

## Perhydrophenanthrenes; Novel Liquid Crystals

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Some perhydrophenanthrenes, prepared in order to fill the gap between bicyclohexanes and cholesteryl esters as liquid crystals, show nematic phases.

Recently Eidenschink *et al.*<sup>1,2</sup> demonstrated liquid crystalline behaviour for bicyclohexanes possessing wide nematic ranges, *e.g.* (1). Bearing in mind that cholesteryl (and cholestanyl) esters (2) are well known to form cholesteric mesophases, we felt that the novel perhydrophenanthrenes (3)—(9) should represent a link between these two types and may be of interest for practical applications.

The synthesis of the key ketones (15) ( $R = n-C_4H_9$  through  $n-C_8H_{17}$ ) was accomplished as shown in Scheme 1. Simple Birch reduction of (15) gave (17); further Birch reduction after intermediate addition of methanol gave (16).<sup>5</sup> The strong bases applied and Birch reductions are known to give the thermodynamically stable configurations of substituents (equatorial) and ring connections (*trans*). This could be confirmed by single peaks in the g.l.c. and <sup>13</sup>C-n.m.r. spectra for compounds (12) to (17). Acetylation of (16) ( $R = n-C_6H_{13}$ ) afforded the acetate (3) which showed nematic but monotropic

behaviour on cooling the molten compound of m.p. 74 °C to below 65 °C. The hexanoic esters (4)—(8) [from (16) with hexanoyl chloride and pyridine] revealed the nematic phase ranges given in Table 1.

There is a considerable alternation of  $T_{CN}$  with chain length of R whereas the influence on  $T_{NI}$  is rather small. As a consequence the nematic range  $\Delta T = T_{NI} - T_{CN}$  is widest in the case of even- and not odd-numbered side chains. Initial investigations show that the birefringence values of the esters are very low ( $\Delta n \leq 0.035$ ); more detailed determinations of their physical properties will be collected in the near future.

Treatment of (16) ( $R = n-C_6H_{13}$ ) with triphenylphosphine dibromide and potassium cyanide gave only inseparable mixtures of the  $\alpha$ - and  $\beta$ -nitrile epimers; however, reduction of (17) ( $R = n-C_6H_{13}$ ) with K-Selectride (tetrahydrofuran, -80 °C)<sup>6</sup> gave the axial alcohol (18) ( $R = n-C_6H_{13}$ ) the toluene-*p*-sulphonate of which afforded a 6% yield of pure equatorial nitrile (9)<sup>7</sup> together with higher amounts of elimination products. Compound (9) proved to be nematic in only a small range between 89 and 91 °C.

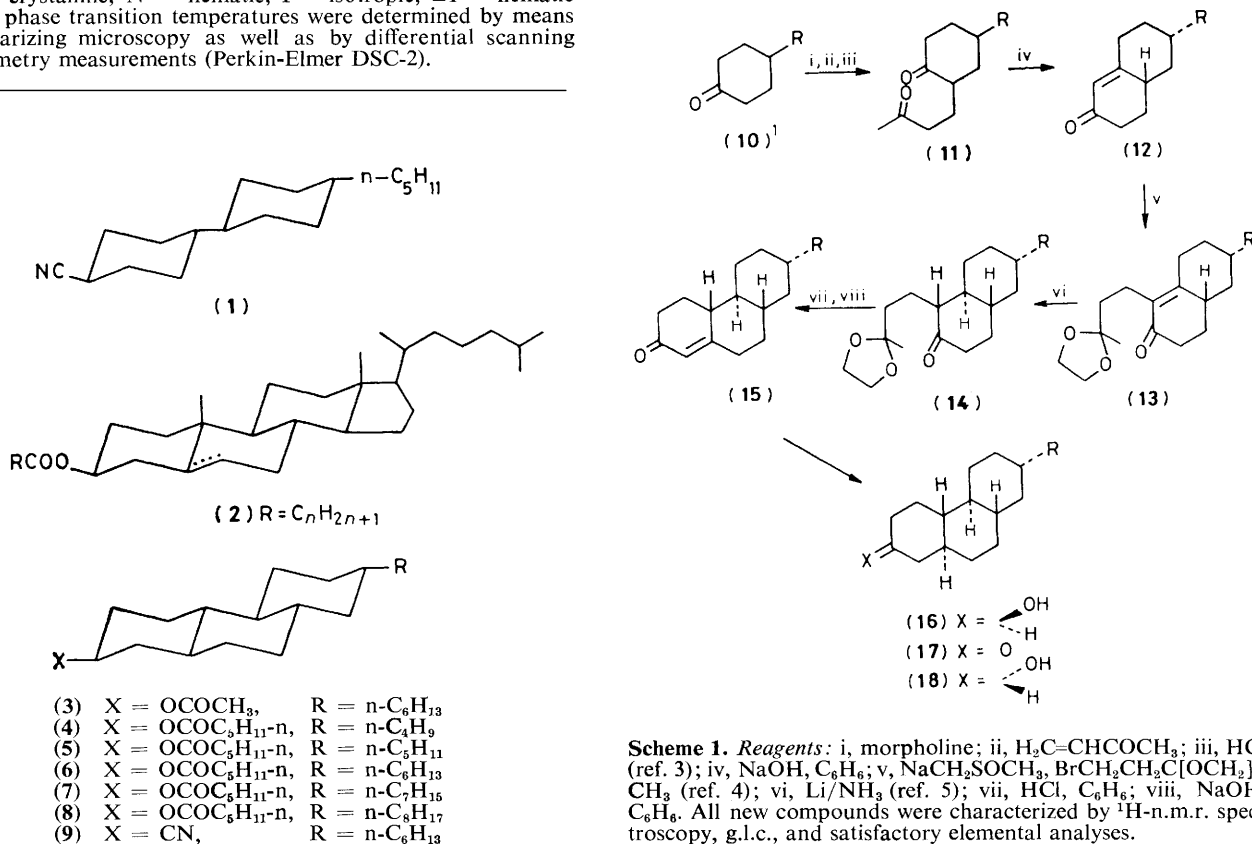
From these results it is concluded that the perhydrophenanthrenes so far investigated resemble the cholesterol-based liquid crystals more than those of the bicyclohexane type.

We thank the State of Nordrhein-Westfalen for a research grant and Prof. P. F. Casals, Université du Maine, Le Mans, France, for a gift of the cyclohexenones from which we

Table 1. Phase transitions (°C) of compounds (4)—(8).<sup>a</sup>

	C	N	I	$\Delta T$
(4)	68	(60)		Monotropic
(5)	70	78		8
(6)	57	76		20
(7)	66	80		14
(8)	57	79		22

<sup>a</sup> C = crystalline, N = nematic, I = isotropic,  $\Delta T$  = nematic range; phase transition temperatures were determined by means of polarizing microscopy as well as by differential scanning calorimetry measurements (Perkin-Elmer DSC-2).



prepared compounds (10). The assistance of Mr. T. Blümel in obtaining the phase transition data is gratefully acknowledged.

*Received, 7th August 1981; Com. 961*

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