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New Chiral 2-Arylidene-*p*-Menthane-3-Ones

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Methylation of 1*R*,4*R*-2-arylidene-*p*-menthane-3-ones by methyl iodide stereo specifically yields 4-methyl derivatives with 1*R*,4*R*-configuration. An alternative way, (-)-menthone methylation and further crotonic condensation with aromatic aldehydes, leads to 1:1 mixture of 1*R*,4*R*- and 1*R*,4*S*-diastereomers. The properties of new 2-arylidene-4-methyl-*p*-menthane-3-ones as chiral components of the induced LC systems based on MBBA or 5CB have been compared with those for their 4-unsubstituted analogues and the corresponding 4-bromo derivatives.

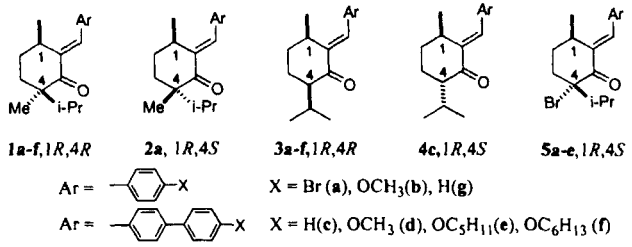
Keywords: 2-arylidene-4-methyl-*p*-menthane-3-ones; synthesis; induced cholesteric systems; helical twisting power; the temperature dependence of the helical pitch

INTRODUCTION

The 1*R*,4*R*-2-arylidene-*p*-menthane-3-ones are known as chiral components of induced cholesteric LC systems which possess high helical twisting power. An influence of the 2-arylidene grouping structure both on the helical twisting power (β) of these chiral dopants and on their disordering effect in mesophase has been studied [1-6]. At the same time, there is little information concerning an influence of structural changes in the cyclic fragment of those compounds on their properties as chiral dopants [1-3]. In this connection, the main objectives of present work are following:

- To obtain of the new 2-arylidene-4-methyl-*p*-menthane-3-ones (**1** and **2**) that differ in C-4 configuration and *p*-substituent in the 2-arylidene fragment.

- To compare of the helical twisting power (β) of chiral dopants **1, 2** with that for their unsubstituted analogues (**3, 4**) and the corresponding 4-bromo derivatives (**5**). In addition, the temperature dependence of the induced helical pitch (*P*) for the LC systems which include the above mentioned chiral compounds has been studied.



1a-f, 1*R*,4*R* **2a**, 1*R*,4*S* **3a-f**, 1*R*,4*R* **4c**, 1*R*,4*S* **5a-e**, 1*R*,4*S*

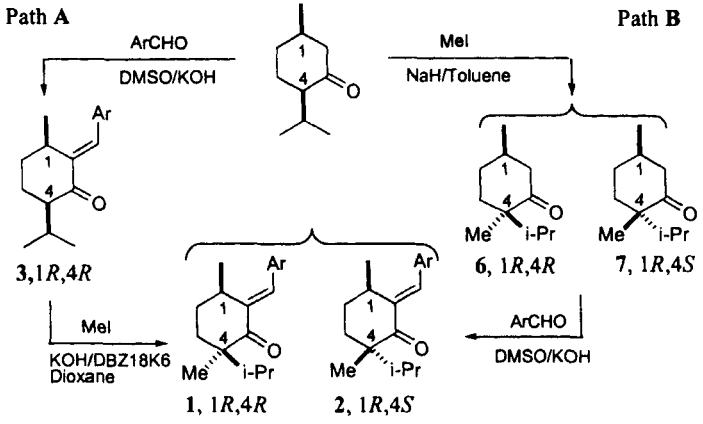
Ar = X X = Br (**a**), OCH_3(**b**), H(**g**)

Ar = X X = H(**c**), OCH_3 (**d**), OC_5H_{11}(**e**), OC_6H_{13} (**f**)

RESULTS AND DISCUSSION

Synthesis

Two possible paths leading to the desired compounds **1, 2** in the instance to obtain 4-bromobenzylidene derivatives **1a** and **2a** have been tested (**Scheme 1**).



