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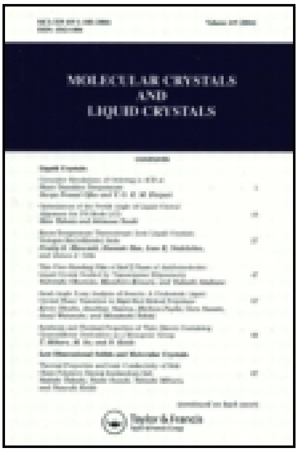

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3,6-Disubstituted Cyclohexenones in the Synthesis of New Three Ring Liquid Crystalline Compounds with the Negative Dielectric Anisotropy

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3,6-Disubstituted Cyclohexenones in the Synthesis of New Three Ring Liquid Crystalline Compounds with the Negative Dielectric Anisotropy

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New improved approach for preparation of the three ring liquid crystalline compounds with 2,3-difluorobenzene moiety is proposed. The key stage is the synthesis of 3,6-disubstituted 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 base. The chlorination with phosphrous pentachloride of these cyclohexenones or methylation with methylmagnesium iodide followed oxidative aromatization give new three ring compounds, which could be used in the LC compositions with negative dielectric anisotropy.

Keywords 2,3-Difluorobenzene derivatives; 3,6-disubstituted cyclohex-2-en-1-ones; liquid crystal; synthesis

1. Introduction

The liquid crystalline compounds containing 2,3-difluorobenzene moiety are very useful as the components for LC mixtures because of their negative dielectric anisotropy [1,2]. The synthesis of these compounds was generally realized according to the scheme, which provides for using of catalytic cross-coupling reaction as a key stage [3–5]. Some syntheses of the bicyclohexylbenzene LC derivatives have been carried out starting from 4-alkylbicyclohexyl-4-one [6]. In this article we show a new pathway to prepare three-ring derivatives possessing 2,3-difluorobenzene moiety. We believe the advantage of our way is that one provides for complete excluding of expensive palladium catalysts and low temperatures reactions.

2. Results and Discussion

2.1. *Syntheses*

We have synthesized a variety of new three-ring derivatives possessing 2,3-difluorobenzene moiety using the Michael-type condensation as a key stage. As it was

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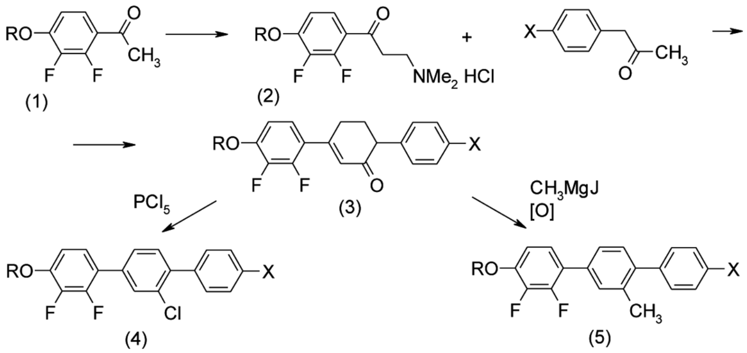
reported in our previous papers 3,6-disubstituted cyclohexenones arriving from the condensation of Mannich salts with the 2-substituted acetoacetic esters (or substituted methyl benzyl ketones) are the convinient semiproducts for the further chemical transformations in liquid crystals synthesis [7–11]. Earlier we have also reported the new cyclopropanol approach for the synthesis of three-ring cyclohexylbiphenyl LC compouds using substituted 1-cyclohexylcyclopropanoles as the precursors instead of Mannich salts in the condensation with acetoacetic esters or methyl benzyl ketones [12].

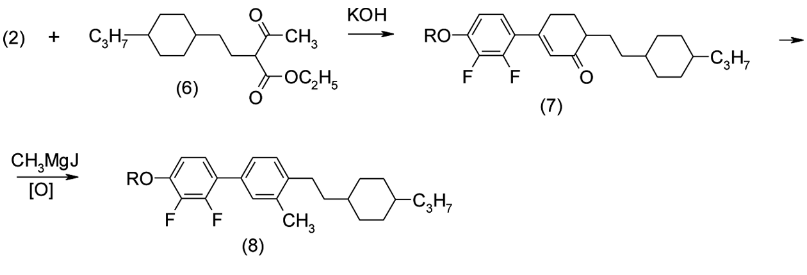
Here three main pathways for the preparation of three ring 3,6-cyclohexenones with 2,3-difluorobenzene moiety have been developed:

a. Condensation of substituted methyl benzyl ketones with the Mannich salts (2) on the base of easily available 4-alkoxy-2,3-difluoroacetophenones (1). This method finally leads to laterally substituted LC terphenyl derivatives (4,5).



