 150, 198, 246, and 390 carbon atoms. Though correctly analysed, they cannot, of course, have their structures confirmed thereby. However, they gave single, narrow peaks on gel-permeation chromatography, their elution volume showing the expected approximately logarithmic relationship to chain length. The efficiency of this test was shown when a second peak was observed revealing the presence of *ca.* 7% of $C_{56}H_{114}$ in the (analytically and spectroscopically pure) $C_{104}H_{210}$ previously described,[4] and when accidental contamination of our otherwise pure C_{294} specimen by *ca.* 8% of, probably, the C_{198} paraffin led to a marked shoulder.

The melting points examined by differential scanning calorimetry were not definable in terms of a single value for a given compound because of the appearance of complex multiple endotherms, sometimes coupled with exotherms. The solution-crystallised C_{198} paraffin, for example, melted at about 118 °C, resolidified and remelted at 127 °C, as shown by a small endotherm, a small exotherm, and a larger endotherm observed during differential scanning calorimetry. It was shown by Ungar, Stejny, and Keller, using Raman spectroscopy, that this behaviour relates to a U-shaped conformer present in the solution-crystallised specimen changing to a straight-chain form in the higher-melting polymorph. Even the C_{150} compound showed spectroscopic evidence of chain-folding, but the C_{102} paraffin did not. This work is described in more detail elsewhere.[6]

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