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NEW SYNTHESIS OF THE LIQUID CRYSTALLINE BICYCLOHEXYLBENZENE DERIVATIVES

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Abstract A new improved approach to prepare the liquid crystalline bicyclohexylbenzene derivatives is proposed. The key stage is the synthesis of 3-(trans-4-arylcyclohexyl)-6-alkyl (or aryl) cyclohex-2-en-1-ones via the condensation of the corresponding Mannich salts with 2-substituted acetoacetic esters (or methyl benzyl ketones) in the presence of a base. The catalytic hydrogenation of these cyclohexenones in base media gives mainly saturated trans-ketones which are promising semiproducts for the preparation of different kinds of the LC compounds containing a bicyclohexyl fragment. The chemical transformations of the prepared cyclohexanones were carried out and as a result a range of LC compounds both known and new ones were synthesized.

INTRODUCTION

The liquid crystalline compounds containing a trans,trans-bicyclohexylbenzene moiety are very useful in LC mixtures because of their low viscosity and low birefrigence.[1, 2] The synthesis of these compounds was generally realized according to scheme which provides for using of catalytic cross-coupling reaction as a key stage.[3-6] The range of bicyclohexylbenzene derivatives containing the 4-fluorophenyl,[7] 3,4-difluorophenyl,[8,9]

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3,4,5-trifluorophenyl,[10] 4-cyanophenyl,[11] or 4-difluorochloromethoxyphenyl fragment[12] is prepared using the mentioned approach.

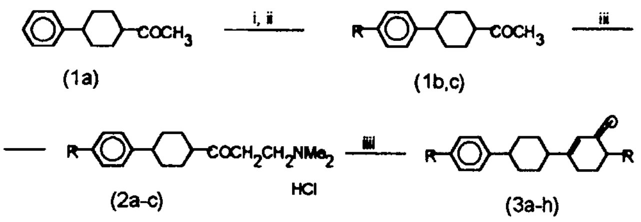
In this report we propose a new pathway to prepare derivatives of bicyclohexylbenzene.

RESULTS AND DISCUSSION.

We have synthesized a variety of both known and new bicyclohexylbenzene derivatives using the Michael-type condensation as a key stage. As it was reported in our previous papers 3,6-disubstituted cyclohexenones arriving from the condensation of Mannich salts with the 2-substituted acetoacetic esters (or methyl benzyl ketones) are the convenient semiproducts for further chemical transformations in liquid crystals synthesis.[13,14] Here we use as the starting reactant trans-1-acetyl-4-phenylcyclohexane (1a) which is easily available from the Nenitcescu reaction.

Compound (1a) was converted in the usual way with dimethylamine hydrochloride and paraform to the corresponding Mannich salt (2a) (R = H). The condensation of salt (2a) with 2-alkylsubstituted acetoacetic esters in a basic medium gives three-ring cyclohexenones (3a-c) as well as analogous condensation of (2a) with methyl 4-methoxybenzylketone gives the four-ring cyclohexenone (3h) (R = $C_6H_4OCH_3$).

To introduce alkyl substituent in position 4 of phenyl ring the starting ketone (1a) was acylated and then catalytically hydrogenated. The prepared in this way ketones (1b, c) (R = C_3H_7; C_5H_{11}) were converted into Mannich salts (2b,c) and then into corresponding cyclohexenones (3d-f) in the same way as (1a).



i. R COCl/$AlCl_3$;

ii. H_2 /Pd, ethanol;

iii. Me_2NH HCl/$(CH_2O)_n$, isopropanol;

iiii. $RCH(COCH_3)COOC_2H_5$ (or $CH_3OC_6H_4CH_2COCH_3$), base.

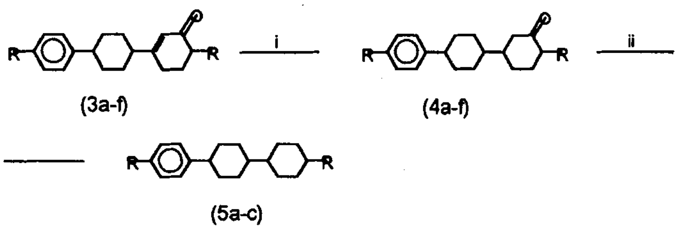
The highest yield of cyclohexenone (3a) (R = C_5H_{11}) was achieved as follows: the mixture of equimolar quantities of Mannich salt and 2-pentylacetoacetic ester in diglyme was refluxed during 5 h in the presence of potassium hydroxide (table 1).

TABLE 1 Yields of cyclohexenone (3a) depending of the reaction conditions

Solvent:	dioxane	isopropanol	glyme	diglyme
Base:	KOH	i-PrONa	KOH	KOH
Yield of (3a), %:	52	13	26	68

For further transformations of cyclohexenones (3) standard procedures were used. Ketones (3a-f) were hydrogenated in the presence of palladium on carbon to give the corresponding saturated cyclohexanones (4a-f). As in the case of other 3,6-disubstituted cyclohexenones the highest yields of trans,trans-isomers (4a-f) (about 85%) were achieved in base media. Earlier we have shown [15] that the catalytic hydrogenation of 6-aryl substituted cyclohex-2-en-1-ones gives a complicated mixture of reduction products. The same result was obtained here. Our attempts to prepare trans-2-(4-methoxy-phenyl)-5-[trans-4-(4-propylphenyl)cyclohexyl]cyclohexan-1-one from cyclohexenone (3h) failed.

