Novel Nematic all-*trans*-Perhydrochrysenes

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Abstract: The fifteen all-*trans*-perhydrochrysenes **1ab**–**1cf** were prepared on a stereoselective route and their nematic phases recorded.

Liquid crystalline alicyclic compounds like bicyclohexyl[1] or all-*trans*-perhydrophenanthrene[2,3] derivatives may be considered as parts of the cholestanol or cholesterol skeleton. Like cholesteryl esters[4], they exhibit low melting and clearing points and nematic ranges up to 30 °C. Cyclohexyldecalins[5] behave in a similar way, but show nematic ranges up to 66 °C.

We wondered how the introduction of an additional ethylene bridge as in all-*trans*-perhydrochrysenes would change this general pattern and set out to synthesize compounds **1ab**–**1cf**. As starting materials we selected compounds **2a**–**c**, which we had previously used to synthesize perhydrophenanthrenes[2]. Alkylation with *m*-methoxyphenylethyl bromide gave **3a**–**c** in moderate yields[6], Birch reduction led to **4a**–**c**[7], which were cyclized with methanesulfonic acid to **5a**–**c**[8]. Another Birch reduction gave the enol ethers **6a**–**c**[9], which on hydrolysis with acid afforded the unsaturated ketones **7a**–**c**[10]. These were subjected to a Birch reduction with an excess of lithium to give the desired alcohols **1aa**–**1ca**[11]. All steps from **4a**–**c** to **1aa**–**1ca** proceeded in good yields[12]. The desired *trans*-configurations were achieved by spontaneous equilibrations of the carbonyl compounds **4a**–**c** and **7a**–**c** and by Birch reductions in a similar way as with the preparation of the perhydrophenanthrenes, the structure of one of which has meanwhile been confirmed by an X-ray analysis[13].

Expectedly, the melting and clearing points of ester derivatives are high, as shown by the butyrates **1ab**–**1cb** (Table 1). For that reason the ether derivatives **1ac**–**1cf** were prepared using potassium hydride in tetrahydrofurane (THF)[14]. These do not show this disadvantage to the same degree (Table 1). The nematic character is expressed in relatively broad ranges[15], comparable to those of the cyclohexyldecalins. While the high melting and clearing points probably exclude these novel nematic compounds from practical application they do provide another example of how nematic phase ranges depend upon the structure of aliphatic molecules.

R' \ R	*n*-C_3H_7	*n*-C_5H_{11}	*n*-C_6H_{13}
H	**1aa**	**1ba**	**1ca**
C(O)-*n*-C_3H_7	**1ab**	**1bb**	**1cb**
CH_3	**1ac**	**1bc**	**1cc**
n-C_3H_7	**1ad**	**1bd**	**1cd**
n-C_4H_9	**1ae**	**1be**	**1ce**
n-C_5H_{11}	**1af**	**1bf**	**1cf**

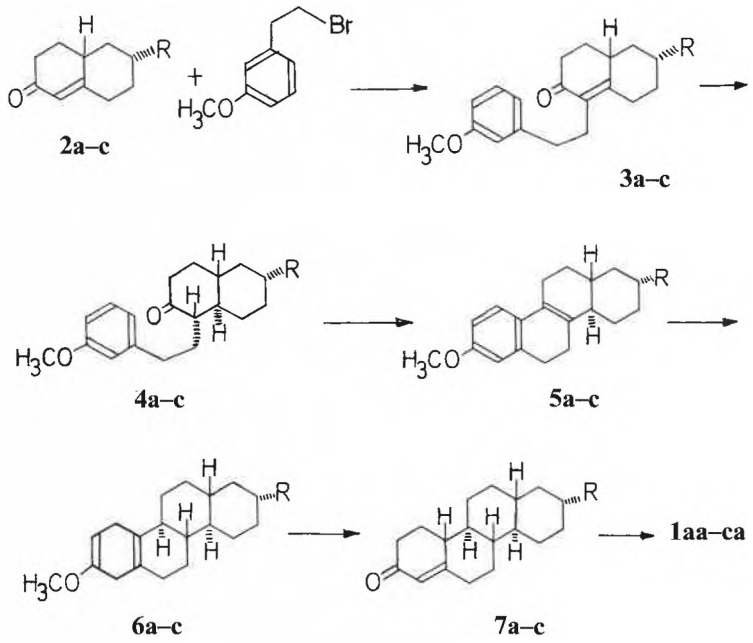

Table 1. Phase Transitions (°C) of Compounds **1ab**–**1cf** [a].

‹c›	‹n›	‹i›	ΔT	‹c›	‹n›	‹i›	ΔT
1ab	142	200	58	**1be**	135	182	47
1ac	155	184	29	**1bf**	115	165	50
1ad	157	185	28	**1cb**	132	195	63
1ae	134	180	46	**1cc**	108	162	54
1af	112	167	55	**1cd**	117	177	60
1bb	145	200	55	**1ce**	119	172	53
1bc	103	169	66	**1cf**	119	169	50
1bd	138	182	44				

[a] ‹c› = crystalline, ‹n› = nematic, ‹i› = isotropic; ΔT = nematic range.

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[6] Alkylation in *t*-BuOH/*t*-BuOK under reflux. Yields after chromatography (petrol ether, CH_2Cl_2, ether 5:3.5:1.5) 26–33%; oils.
[7] Addition of **3a**–**c** in THF to lithium and 1 eq *t*-BuOH in NH_3, after 90 min quenching with isoprene. Yields 51–78%; oils.
[8] Cyclization with a catalytical amount of CH_3SO_3H in benzene. Yields after recrystallization from EtOH 77–84%; *m.p.*: **5a** 86 °C, **5b** 70 °C, **5c** 73 °C.
[9] Addition of lithium to a mixture of **5a**–**c** in NH_3, THF, EtOH. Yields 68–70%; *m.p.*: **6b** 82 °C, **6c** 105 °C (EtOH).
[10] Hydrolysis of **6a**–**c** with 7N HCl in MeOH under reflux for 20 min. Yields 89–90%; *m.p.*: **7a** 78 °C, **7b** 117 °C, **7c** 103 °C (MeOH).
[11] Treatment of **7a**–**c** in THF, EtOH with a large excess of lithium in NH_3. Yields 81–93%; *m.p.*: **1aa** 169 °C, **1ba** 173 °C, **1ca** 178 °C (hexane); **1ba** showed the expected number of 23 single peaks in the completely proton decoupled ^{13}C-NMR spectrum from δ = 14.0 to 70.6.
[12] All new compounds were characterized by ^1H-NMR spectroscopy and satisfactory elemental analyses and showed single peaks in GL chromatography.
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[14] Ethers from **1aa**–**1ca** with KH (35% dispersion in mineral oil) in boiling THF, followed by addition of alkyl bromide and subsequent boiling for 2.5 h. Yields 80–90%.
[15] We thank Mr. H.-J. Kersting, Paderborn, for recording the phase transition data.

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