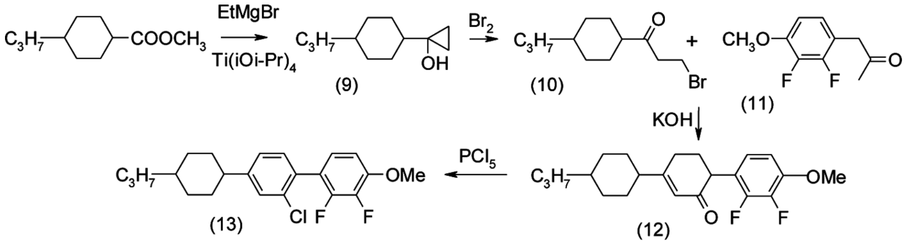
$R=C_2H_5$, C_4H_9; $X=Cl$, OCF_3, C_2H_5, C_5H_{11};

b. Condensation of Mannich salt (2) on the base of 4-alkoxy-2,3-difluoroacetophenone. (1) with 2-[2-(trans-4-alkylcyclohexyl)ethyl]acetoacetic ester (6). The resulting cyclohexenones (7) are precursors for the three ring LC compounds with the dimethylene bridge (8).



$R=C_2H_5$, C_4H_9;

c. Starting from alkyl trans-4-alkylcyclohexanecarboxylate as the precursor for the corresponding cyclopropanol (9) (according Kulinkovich reaction [13]), which was brominated and then condensed with 4-methoxy-2,3-difluorobenzyl methyl ketone (11).

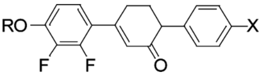


2,3-Difluorosubstituted acetophenones (1) prepared from the available 2,3-difluoroalkoxybenzenes in the Friedel-Crafts reaction conditions can be converted in the usual way with dimethylamine hydrochloride and paraform to the corresponding Mannich salts (2). The condensation of salts (2) with 2-alkylsubstituted acetoacetic esters in basic media gives three-ring cyclohexenones (7) as well as analogous condensation of (2) with 4-substituted methylbenzylketones affords the three-ring cyclohexenones (3).

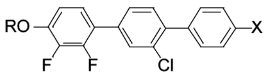
Using Kulinkovich reaction we have made the successful attempt to apply this synthetic approach to prepare three-ring cyclohexenones (12) possessing 2,3-difluorobenzene moiety.

For the further transformations of cyclohexenones (3,7,12) standard synthetic organic chemistry procedures were used. The chlorination with phosphrous pentachloride of these cyclohexenones or methylation with methylmagnesium iodide

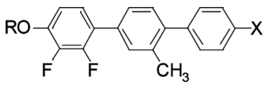
Table 1. Phase transition temperatures [°C] of prepared compounds.



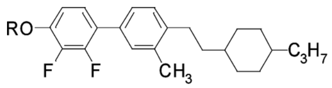
No	R	X	T,°C
3a	C_2H_5	Cl	Cr 145 Iso
3b	C_2H_5	OCF_3	Cr 124 Iso
3c	C_4H_9	Cl	Cr 110 Iso
3d	C_4H_9	OCF_3	Cr 121 Iso
3e	C_4H_9	C_2H_5	Cr 99 Iso
3f	C_4H_9	C_5H_{11}	Cr 79 Iso



No	R	X	T,°C
4a	C_2H_5	Cl	Cr 152 Iso
4b	C_2H_5	OCF_3	Cr 118 Iso
4c	C_4H_9	Cl	Cr 96 (N 68) Iso
4d	C_4H_9	OCF_3	Cr 79 SmA 71 Iso
4e	C_4H_9	C_2H_5	Cr 78 Iso
4f	C_4H_9	C_5H_{11}	Cr 51 N 60 Iso



No	R	X	T,°C
5a	C_4H_9	Cl	Cr 79 (N 59) Iso
5b	C_4H_9	OCF_3	Cr 50 Iso
5c	C_4H_9	C_2H_5	Cr 55 (N 47) Iso
5d	C_4H_9	C_5H_{11}	Cr 52 N 72 Iso



No	R	T,°C
8a	C_2H_5	Cr 74 N 101 Iso
8b	C_4H_9	Cr 67 N 98 Iso

followed oxidative aromatization give new laterally substituted three ring compounds (4,5,8,13).