Scheme 1

The methylation of 1*R*,4*R*-2-(4-bromobenzylidene)-*p*-menthane-3-one (**3a**) by methyl iodide under basic conditions (path **A**) yields the 4-methyl derivative with the 1*R*,4*R*-configuration (**1a**) stereospecifically. Using path **A** the series of *cis*-1*R*,4*R*-2-arylidene-4-methyl-*p*-menthane-3-ones (**1b-f**) has been obtained (Table I).

By the path **B** the 1:1 mixture of the diastereomeric 4-methyl-*p*-menthane-3-ones (**6**, **7**) is formed. Further condensation of this mixture with 4-bromobenzaldehyde leads to the mixture in the same ratio of the corresponding 2-arylidene derivatives **1a**, **2a**. From this mixture, 1*R*,4*S*-2-(4-bromobenzylidene)-4-methyl-*p*-menthane-3-one (**2a**) is isolated by preparative liquid chromatography.

The structures of both 4-bromobenzylidene derivatives (**1a**, **2a**) were established by X-ray analysis [7].

Table I Characteristics of 2-arylidene-4-methyl-*p*-menthan-3-ones **1**, **2**

Compound	X	Yield (%)	m.p. (°C)	IR (cm^{-1})[a]	
				$\nu_{C=O}$	$\nu_{C=C}$, ν_{Ar}
1a	Br	77	139–140	1682	1605, 1578
2a	Br	18	32–33	1688	1618, 1578
1b	OCH_3	51	109–110	1675	1600
1c	Ph	81	122–123	1668	1596, 1587
1d	$C_6H_4OCH_3$	22	152–154	1682	1603
1e	$C_6H_4OC_5H_{11}$	29	91–92	1679	1605
1f	$C_6H_4OC_6H_{13}$	43	85.5–86.5	1680	1603

[a] for KBr pellets

The Molecular Structure of the Chiral Dopants

According to X-ray data [7], the molecular structures of the diastereomeric compounds **1a** and **2a** in the crystals differ in the cyclohexanone ring conformation and the alkyl substituents orientation. In the compound **1a** the ring has a *chair*-like

conformation with the axial 1-methyl and the equatorial 4-isopropyl groups; 4-methyl one occupies the axial position. Taking into account the results of molecular mechanics (MM) simulation for the model compound **1g** [7], the *chair*-like conformation, an analogue to that in the crystal of **1a**, is believed to be dominant for the 1*R*,4*R*-*cis*-diastereomers in solution including LC as well. Therefore, compounds **1a-f**, as well as other compounds of the *cis* series (**3** and **5**) [8,9] can be considered to be conformationally homogeneous. The same orientation of the substituents Y at the C-4 atom make it possible to consider that the molecular anisometry of the *cis*-compounds decreases in sequence variation of Y: H > Br ≈ Me with increasing of effective Van-der-Waals radius for these substituents.

In contrast to the conformationally homogeneous *cis*-diastereomers **1**, the molecules of the *trans*- ones **2** are conformationally labile in solution as evidenced by the MM simulation for model compound **2g** [7]. The simulated *chair*-like conformation of **2g** with the axial 1-methyl and 4-isopropyl groups and the equatorial 4-methyl is the most favourable. However, only 0.87 kcal/mol of the MM sterical energy for such a conformation is lower as compared to that of the nearest *twist*-form. The same conformational lability have been noted for the diastereomeric pair **3c** and **4c** [11].

It is also important to note that the cinnamoyl fragment of all compounds considered have *E*-configuration [7-10]. Therefore the introduction of an oxyalkyl substituent into the *p*-position of the terminal benzene ring of the compounds **1c** as well as **3c** and **5c** should lead to the increase of molecular anisometry.

New Chiral Compounds in the Induced Cholesteric Systems

All new chiral dopants obtained induce the left cholesteric helix in MBBA and 5CB. An influence of the structural variation on the β values in a series of the chiral dopants **1** (Y = CH_3) (see Table II) is analogous to that in the series of compounds **3** (Y = H) and **5** (Y = Br) [1]. The most significant increase of the |β| values is observed

as the second benzene ring containing a *p*-oxyalkyl substituent especially is incorporated in the chiral dopant molecules (cf. **1b** and **1d–f**; **3b** and **3d–f**; **5b** and **5d, e**).

