New Liquid Crystalline Tolanes from (-)-Menthone

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Synthetic manipulations were carried out with the aim of obtaining an advanced linear fragment for production of thermotropic liquid crystals. The chiral fragment synthesised was introduced in a tolanbenzoate mesogenic core by coupling of Sonogashira. The final chiral tolans showed smectic A and C and nematic liquid crystalline phases. The crystallographic structure of lactone from (-) menthone is presented.

I Introduction

The design and synthesis of new chiral liquid crystals has experienced a great growth, especially of ferroelectric liquid crystals (FLCs). This is due to practical applications of FLCs as high resolution displays and in photonical technologies for storage and reproduction of information based on non-linear optical (NLO) effects [1]. The correlation between molecular chirality and physical properties has been well studied and some models proposed [2]. Conventionally, natural abundant materials like amino acids or commercially available alcohols and esters such as (S)-2-methylbutan-1-ol, (S)-2-methyloctan-1-ol and (S)-ethyl lactate are used to synthesize chiral liquid crystals [3]. (-)-Menthone derivatives have been used only as chiral dopants, to induce ferroelectricity in smectic C (S_C) liquid crystals or more recently, in photochromic polymers [4]. In all cases the original cyclic structure of (-)-menthone was maintained. In the present work we describe a efficient synthetic approach to transform the (-)-menthone to an appropriate chiral structure which can provide high stereo- and regio-control for liquid crystals synthesis. To verify the efficiency of the chiral chain, we present the synthesis of new liquid crystalline tolanes (diphenylacetylenes) as a continuation of our most recent study [5].

II Experimental

II.1 Tecniques

^{1}H-NMR and ^{13}C-NMR spectra were obtained in CDCl$_3$ with 270 MHz (Bruker HX-270) spectrometer using TMS as internal standard. IR Spectra were recorded in KBr discs, nujol dispersions or films with a Perkin-Elmer model 283 spectrometer. Elemental analysis was done using a Perkin Elmer 2400CHN. Optical rotations were measured on a Perkin-Elmer 341 polarimeter at the sodium D line. GC analysis was conducted in a Varian 2 equipped with a FID detector using H$_2$ as carrier gas; capillary column used β-DEX 120 (30m x 0.25mm). X-ray data were collected in a difratometer Nonius CAD-4; refinement: full-matrix least-squares on F^2, GooF (F^2), programs: solution $\rightarrow$ SHELXS97; refinement $\rightarrow$ SHELXL97; molecular drawing $\rightarrow$ ZORTEP. The thermal transitions and the mesomorphic textures were determined using a Olympus BX 50 polarising microscope in conjunction with a Mettler Toledo FP-90 heating stage and Perkin Elmer DSC-2, using indium as a standard calibration.

The synthetic methodology used was very convenient, it is depicted in scheme 1.

Baeyer-Villiger oxidation afforded the correspondent lactone (1) [6]. Three oxidation systems were tested on a preparative scale (ca. 10 g of ketone) and the results obtained are summarized in Table 1. This is the most important step in the synthesis because the stereo- and regio-control must be guaranteed. NMR experiments (^{1}H, DEPT, COSY ^{1}H-^{1}H and HETCOR), chiral capillary GC and X-ray crystal analysis were used for controlling the structure of Baeyer-Villiger oxidation product **1** (Fig. 1 and Table 2).
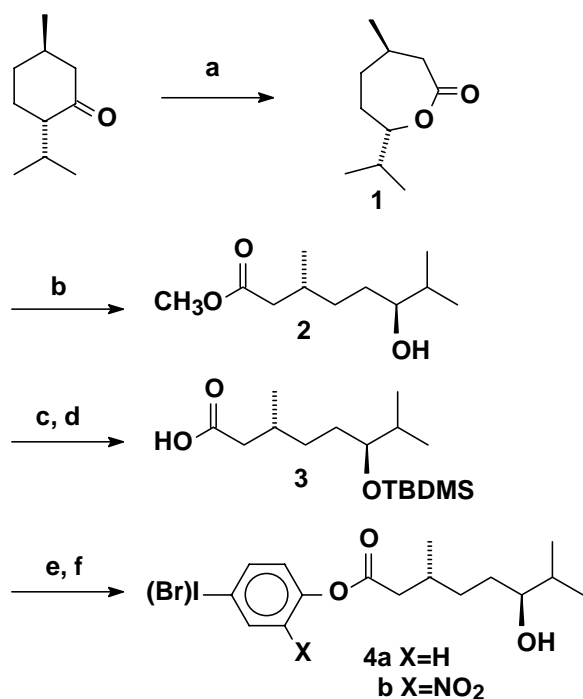
Scheme 1: *Regents and conditions* a. Baeyer-Villiger oxidation (see table 1). b. MeOH, H_2SO_4 conc., rt, overnight, (83%). c. TBDMSCl, imidazol, DMF, rt, 24h (88%). d. MeOH, 2.9M KOH, reflux, 3h (73%); e. 4-iodophenol or 2-nitro-4-bromophenol, DCC, DMAP, CH_2Cl_2, rt, overnight (73% and 66% respec.). f. HF48%/CH_3CN, rt, 15 min, (>95%).

