Liquid-crystalline allene derivatives

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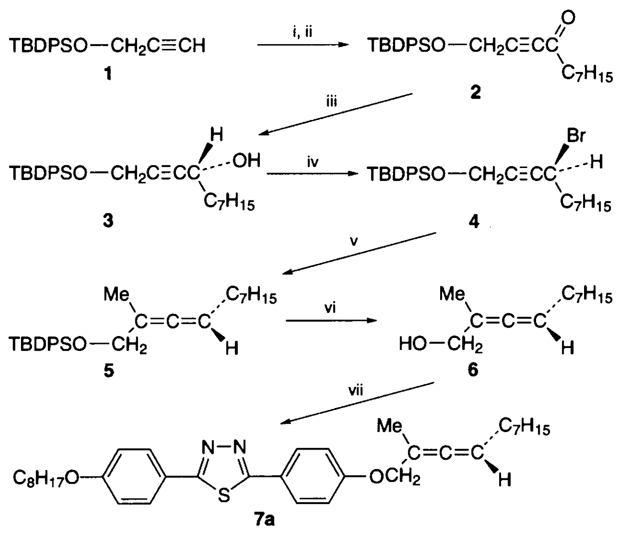
The synthesis of the first liquid-crystalline allene derivatives with chiral smectic C-phases is reported.

Ferroelectricity in liquid crystals was first reported and afterwards experimentally demonstrated by Meyer *et al.*[1] In recent years ferroelectric liquid crystals have attracted considerable interest because of their unique properties and their potential technical applications.[2] The basis of ferroelectricity in liquid crystals are a tilted arrangement of the molecules in layers (*e.g.* smectic C-phase) and molecular chirality. Particularly with the recent discovery of new mesophases, for example, the twisted-grain-boundary phase and the antiferroelectric and ferrielectric phases, chirality in liquid crystals has grown to be a topical subject in liquid-crystal research.[3,4] Nevertheless, to date most of the chiral liquid crystals represent molecules incorporating a centre of chirality. Only some rare examples of mesogens with an axis of chirality[5–9] or with a plane of chirality[10–12] have been reported. Here we describe the first axial chiral allene derivatives, which display liquid-crystalline properties.

The optically active allene derivatives were prepared as shown in Scheme 1. In this Scheme the optically active prop-2-ynyl alcohol **3** was obtained by (*R*)-Alpine borane reduction[13] of the alkynone **2** (88% ee).[14] **3** was then transformed to the corresponding bromide **4** with inversion of the configuration.[15] Anti-S_N2' substitution with a complex organocopper agent [MeCu·LiBr·MgBrI][16–19] gave the TBDPS-protected chiral allenic alcohol **5** with an ee of 52%.[14] After deprotection[20] the allenic alcohol **6** was etherified with different phenols using the Mitsunobu method.[21]

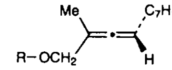


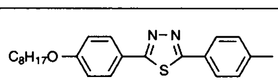
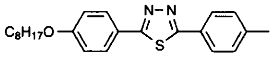
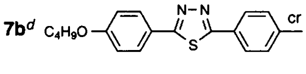
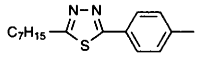
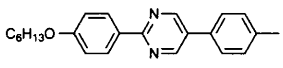
Scheme 1 *Reagents and conditions*: i, Bu^nLi, THF, 0.5 h, −78 °C, then *n*-octanal, 3 h, −78 °C, H_2O–HCl, 65%; ii, PCC, CH_2Cl_2, 4 h, 20 °C, 70%; iii, (*R*)-Alpine borane, THF, 4 days, 20 °C, 63% (88% ee); iv, CBr_4, PPh_3, pyridine, THF, 2 h, 20 °C, 63%; v, LiBr, Cu_2I_2, MeMgBr, THF, 1 h, 0 °C, 80%; vi, Bu_4NF, THF, 24 h, 20 °C, 70% (52% ee); vii, 4-[5-(4-octyloxyphenyl)-1,3,4-thiadiazol-2-yl]phenol, PPh_3, DEAD, THF, 20 h, 20 °C, 28%.

The racemic allenes *rac*-**7a,c,d** were obtained starting from the racemic alcohol *rac*-**3** which was obtained by treatment of octanal with lithium 3-(*tert*-butyldiphenylsilyloxy)propynide. Transformation of *rac*-**3** into the racemic allenic alcohol *rac*-**6** was performed in the same way as described for the optically active compounds. The phase-transition temperatures of these new allene derivatives† incorporating a thiadiazole[22] or a pyrimidine[23] ring are summarised in Table 1.

The racemic three-ring compounds *rac*-**7a** and *rac*-**7d** exhibit a smectic C-phase and a nematic phase. The optically active thiadiazole derivatives **7a** and **7b** display smectic C*-phases, cholesteric phases and also small regions of blue phases at the transition to the isotropic liquid. Due to a substantial electric

Table 1 Phase-transition temperatures *T* (°C)[a] and corresponding enthalpy values Δ*H* (kJ mol^{-1})[b] of the chiral allene derivatives **7**.