TABLE II The helical twisting power (β, $m\mu^{-1}$ mol.fr.$^{-1}$) and of dP_{rel}/dT (grad^{-1}) parameter [11] of the chiral dopants **1–5** in MBBA and 5CB.

Compound			MBBA		5CB	
	X	Y	−β	$dP_{rel}/dT \times 10^4$	−β	$dP_{rel}/dT \times 10^4$
1a	Br	CH_3	29.5 ± 1.1	—	29.2 ± 1.4	—
2a[*)]	Br	CH_3	25.6 ± 1.1	—	29.4 ± 0.8	—
1b	OCH_3	CH_3	29.3 ± 1.1	8.9 ± 1	—	−11 ± 3
1c	C_6H_5	CH_3	37.8 ± 2.8	24 ± 3	41.6 ± 2.3	−38 ± 3
1d	$C_6H_4OCH_3$	CH_3	34.8 ± 1.0	−3.5 ± 1	30.6 ± 2.8	−85 ± 4
1e	$C_6H_4OC_5H_{11}$	CH_3	42.9 ± 3.3	−65 ± 5	—	—
1f	$C_6H_4OC_6H_{13}$	CH_3	47.5 ± 2.2	−54 ± 2	46.5 ± 2.0	−88 ± 3
3a	Br	H	32.6 ± 2.0	—	28.0 ± 1.1	—
3b	OCH_3	H	30.5 ± 1.1	10.6 ± 2	—	−38 ± 2
3c	C_6H_5	H	41.9 ± 1.4	0.4 ± 2	36.9 ± 0.6	−39 ± 1
4c[*)]	C_6H_5	H	—	—	39.8 ± 1.6	—
3d	$C_6H_4OCH_3$	H	48.9 ± 1.5	−28 ± 3	40.1 ± 2.4	−69 ± 3
3e	$C_6H_4OC_5H_{11}$	H	54.0 ± 4.0	−64 ± 2	41.2 ± 2.9	−110 ± 4
3f	$C_6H_4OC_6H_{13}$	H	52.7 ± 1.7	−64 ± 3	42.4 ± 2.4	−33 ± 2
5a	Br	Br	32.2 ± 1.0	—	—	—
5b	OCH_3	Br	32.8 ± 0.7	10 ± 2	—	−14 ± 3
5c	C_6H_5	Br	44.5 ± 3.1	−18 ± 3	46.5 ± 1.2	−40 ± 2
5d	$C_6H_4OCH_3$	Br	49.6 ± 1.9	−52 ± 5	50.7 ± 1.2	−119 ± 3
5e	$C_6H_4OC_5H_{11}$	Br	52.4 ± 1.1	−69 ± 6	54.1 ± 1.6	−138 ± 6

[*)] Compounds have 1*R*,4*S* configuration, the rest are the 1*R*,4*R* diastereomers.

The helical twisting power of the chiral dopants studied does not significantly depend on the configuration (*R* or *S*) of the C-4 chiral centre and on molecular conformational features mentioned above (the compound pair **1a**, **2a** or **3c**, **4c**). The variation of the substituent Y at the C-4 atom influences on the β value only slightly. One can notice, twisting power for the 4-methyl derivative **1** as a rule just lower compared to that for their 4-H (**3**) and 4-Br (**5**) analogs with the same substituent X.

These data combined with our previous results [1-6] prove that the twisting power of the different 2-arylidene-*p*-menthane-3-one derivatives is determined mainly by the structure of the 2-arylidene fragment.

The LC systems based on MBBA which include the compounds **1c** and **1d** in the contrast to the other chiral dopants are characterised by some increase of the *P* value with temperature growth (the positive dP_{rel}/dT values, Table II). The introduction of a *p*-oxyalkyl substituent into the molecules **1c**, **3c** or the replacement of OCH_3 group by a phenyl one (**5b** → **5c**) leads to the negative dP_{rel}/dT values.