Table 1. Baeyer-Villiger oxidation of (-)-menthone.

Entry	Peracid	Time (h)	T (°C)	Conversion[a]	Yield (%)	Ketone recov. (%)
1	b	66.5	25	Incomplete	32	41
2	c	96.0	25	Incomplete	70	13
3	d	7.5	25	Complete	90	-

[a] Monitored by TLC using hexanes/ethyl acetate (7:3) as eluent.
[b] MCPBA (3-Chloroperoxybenzoic acid).
[c] MMPP (Magnesium monoperoxyphtalate hexahydrate).
[d] MCPBA/CF_3CO_2H.

The chiral precursors (**4a** and **4b**) were coupled with a tolanebenzoate mesogenic core to investigate its efficiency in the production of liquid crystals. Scheme 2 illustrates the synthesis of the mesogenic core and the target molecules.
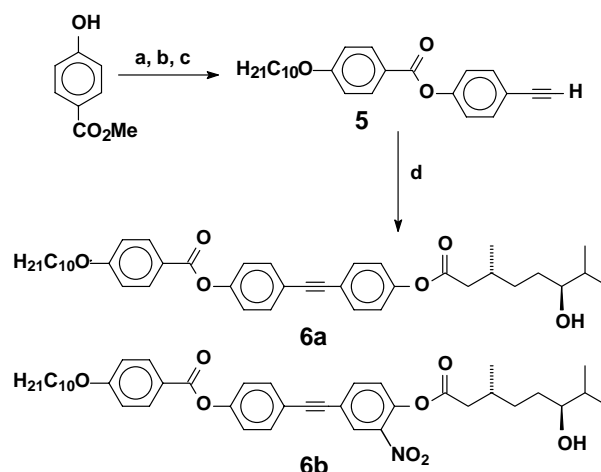
Scheme 2: a. *n*-decylbromide, K_2CO_3, butanone; b. i. MeOH, KOH; ii. conc. HCl (74% two steps); c. 4-ethynylphenol, DCC, DMAP, CH_2Cl_2 (82%); d. **4a** or **4b**, $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N/THF (3:1), (51-55%).

Methyl 4-hydroxybenzoate was alkylated with n-decylbromide by a traditional method. After hydrolysis the resultant acid was esterificated with 4-ethynylphenol [7] furnishing the alkyne **5**. Palladium catalysed cross-coupling between **5** and **4a** or **4b** led to the desired compounds **6a** and **6b**. Selected data for final compounds are displayed in the Table 3.
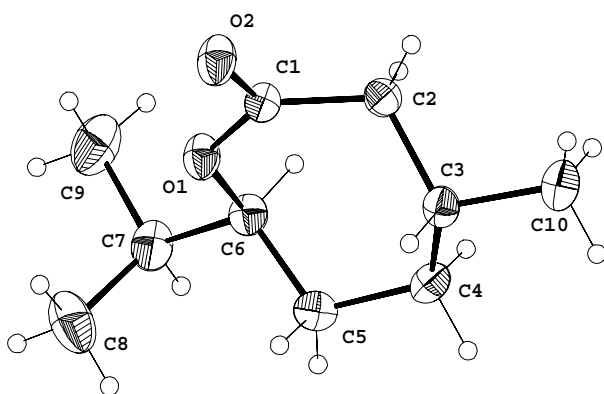

Figure 1. Molecular structure of the lactone from (3R,6S)-(-)-6-hydroxy-3,7-dimethyloctanoic acid (1) with atom-labelling scheme. Thermal ellipsoids are shown at 40% probability level.

