Synthesis and Properties of New Optically Active γ-Lactones as Chiral Dopants for Ferroelectric Liquid Crystals

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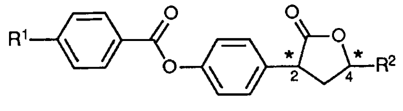
Optically active α-aryl-γ-alkyl-γ-lactones were synthesized through the reaction of chiral 1,2-epoxyalkanes with the carbanion derived from 4-methoxyphenylacetonitrile or 4-methoxyphenylacetic acid and shown to be good chiral dopants for ferroelectric liquid crystals.

It has recently been suggested that thin cells containing ferroelectric liquid crystals (FLCs) can be applied to high-speed switching devices.[1] The switching time depends on the magnitude of spontaneous polarization (P_s) and viscosity of the FLCs. The FLC materials are usually prepared by mixing chiral dopants possessing large P_s values with achiral smectic C (S_C) host liquid crystal mixtures having low viscosity. For chiral dopants various optically active compounds have been designed. In particular, we have proposed chiral dopants containing a chiral centre connected directly both to a core aromatic ring and to a polar group and have shown that these actually exhibit large P_s values.[2–5] Examples are compounds with the structure ArCHMeCO$_2$R.[2] To improve the P_s values further, we have designed FLCs having an optically active lactone ring, *e.g.* **1** and **2**, wherein two polar groups C=O and C–O–C are disposed so that each dipole is fixed in a nearly parallel direction. In addition, free rotation of the lactone ring is apparently more restricted than it is in ArCHMeCO$_2$R because this ring is directly connected to the core aromatic ring. We report herein the synthesis of compounds **1** which are indeed found to be superior chiral dopants.

The chiral γ-lactone **1a** was prepared according to the route shown in Scheme 1. The carbanion of 4-methoxyphenylacetonitrile **3** was allowed to react with (*R*)-1,2-epoxyoctane to give **4** as a *ca.* 1:1 mixture of diastereoisomers (70% yield). Hydrolysis of the cyano group using KOH in diethylene glycol followed by esterification with thionyl chloride afforded lactones **5a** (52%) and **5b** (44%). The diastereoisomers were easily separated by silica gel column chromatography. Alternatively, **5a** and **5b** were available by the reaction of (*R*)-1,2-epoxyoctane with the dianion of 4-methoxyacetic acid **6** and subsequent lactonization (45 and 48% yield respectively). Selective demethylation of **5a** was effected with EtSH–AlCl$_3$[6] to give the phenol derivative **7** (90% yield) which was esterified with 4-octyloxybenzoyl chloride to give **1a** (70% yield). Compounds **1b** and **1c** were synthesized similarly. Lactone **1e** was obtained from (*S*)-propylene oxide in a similar manner, whereas **1d** was prepared using a chiral epichlorohydrin. The cyano epoxide **8** (77% yield, *ca.* 1:1 diastereoisomer mixtures), obtained through the reaction of (*R*)-epichlorohydrin with the carbanion of **3**, was allowed to react with propylmagnesium bromide in the presence of CuI to give **9** in 59% yield. This cyano alcohol was converted into **1d** as described above.

Although compounds **1a**–**1e** did not exhibit a chiral smectic C phase (S_C*), they were employed as chiral dopants for



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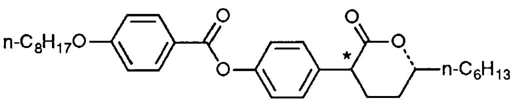

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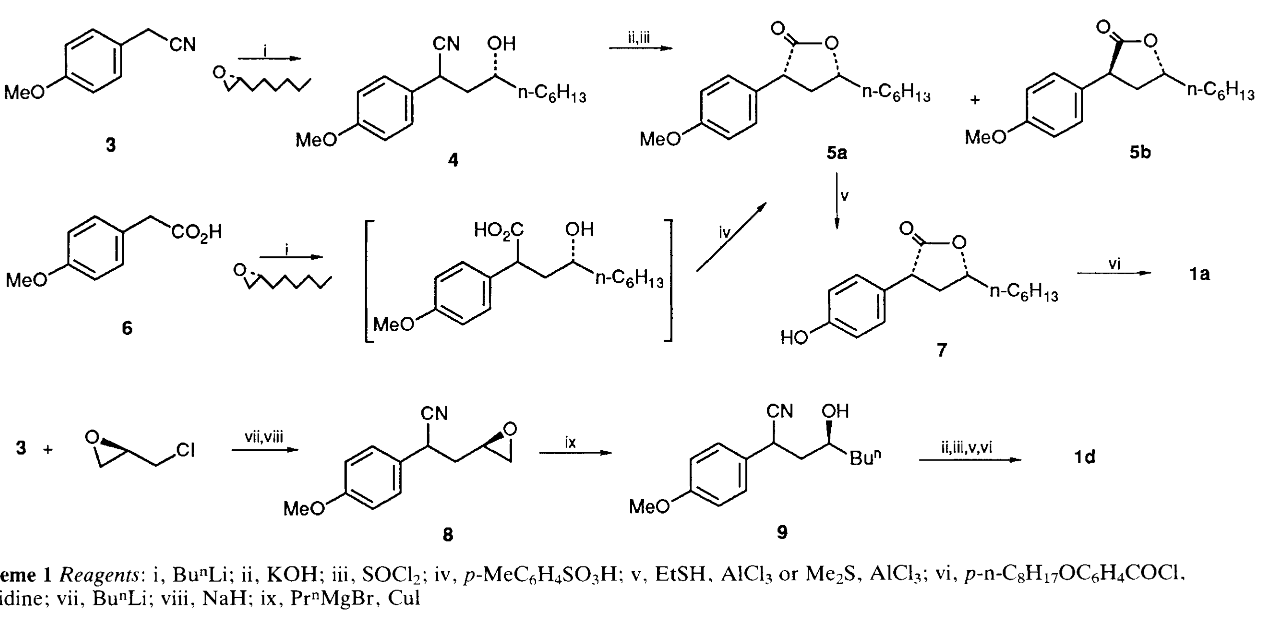
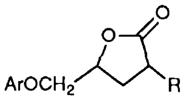
a; 2*R*,4*R* (*cis*), R^1 = n-$C_8H_{17}O$, R^2 = n-C_6H_{13}
b; 2*S*,4*R* (*trans*), R^1 = n-$C_8H_{17}O$, R^2 = n-C_6H_{13}
c; 2*R*,4*R* (*cis*), R^1 = n-C_8H_{17}, R^2 = n-C_6H_{13}
d; 2*S*,4*S* (*cis*), R^1 = n-C_8H_{17}, R^2 = Bu^n
e; 2*S*,4*S* (*cis*), R^1 = n-C_8H_{17}, R^2 = Me



