

## The Synthesis of Long-chain Unbranched Aliphatic Compounds by Molecular Doubling

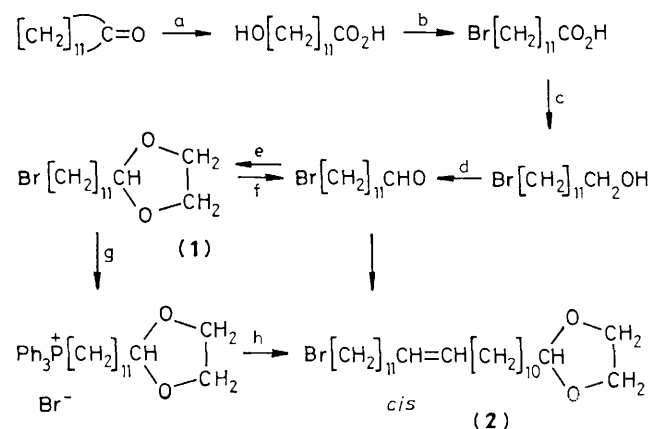
Oliver I. Paynter, Derek J. Simmonds, and Mark C. Whiting\*

*Department of Organic Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.*

A convenient general synthesis, applicable to alkanes and terminally mono- and di-substituted alkanes of any chain length, is described; cyclododecanone is used as the starting material, and the C<sub>12</sub> chain is doubled in length as often as required and adjusted first to a multiple of 12, and then to any desired length.

Surprisingly few pure aliphatic compounds having >50 carbon atoms in a straight chain have been reported,<sup>1</sup> yet they, and especially the alkanes, are obviously important as analogues of polyethylene. It is difficult to obtain pure compounds derived ultimately from natural fats or waxes or from ethylene oligomers, which are mixtures of homologues, or by routes involving partial reactions of symmetrical intermediates. In a strategy which avoids these problems, Baeyer–Villiger reaction of cyclododecanone and subsequent straightforward transformations led, after optimisation, to a *ca.* 50% overall yield of the bromo-acetal (**1**), m.p. 24 °C (Scheme 1). The bromo-acetal was readily converted into a triphenylphosphonium salt, which with dimethyl sodium gave a Wittig reagent extractable with diethyl ether. This reacted with the C<sub>12</sub> bromo-aldehyde regenerated from the acetal (**1**) (in ether; in

dimethyl sulphoxide the –CH<sub>2</sub>Br group caused problems) to give a C<sub>24</sub> bromo-acetal (**2**), m.p. 25 °C. Repetition of the same three reactions converted acetal (**2**) into a C<sub>48</sub> triene-acetal, m.p. 40 °C. This was converted by similar reactions with the C<sub>12</sub> phosphonium salt into a C<sub>60</sub> analogue, or with its own triphenylphosphonium salt to a C<sub>96</sub> acetal, m.p. 45 °C. These moderate melting-points, the results of intermittent *cis* olefinic links, implied sufficient solubility in organic solvents at low temperatures, in contrast to the very low solubility of saturated alkanes of such chain lengths. The structure and purity of these compounds were verified by elementary analysis, i.r. spectra, <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra, and observation of molecular ions with appropriate isotopic profiles in mass spectra. Electron impact was satisfactory for C<sub>48</sub> and C<sub>60</sub> chains, but fast-atom bombardment was needed to ionise the



**Scheme 1.** Reagents: a,  $\text{HO}_3\text{C.CH=CH.CO}_3\text{H}$ ;<sup>2</sup> b,  $\text{HBr} \cdot \text{HOAc}$ ; c,  $\text{BH}_3 \cdot \text{Me}_2\text{S}$ ;<sup>3</sup> d,  $(\text{COCl})_2$ ,  $\text{Me}_2\text{SO}$ ,  $\text{NEt}_3$ ;<sup>4</sup> e,  $(\text{CH}_2\text{OH})_2$ ,  $\text{C}_7\text{H}_7\text{SO}_3\text{H}$ ; f,  $\text{H}_2\text{O}$ ,  $\text{C}_7\text{H}_7\text{SO}_3\text{H}$ ; g,  $\text{Ph}_3\text{P}$ ,  $\text{MeCN}$  or  $\text{PrCN}$ ; h,  $\text{NaCH}_2\text{SOMe}$ ,  $\text{Me}_2\text{SO}$ .<sup>5</sup>

$\text{C}_{96}$  bromo-acetal. This last compound was converted by the same sequence of reactions into a  $\text{C}_{102}$  bromo-acetal, m.p.  $45^\circ\text{C}$ , characterised by analysis and by correct ratios for the variety of protons present in the  $^1\text{H}$  n.m.r. spectra, including triplets for  $-\text{CH}(\text{O}_2\text{C}_2\text{H}_4)$  and  $\text{CH}_2\text{Br}$  with intensities approximating to 1/357 and 2/357, respectively, of the total.

Removal of the aldehyde function was conveniently effected with a monofunctional Wittig reagent, which also adjusts the chain length. The terminal bromine atom was easily displaced by lithium triethylborohydride.<sup>6</sup> Using octyltriphenylphosphonium salts, a  $\text{C}_{56}$  tetraene and a  $\text{C}_{104}$  octaene were prepared, which on hydrogenation at  $150^\circ\text{C}$  in ethyl palmitate (used to prevent crystallisation of incompletely hydrogenated material) gave  $\text{C}_{56}$  and  $\text{C}_{104}$  alkanes, m.p.  $90$  and  $115^\circ\text{C}$ , respectively. The latter is the longest chain yet reported. The main value of this method, however, is its obvious generality, given the range of reactions available to intermediates of type (2), and its applicability to the expeditious preparation of really long-chain compounds.

Received, 16th August 1982; Com. 978

## References

- 1 G. Ställberg, S. Ställberg-Stenhagen, and E. Stenhagen, *Acta Chem. Scand.*, 1952, **6**, 313; R. R. Reinhard and J. A. Dixon, *J. Org. Chem.*, 1965, **30**, 1450.
- 2 R. W. White and W. D. Emmons, *Tetrahedron*, 1962, **17**, 31.
- 3 C. F. Lane, *Aldrichimica Acta*, 1975, **8**, 20; H. C. Brown, P. Heim, and N. M. Yoon, *J. Am. Chem. Soc.*, 1970, **92**, 1637.
- 4 K. Omura and D. Swern, *Tetrahedron*, 1978, **34**, 1651.
- 5 E. J. Corey and M. Chaykowski, *J. Am. Chem. Soc.*, 1962, **84**, 866.
- 6 H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, 1973, **95**, 1669.