Table 2. Crystal data for the lactone from ($3R,6S$)-(-)-6-hydroxy-3,7-dimethyloctanoic acid (1).

Empirical formula	$C_{10}H_{18}O_2$
Formula weight	170.24
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, $P2_12_12_1$
a (Å)	9.632(2)
b (Å)	10.273(2)
c (Å)	10.527(2)
Volume ($Å^3$)	1041.6(4)
Z, Calculated density (g.cm^{-1})	4, 1.086
Absorption coefficient (mm^{-1})	0.073
F(000)	376
Crystal size (mm)	0.50 x 0.40 x 0.40
Reflections collected / unique	1074 / 1074
Data / restraints / parameters	1074 / 0 / 110
GOOF (F^2)	1.098
Final indices	R1 = 0.0409, $_wR2 = 0.1006$

Table 3: Selected physical and spectroscopic data used to characterize the final compounds.

Com-pound	Optical rotation	Elemental analysis		^{1}H-NMR (δ, ppm)	^{13}C-NMR (δ, ppm)
		Calcd for	Found		
6a	$[\alpha]_D^{20}$ -2.0	$C_{41}H_{52}O_6$		δ 0.93 (m, 9H, 3CH$_3$), 1.08 (d, 3H, J=6.5Hz, CH$_3$), 1.50 (m, 21H, 10CH$_2$ and CH), 2.10 (m, 1H, CH), 2.40 (dd, 1H, J_{ab}=15.0Hz and J_{ax}=7.8Hz, -CH$_a$HCOOAr, A part of ABX syst.), 2.60 (dd, 1H, J_{ab}=15.0Hz and J_{bx}=6.0Hz, -CHH$_b$COOAr, B part of ABX syst.), 3.35 (m, 1H, -CH(CH$_3$)$_2$OH, 4.05 (t, 2H, J=6.4Hz, -CH$_2$OAr), 6.97 (d, 2H, J=8.7Hz, Ar), 7.09 (d, 2H, J=8.5Hz, Ar), 7.21 (d, 2H, J=8.5Hz, Ar), 7.56 (m, 4H, Ar), 8.14 (d, 2H, J=8.7Hz, Ar)	δ 17.0, 18.9, 19.9, 22.6, 25.9, 29.3, 29.5, 30.7, 31.5, 31.9, 33.4, 41.6 (–OCH$_2$C$_9$H$_{19}$), 68.3 (-CH(CH$_3$)$_2$OH), 88.6 (Ar$_1$C≡CAr$_2$), 88.7 (Ar$_1$C≡CAr$_2$), 114.3, 120.6, 120.7, 121.2, 121.7, 121.9, 132.3, 132.7, 150.5, 150.9, 163.6, 164.6 (ArCO$_2$Ar), 171.3 (ArOC=OCH$_2$-)
	(c 0.65, CHCl$_3$)	C 76.87	C 76.23		
		H 8.12	H 8.12		
6b	$[\alpha]_D^{20}$ -1.0	$C_{41}H_{51}NO_8$		δ 0.92 (m, 9H, 3CH$_3$), 1.08 (d, 3H, J=6.6Hz, CH$_3$), 1.48 (m, 21H, 10CH$_2$ and CH), 2.15 (m, 1H, CH), 2.45 (dd, 1H, J_{ab}=15.0Hz and J_{ax}=7.8Hz, -CH$_a$HCOOAr, A part of ABX syst.), 2.7 (dd, 1H, J_{ab}=15.0Hz and J_{bx}=6.0Hz, -CHH$_b$COOAr, B part of ABX syst.), 4.05 (t, 2H, J=6.5Hz, -CH$_2$OAr), 6.97 (d, 2H, J=8.8Hz, Ar), 7.21 (d, 2H, J=8.7Hz, Ar), 7.24 (d, 2H, J=8.5Hz, Ar), 7.60 (d, 2H, J=8.5Hz, Ar), 7.75 (dd, 1H, J=8.7 and 1.9Hz, Ar), 8.13 (d, 2H, J=8.8Hz, Ar), 8.22 (d, 1H, J=1.9Hz, Ar)	δ 14.2, 17.1, 19.0, 20.0, 22.8, 26.0, 29.2, 29.4, 29.6, 30.3, 31.5, 32.0, 33.0, 33.5, 41.3 (–OCH$_2$C$_9$H$_{19}$), 68.4 (-CH(CH$_3$)$_2$OH), 86.3 (Ar$_1$C≡CAr$_2$), 91.3 (Ar$_1$C≡CAr$_2$), 114.4, 119.6, 121.1, 122.3, 125.5, 128.6, 132.4, 133.1, 137.2, 141.8, 143.6, 151.6, 163.8, 164.7 (ArCO$_2$Ar), 170.6 (ArOC=OCH$_2$-)
	(c 0.69, CHCl$_3$)	C 71.82	C 71.21		
		H 7.44	H 7.45		
		N 2.04	N 1.95		