Compound	R	Transition temperatures *T* / °C (transition enthalpies Δ*H* / kJ mol^{-1})
rac-**7a**		cr 64 S_C 98 N 101 is (35.4) (3.2) (1.8)
7a		cr 67 S_C* 99 N* 100 BP 101 is (35.5) (3.0) (1.4)[c]
7b[d]		cr 60 S_{C1}* 72 S_{C2}* 73 S_{C3}* 90 N* 97 BP 98 is (25.0) (0.04)[c] (1.3) (0.9)[c]
rac-**7c**		cr 13 is (22.2)
rac-**7d**		cr 59 S_C 95 N 96 is (35.1) (7.1)[c]

[a] Phase-transition temperatures were determined by optical microscopy between crossed polarizers using a Mettler FP HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope; abbreviations: cr = crystalline solid, S_c = smectic C-phase, S_c* = chiral smectic C-phase, N = nematic phase, N* = cholesteric phase, BP = blue phase, is = isotropic liquid. [b] Determined by differential scanning calorimetry using a Perkin Elmer DSC-7 calorimeter (10 K min^{-1}). The transition enthalpies were taken from the first heating scans. [c] Not resolved. [d] Compound **7b** displays a more complex phase behaviour. Two additional phase transitions (S_{C1}*–S_{C2}*–S_{C3}*) with very low transition enthalpies were found within the S_C*-phase region of this compound. These phase transitions are accompanied by significant changes of the optical texture observed between crossed polarizers. Depending on the sample preparation different broken fan textures or schlieren textures were observed for all three phases. However, no changes could be detected in the X-ray diffraction pattern. The X-ray pattern in all three phases shows one sharp reflection in the small-angle region and a diffuse scattering in the wide-angle region, suggesting a smectic layer structure without order in the layers. The layer thickness within the C-phase continuously decreases with decreasing temperature (27.5 Å at 75 °C, 27.35 Å at 72 °C and 27.1 Å at 60 °C). Because of the rather high conductivity of the samples a distinction between ferroelectric, antiferroelectric and ferrielectric C-phases was not possible on the basis of the switching behaviour.

conductivity we were not able to measure the switching behaviour of **7a** or **7b** in the Sc*-phases.

Nevertheless, compounds **7** represent the first liquid-crystalline allene derivatives. The optically active compounds **7a** and **7b** are the first allenes which exhibit chiral smectic C-phases. Further investigations of the liquid-crystalline phases and the preparation of other chiral allene derivatives are in progress.

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Footnote

† Correct CHN analyses, and ^{1}H and ^{13}C NMR spectra have been recorded. **7a**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.90 (t, 6 H, CH_3), 1.26–1.36 (m, 18 H, CH_2), 1.49–1.52 (m, 2 H, $\mathit{CH_2}C=$), 1.82 (d, 3 H, $=CCH_3$), 1.85 (dt, 2 H, CH_2), 2.01 (dt, 2 H, CH_2), 4.06 (t, 2 H, CH_2O), 4.60 (s, 2 H, $OCH_2C=$), 5.21–5.22 (m, 1 H, $=CH$), 7.02 (d, 2 H, ArH), 7.05 (d, 2 H, ArH), 7.92 (d, 2 H, ArH), 7.96 (d, 2 H, ArH); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 202.68 (C=*C*=*C*), 167.15 (thiadiazole), 167.07 (thiadiazole), 161.43 (quat Ar), 160.88 (quat Ar), 129.34 (2C, Ar CH), 129.22 (2C, Ar CH), 123.09 (quat Ar), 122.86 (quat Ar), 115.60 (2C, Ar CH), 115.04 (2C, Ar CH), 95.32 (*C*=C=*C*), 92.06 (*C*=C=*C*), 70.49 (OCH_2), 68.31 (OCH_2), 31.87 (CH_2), 31.80 (CH_2), 29.33 (CH_2), 29.21 (2C, CH_2), 29.17 (CH_2), 29.14 (CH_2), 29.03 (CH_2), 28.76 (CH_2), 26.01 (CH_2), 22.65 (CH_2), 16.08 ($\mathit{C}H_3=$), 14.06 (2C, CH_3); MS *m*/*z* (rel. intensity, %): 546 (52, M^+), 531 (14), 461 (15), 447 (29), 382 (78), 363 (21), 270 (100), 199 (21), 137 (25), 95 (11), 81 (26), 55 (22). *rac*-**7d**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.90 (t, 3 H, CH_3), 0.96 (t, 3 H, CH_3), 1.2–1.4 (m, 14 H, CH_2), 1.53 (m, 2 H, $CH_2C=$), 1.83 (d, 3 H, $=CCH_3$), 1.86 (dt, 2 H, CH_2), 2.02 (dt, 2 H, CH_2), 4.08 (t, 2 H, CH_2O), 4.59 (s, 2 H, $OCH_2C=$), 5.21 (m, 1 H, $=CH$), 7.04 (d, 2 H, ArH), 7.10 (d, 2 H, Ar H), 7.57 (d, 2 H, Ar H), 8.44 (d, 2 H, Ar H), 8.96 (s, 2 H, Py H).

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