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# SYNTHESIS OF OPTICALLY ACTIVE α-CYANOBENZYL ALKYL ETHERS

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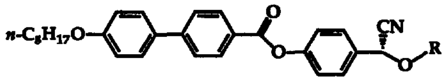
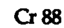
*The title ethers, expected chiral dopants for ferroelectric liquid crystals, were prepared by the allylation of chiral cyanohydrins under the acidic conditions followed by hydrogenation, or alternatively by the Johnson's cyanation of chiral acetals followed by fluorination.*

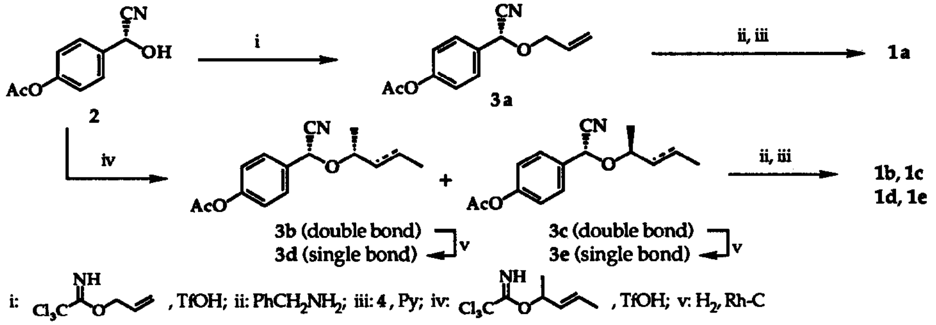
We have shown that the ferroelectric liquid crystals having a chiral center connected directly to the core aromatic ring exhibit much enhanced spontaneous polarization (Ps) requisite to high-speed switching devices.1,2) Optically active a-cyanobenzyl esters realized short response time useful for practical applications.3) For related studies, chiral cyanohydrin ethers of type **1** became required. However, the Williamson conditions cannot be applied to their synthesis, because under the basic conditions cyanohydrins readily decompose and the optical activity of the expected product is lost quickly. We report herein two solutions for the synthesis of the title ethers.



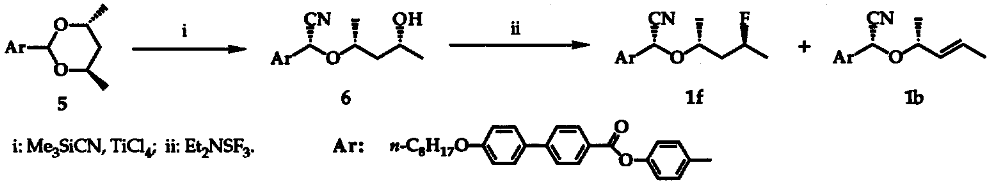
**1**

| | | | | | |
|---|---|---|---|---|---|
| **a**: R = |  | Cr 101 $S_C$* 106 $S_A$ 143 I | **d**: R = |  | Cr 100 $S_A$ 110 I |
| **b**: |  | Cr 88 $S_A$ 117 I | **e**: |  | Cr 84 $S_A$ 124 I |
| **c**: |  | Cr 99 $S_A$ 133 I | **f**: |  | Cr 94 ($S_C$* 84) $S_A$ 103 I |

The optically active cyanohydrin **2** (94% ee)4) was allowed to react with allyl trichloroacetoimidate5) in *c*-$C_6H_{12}$-$CH_2Cl_2$ at room temperature in the presence of trifluoromethanesulfonic acid (TfOH) to give the corresponding *O*-allyl cyanohydrin **3a** in 36% yield without any trace of racemization. Deacetylation of **3a** was carried out with benzylamine (86% yield) to afford the corresponding phenol which was esterified with 4'-octyloxybiphenylcarbonyl chloride (**4**) to give rise to **1a** (81% yield). When 1-methyl-2-butenyl trichloroacetoimidate6) was allowed to react with **2**, the corresponding ethers **3b** (38%) and **3c** (23%) were obtained. The combined yields were higher than that of **3a** due possibly to the stabilization effect of an intermediate allylic cation by the two methyl groups. Each diastereomer was easily separated by column chromatography. Hydrogenation of **3b** or **3c** was achieved with the cyano group totally intact by means of Rh-C to give an alkyl ether **3d** or **3e** in 49% or 74% yield, respectively. A Pd-C catalyst reduced the CN group also; $PtO_2$ turned out less active. Compounds **1b**-**1e** were prepared from **3b**-**3e** in the same manner as **1a**.



The cyanohydrin ethers of type **1** were prepared alternatively. The chiral acetal **5** was prepared from the corresponding aldehyde with (*R*,*R*)-2,4-bis(trimethylsilyloxy)pentane using $Me_3SiOTf$ in 91 % yield.[7] The reaction of **5** with $Me_3SiCN$ gave **6** stereoselectively (95% de) in 57% yield with $TiCl_4$ as the catalyst.[8,9] The alcohol **6** was fluorinated with diethylaminosulfur trifluoride[10] to afford **1f** (61%) along with **1b** (13%).



The phase transition temperatures[11] of **1** are shown in the previous page. Of the compounds we prepared, **1a** exhibited $S_C$* phase, the Ps being 58 $nC/cm^2$ at 98 °C comparable to the Ps's of ArCHMeCOOR or ArCHMeOR.[1] Compounds **1a-f** were found to be useful chiral dopants for ferroelectric liquid crystals. Details will be discussed elsewhere.

## References and Notes

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2) K. Nishide, A. Nakayama, T. Kusumoto, T. Hiyama, S. Takehara, T. Shoji, M. Osawa, T. Kuriyama, K. Nakamura, and T. Fujisawa, *Chem. Lett.*, **1990**, 623.
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4) Prepared according to the Narasaka's method: H Minamikawa, S. Hayakawa, T. Yamada, N. Iwasawa, and K. Narasaka, *Bull. Chem. Soc. Jpn.*, **61**, 4379 (1989).
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6) Prepared in 80% yield from trichloroacetonitrile with 3-penten-2-ol in the presence of NaH.
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8) J. D. Elliott, V. M. F. Choi, and W. S. Johnson, *J. Org. Chem.*, **48**, 2295 (1983); V. M. F. Choi, J. D. Elliott, and W. S. Johnson, *Tetrahedron Lett.*, **25**, 591 (1984).
9) Cyanation with $BF_3{\bullet}OEt_2$ catalyst gave a 3 : 2 diastereomeric mixture.
10) W. J. Middleton, *J. Org. Chem.*, **40**, 574 (1975); M. Hudlicky, *Org. Reactions*, **35**, 513 (1988).
11) Given in °C. Cr: crystalline phase, $S_C$*: chiral smectic C phase, $S_A$: smectic A phase, N*: chiral nematic phase, I: isotropic liquid phase, $S_C$: smectic C phase, N: nematic phase. The value and the phase in the parenthesis refer to those observed under cooling.

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