In all induced cholesteric systems based on 5CB, the $P(T)$ dependence with the negative dP_{rel}/dT value are observed (Table II). Consequently, the character of the $P(T)$ dependence is caused not only by the chiral dopant nature, but by the ordering extent of nematic solvent.

EXPERIMENTAL

Materials

The composition of reaction mixtures was determined by high performance liquid chromatography (HPLC) and by gas chromatography (GC). The Milichrom-2 liquid chromatograph equipped with a 2×6 mm Silasorb 600 column (a 99.5 : 0.5 octane/buthylacetate mixture was used as eluent and 4-carbomethoxybiphenyl as internal standard) and the Tsvet-500 gas chromatograph equipped with a 5mm×3m column were used (stationary phase was 10 % of 1,2,3-*tris*-cyanoethoxypropane on

Silachrom). IR spectra was recorded on Specord M80 spectrometer.

The compounds **3a-e**, **4b**, and **5a-e** were synthesized as described in Refs.[3,10,12]. Methylation of (–)-menthone (path **B**, Scheme 1) were carried out as described in Ref. [13].

1*R*,4*R*-2-arylidene-4-methyl-*p*-menthane-3-ones 1a-f (path A, Scheme 1, typical procedure)

To the solution of 1*R*,4*R*-2-arylidene-*p*-menthane-3-one (6.2 mmol), 5 ml of methyl iodide and 0.1 g of dibenzo-18-crown-6 in 25 ml dioxane, 1 g of powdered KOH was added and the solution was stirred at 25 °C. The progress of reaction was monitored by HPLC. When the reaction was completed (5-8 h usually), the reaction mixture was diluted by solution of aqueous HCl (5 ml of conc. HCl in 200 ml of ice water), the precipitate was filtered, washed with water and dried. The crude product was purified by recrystallisation from 2-propanole or hexane. All compounds gave a satisfactory elemental analysis data. The yield, melting point and IR data for the compounds prepared by this typical procedure are listed in the Table I.

1*R*,4*S*-2-(4-bromobenzylidene)-4-methyl-*p*-menthane-3-one 2a (path B, Scheme 1)

To a solution of 0.9 g (≈5.3 mmol) of the resultant mixture of methylation and 1.1 g (5.3 mmol) of 4-bromobenzaldehyde in 3 ml DMSO, 0.2 g of powdered KOH was added and the solution was stirred at 25 °C during 2 h. The reaction mixture was diluted by 100 ml of 2 % aqueous acetic acid and then was extracted into $CHCl_3$ (3×25 ml). The combined organic extracts were washed with water, dried on $CaCl_2$ and then evaporated. According to HPLC, the residue (1.6 g) contained 30 wt % of compound **1a** and 29 % of **2a**, that corresponded to 59 % of the overall yield of diastereomers **1a** and **2a**. Recrystallization from hexane yielded 0.3 g of **1a**. The

1*R*,4*S*-diastereomer **2a** was isolated from the mother liquor after recrystallisation of **1a** by column chromatography on silica gel (Woelem, 5-40 μm, 60×3 cm) using benzene as eluent and by recrystalization from methanol (cooling to −10 °C) to yield pure **2a** (0.35 g).

Liquid Crystalline Properties Measurements

The measurements of the *P* values were carried out by Grandjean–Cano method as described in the previous report [11]. The values of helical twisting power were calculated from $\beta = (Pc)^{-1}$ equation, where *c* is the concentration of chiral dopant in mole fraction.

CONCLUSION

The helical twisting power of the diastereomeric 2-arylidene-4-methyl-*p*-menthane-3-ones does not depend on the C-4 chiral centre configuration. Variation of the substituent at the C-4 chiral centre (Y = CH_3, H, Br) leads to only slight changes of the helical twisting power. The structure of 2-arylidene fragment is the most important in this regard.

In the LC systems which include the new chiral dopants, both increase and decrease of the helical pitch with temperature growth is observed. The different character of *P*(*T*) dependence found is caused by the distinction in the molecular anisometry of the chiral dopants and, consequently, by their different influence on the nematic ordering.

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