III Results and Discussion

Conventional chiral terminal groups are almost always linear and possess contiguous stereogenic centers. The unique branching points are only the chiral centers. From this point of view the compound **3** is not a "conventional" chiral tail such as 2-methyloctanol or aminoacids are. In the compound **3** the asymmetric centers are spaced by two atoms of carbon and additionally is present a methyl group at the end of the hydrocarbon chain. However, important factors such as a straight chain and the presence of good linking carboxylate group remain. Methyl branched systems generally show lower clearing points than their linear analogs [8]; presumably because the methyl group sticks out at an angle from the molecular rotational cylinder, and thereby disrupts efficient packing by increasing the separation between neighboring molecules. However, as the methyl branch is moved further away from the core of the mesogen, the clearing point depression is reduced. This demonstrates the greater degree of conformational freedom further away from the core since the effect of branching is less marked [9]. Thus we believe that the methyl group, placed at the last carbon of the main chain in **3**, does not significantly take effect on the mesomorphic behavior. Also the hydroxyl group may behave in the same way or even help molecular packing by establishing intermolecular hydrogen bonds.

The mesomorphic behavior of the final tolanes was investigated by optical microscopy and the thermal properties are compiled in Table 4. These compounds exhibited chiral nematic (N^*), smectic A (S_A) and ferroelectric (S_C^*) liquid crystalline phases.

Table 4: Selected physical and spectroscopic data used to characterize the final compounds.

Compound	K	S_A	$S_C{}^*$	N^*	I
6a	•	113.2	• (108.5)	• 164.4	•
6b	•	78.6 • 105.1		• 128.1	•

The triple bond between two aromatic rings is interesting, because it contributes to the polarizability, linearity and rigidity of the final molecules. These factors are important and determine many physical properties, such as thermal stability and viscosity in liquid crystals. The presence of the nitro group decreased the melting point expressively (compare 113.2 °C for compound **6a** and 78.6 °C for compund **6b**) and also reduced the thermal stability (compare 164.4 °C for compound **6a** and 128.1°C for compound **6b**). Such behaviour is due the greater van der Waals volume of the nitro group and its effect on molecular packing.

IV Conclusions

(-)-Mentone has been transformed into a nearly linear moiety through several chemical reactions including the Baeyer-Villiger oxidation. Two new chiral tolanes were synthesised, one non-laterally substituted **6a** and the other nitro-laterally substituted **6b**, using the chiral compound from (-)-mentone. Both compounds showed a N^* mesophase and **6b** shows also an enantiotropic S_A phase. But undoubtedly, the more exciting result is the S_C^* ferroelectric mesophase observed for compound **6a**, because it proves that compound **3** is efficient for producing a S_C^* phase.

Acknowledgements

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