

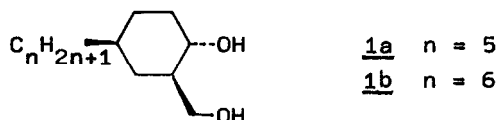
AMPHIPHILIC LIQUID CRYSTALS I. SYNTHESIS OF *trans*-4-*n*-ALKYL-*trans*-2-HYDROXYMETHYLCYCLOHEXANOLS

C. TSCHIERSCHE and H. ZASCHKE^x

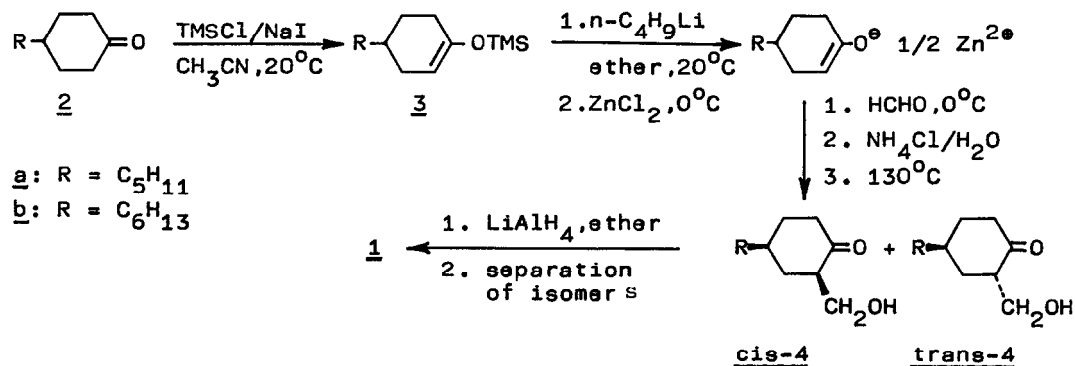
Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg
 Weinbergweg 16, DDR-4050 Halle (Saale), GDR

Abstract: A selective synthesis of *trans*-4-alkyl-*trans*-2-hydroxymethylcyclohexanols is described, the key feature of which is the use of selective aldol addition reaction of cyclohexanone zinc-enolates with formaldehyde. These compounds exhibit liquid crystalline behaviour in the presence of small amounts of water.

We have recently reported about the liquid crystalline properties of some 2-(*trans*-4-alkylcyclohexyl)propane-1,3-dioles 1. In order to get more information about the reasons for this unusual behaviour we decided to synthesize *trans*-4-*n*-alkyl-*trans*-2-hydroxymethylcyclohexanols 1 which have not been described in literature yet.



We synthesized the compounds 1 according to the reaction scheme. It is essential to generate the Li-enolates by the reaction of the corresponding silylenolates with *n*-butyllithium or methyllithium ². (The deprotonation with LDA gives only low yields of 4). These Li-enolates were treated with 0,5 equ. ZnCl₂ in ether ^{3,4}



to give the corresponding Zn-enolates which were treated with an Ar-HCHO-gas mixture, generated by thermal depolymerization of α -polyoxymethylene in an Ar stream at 170°C. This kinetically controlled aldol reaction yields a diastereomeric mixture consisting of 90 % trans-4 and only 10 % of the desired cis-isomer 4. This crude reaction product was easily equilibrated to a mixture containing 70 % of the thermodynamically more stable diastereomer cis-4 simple by heating to about 130°C for 15 min or by distillation at this temperature presumably by a retro-aldol process, catalyzed by traces of basic Zn-compounds. No equilibration was observed when the product was carefully distilled in a kugelrohrapparatus before heating. The cis-4 enriched mixture was reduced with LiAlH₄ in ether and the compounds 1 were purified by repeated recrystallization from n-hexane. In a typical run 0.1 mol (25,4 g) 3b, dissolved in 100 ml ether was lithiated by slow addition of 0,1 mol (45,3 ml of a 2,21 molar solution in n-hexan) n-butyl-lithium at 20°C. The mixture was stirred for 1 h at 20°C and then cooled to 0°C. 0,05 mol ZnCl₂ (73 ml 0,73 molar solution in ether) was added at 0°C. Afterwards it was stirred at this temperature for 30 min and then a formaldehyde-argon mixture was vigorously bubbled through for 5 min at 0°C. After quenching with sat. NH₄Cl solution the product was worked up and distilled under reduced pressure at 130-140°C to yield 15,3 g (72 %, b.p. 125°C at 0,1 mm Hg) 4b. The final products 1a and 1b exhibit no liquid-crystalline behaviour but after treatment with 2,5 mol water a smectic mesophase was observed by polarization microscopy. The transition temperatures are summarized in Table 1. The mesomorphic behaviour of 1a and 1b is being investigated at present.

Table 1 Melting behaviour of 1a and 1b with and without water

Comp.	n	m.p.(°C)	Comp.	C	S	I ¹⁾
<u>1a</u>	5	64,5	<u>1a</u> ·2,5 H ₂ O	. 42	. 44	.
<u>1b</u>	6	67,0	<u>1b</u> ·2,5 H ₂ O	. 48	. 59	.

1) The compounds were saturated with water (ca. 10 % by weight) and now exhibit liquid-crystalline properties; C means crystalline solid; S is a smectic mesophase; I describes the isotropic liquid; the microanalysis, ¹H NMR, ¹³C NMR and IR spectra were accurate.

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