Scheme 1 *Reagents*: i, Bu^{n}Li; ii, KOH; iii, SOCl$_2$; iv, *p*-MeC$_6$H$_4$SO$_3$H; v, EtSH, AlCl$_3$ or Me$_2$S, AlCl$_3$; vi, *p*-n-C$_8$H$_{17}$OC$_6$H$_4$COCl, pyridine; vii, Bu^{n}Li; viii, NaH; ix, Pr^{n}MgBr, CuI



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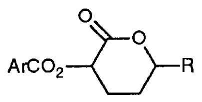

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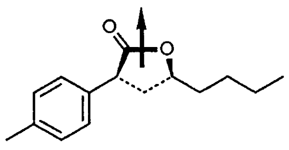
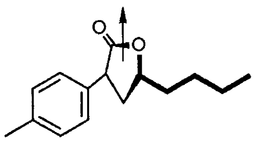


cis



trans

achiral smectic C liquid crystals. Thus, each was added to a host liquid crystals mixture A.† The electrooptical properties of the resulting mixtures are listed in Table 1. The mixture containing 2 wt% *cis*-lactone **1a** showed a very large P_s value (4.5 nC cm^{-2}), a short response time (162 μs) and tilt angle (25 °). Use of 4 wt% of **1a** resulted in a large enhancement of P_s and decrease of the response time: 12.7 nC cm^{-2} and 98 μs respectively. These P_s values are apparently larger than that for the acyclic model ArCHMeCO$_2$R and can be estimated to be comparable or slightly superior to P_s values of the related lactones **10**[7,8] and **11**.[9] Noteworthy is the fact that the *trans*-lactone **1b** showed a very small P_s value whereas the *cis*-lactones **1a** and **1c–1e** exhibited large values. This observation may be ascribed to the conformation of the lactones: the dipole moment of the *cis*-lactones is apparently arranged perpendicular to the axis of the core and alkyl chains, whereas that of the *trans*-lactone is nearly parallel to the planes of the core and alkyl side chain.‡ The former conformation is particularly important for high P_s to be realized, as discussed for **10**.[8] The nature of the group R^1 (octyloxy or octyl) did not influence P_s **1a** *vs.* **1c**, but a short R^2 lowered P_s somewhat (**1c** *vs.* **1d** or **1e**). The sign of the P_s is decisively correlated with the chirality of the lactone ring: (*R,R*), (+); (*S,S*), (−).

In contrast to γ-butyrolactones **1**, δ-valerolactones **2** showed very small P_s values.[10] Thus, the conformational rigidity of the lactone ring seems to be essential for high P_s values. The lactone ring system may thus be considered to be a new chiral core which introduces chirality to the whole molecule in a way different from the chiral centre(s) in alkyl side chains.

Table 1 Electrooptical properties of the chiral dopant **1** in host liquid crystal mixture A at 25 °C[a]

Chiral dopant	(wt%)	P_s[b] /nC cm^{-2}	Response time[c] /μs	Tilt angle/°
1a	(2)	+4.5	162	25
	(4)	+12.7[d]	98	24
1b	(10)	—[e]	891	14
1c	(2)	+4.4	153	26
1d	(2)	−4.2	169	24
1e	(2)	−4.1	171	23

[a] The liquid crystal mixture was sealed in a polyimide rubbing cell of about 2 μm thickness, and a square wave of 10 $V_{p\text{-}p}$/μm was applied to the cell. [b] P_s was measured by the triangular wave method. [c] Change of transmittance (from 0 to 90%) of light was observed. [d] Extrapolation to 100 wt% gives a value > 300 nC cm^{-2} (probably around 1000 nC cm^{-2}). [e] Too small to be measured.

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† The host liquid crystal mixture A consists of 2-(4-nonyloxyphenyl)-5-heptylpyrimidine (30 wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (20 wt%), 2-(4-decyloxyphenyl)-5-octylpyrimidine (30 wt%), and 2-(4-octyloxyphenyl)-5-nonylpyrimidine (20 wt%). The phase transition temperatures (*T*/°C) of the host A were Cr 13 S_CH56 S_A 65 N 70 I.

‡ This conformation was suggested by molecular mechanics calculations (MM2 and MOPAC).