Cyclohexanones (4a-c) were reduced using Huang-Minlong procedure to give the corresponding hydrocarbons (5a-c) containing the bicyclohexyl fragment. It should be noted that during the reaction partial isomerisation of cyclohexanone ring takes place. The resulting product is a mixture of trans,trans- and trans,cis-isomers in ratio 2:1. But the wanted trans, trans-isomers (5a-c) may be easily separated by crystallisation.



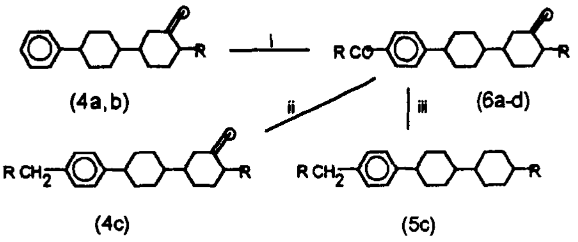
(3a-f) (4a-f) (5a-c)

i. H_2/Pd, KOH, ethanol; ii. N_2H_4 , KOH, diethylene glycol.

The cyclohexanones (4a,b) having no substituent in position 4 of phenyl ring were acylated in the usual way giving the corresponding diketones. Diketones (6) were reduced in two ways.

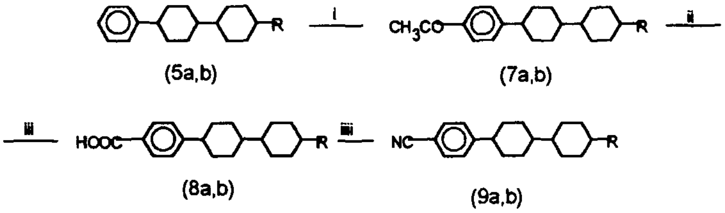
1. Catalytic hydrogenation of ketone (6c) over palladium on carbon provides selective reduction of carbonyl group in α-position to phenyl ring and leads to ketone (4c). This is the other way to obtain substituted ketone (4c).

2. Complete reduction of both carbonyl groups in ketone (6c) using Huang-Minlong procedure gives the substituted hydrocarbon (5c).



i. RCOCl/$AlCl_3$; ii. H_2 /Pd, ethanol; iii. N_2H_4 , KOH, diethylene glycol.

The unsubstituted trans,trans-hydrocarbons (5a,b) were converted in the usual way into cyanoderivatives (9a,b) which have been described earlier. [18]



i. $CH_3COCl/AlCl_3$; ii. NaOBr/NaOH; iii. $SOCl_2$; iiii. NH_4OH; iiiii. $SOCl_2$ /DMF.

The chemical transformations shown above illustrate our approach for an effective and convenient synthesis of various liquid crystalline bicyclohexylbenzene derivatives.

TABLE 2 Properties of prepared compounds (1-7).

No	R	R	Yield (%)	Phase transition temperatures, °C
3a	H	C_5H_{11}	68	Cr 90 I
3b	H	C_3H_7	71	Cr 102 I
3c	C_5H_{11}	C_5H_{11}	60	-
3d	C_3H_7	C_3H_7	58	Cr 89 N 104 I
3e	C_3H_7	C_5H_{11}	57	Cr 44 S_B 51 S_A 65 N 117 I
3f	H	CH_2CH_2 C_4H_9	60	S_X 144 S_B 183 I
3h	C_3H_7	$C_6H_4OCH_3$	54	Cr 144 N 193 I
4a	H	C_5H_{11}	86	Cr 68 N 106 I
4b	H	C_3H_7	82	Cr 84 N 104 I
4c	C_4H_{11}	C_5H_{11}	80	-
4d	C_3H_7	C_3H_7	87	Cr 109 N 155 I
4e	C_3H_7	C_5H_{11}	86	S_X 146 S_B 151 N 168 I
4f	H	CH_2CH_2 C_4H_9	82	S_X 60 S_B 224 I
5a*	H	C_5H_{11}	51	Cr 39 S_B 109 N 110 I
5b*	H	C_3H_7	48	Cr 76 S_B 97 N 103 I
5c*	C_4H_{11}	C_5H_{11}	55	Cr 30 S 191 I
6a	CH_3	C_5H_{11}	80	Cr 107 N 200 I
6b	C_2H_5	C_5H_{11}	60	Cr 69 N 218 I
6c	C_4H_9	C_5H_{11}	58	Cr 70 S_B 74 N 197 I
6d	C_5H_{11}	C_5H_{11}	52	Cr 70 S_B 105 N 187 I
7a	-	C_5H_{11}	66	Cr 108 N 211 I
7b	-	C_5H_{11}	81	Cr 116 N 216 I
8a	-	C_3H_7	70	Cr 263 N 350 I
8b	-	C_5H_{11}	76	Cr 308 N 350 I
9a*	-	C_5H_{11}	56**	Cr 54 S 61 N 234 I
9b*	-	C_3H_7	63**	Cr 80 N 247 I

* The properties of these compounds are given also in [16-18].

** Yields of transformations acid --- nitrile

EXPERIMENTAL

The structures of the prepared compounds are consistent with analytical data including H^1 NMR and mass spectra. Phase transfer temperatures were measured using a heating stage in conjugation with a polarising microscope and also using a Setaram DSC 92.

The compounds were prepared using standard synthetic procedures.

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