2.2. *Mesogenic Properties*

Mesogenic properties of the intermediate cyclohexenones (3,7,12) and transformation products prepared on the base of them (4,5,8,13) have been examinated (Table 1).

The prepared cyclohexenones (3,7,12) are not liquid crystalline. But first of all these compounds are interesting as precursors for the further chemical transformations because of reactive enone moiety presence. An initial examination of the mesophase behaviour of prepared compounds (4,5,8,13) shows that only compounds with the enough long chain in the both terminal positions possess liquid crystalline phases over a narrow temperature range.

3. Experimental

The structures of the prepared compounds are consistent with the analytical data including H^1 NMR and mass spectra. Phase transition temperatures were measured using a Linkam heating stage in conjugation with a polarising PZO microscope and also using a Setaram DSC 141.

Here we describe the example of synthetic procedures as the general one for such compounds. All compounds have been prepared according the analogous instructions.

All used 4-substituted methylbenzylketones have been prepared by reaction of the corresponding 4-substituted phenylacetyl chlorides with magnesium malonic ester followed by hydrolysis in 20% sulphuric acid.

2-(2-(Trans-4-propylcyclohexyl) ethyl) acetoacetic ester (6) has been prepared starting from trans-4-propylcyclohexane carboxylic acid. Synthesis of 1-(trans-4-propylcyclohexyl) cyclopropanol starting from methyl trans-4-alkylcyclohexanecarboxylate and its further bromination are described in [12].

The Condensation General Procedure. The mixture of 0.05 mol Mannich salt (2), 0.055 mol 2-alkylacetoacetic ester (or 4-substituted methyl benzylketone) and 0.15 mol potassium hydroxide in 150 ml of dioxane was refluxed during 6 h under stirring. After cooling 300 ml of 10% sulfuric acid solution was added carefully (evolution of carbon dioxide in the case of acetoacetic ester using) and product was extracted with methylene chloride. Organic layer was washed with water, dried over anhydrous magnesium sulfate and filtered through short column with silica gel. The residue obtained after the solvent evaporation was recrystallized from ethanol. The yields were 45–60%.

2-Bromoketone (10) obtained from 1-(trans-4-propylcyclohexyl)-1-cyclopropanol (9) (0.041 mol) was dissolved together with 2,3-difluoro-4-methoxyphenylacetone (11) (9.0 g, 0.045 mol) in 100 ml of diglyme. After adding of granulated potassium hydroxide (8.4 g, 0.15 mol) the resulting mixture was then refluxed under stirring during 4 h. After cooling to room temperature and treatment with 10% solution of sulphuric acid the product was twice extracted with benzene. After drying over sodium sulphate and removing of the solvent the ketone (12) has been twice crystallized from ethanol. The yield was 52% (isolated product); m.p. 127–128°C.

Ketone (12) was then chlorinated according below general procedure giving (13); yield 39%; Cr 101 Iso.

The Chlorination General Procedure. Phosphorous pentachloride (0,015 mol) was slowly added th the solution of cyclohexenone (3,12) (0,01 mol) in 100 ml of toluene. The reaction mixture was heated under reflux during 5–6 h and then was poured into a mixture of 5% sodium hydroxide solution with ice. The organic layer was separated and washed with water, diluted hydrochloric acid and again with water. The resulting solution was filtered through short column with silica gel. After the solvent had been removed the obtained residue was solved in hexane and purified by filtration throught the column with silica gel. After removing of solvent the product was recrystallized from isopropyl alcohol-hexane mixture. The yields were 35–42%.

The Methylation General Procedure. Methylmagnesium iodide (approx. 0.02 mol) prepared in the usual way in ether was slowly added to the solution of 3,6-disubstituted cyclohexenone (3,7) (0.01 mol) in 30 ml of dry THF at room temperature. The reaction mixture was stirred for 2 h and then kept overnight. Diluted sulphuric acid was carefully added and water layer was separated and twice extracted with ether. Combined organic layer was washed with water and dried over anhydrous magnesium sulfate. After evaporation of the solvent the residue was solved in 50 ml of toluene and air was bubbled through the solution at boiling temperature. The reaction completion was tested by chromatographic method. Toluene solution was filtered through short column with silica gel and solvent was removed completely. The residue was solved in hexane and again filtered through short column with silica gel. After removing of solvent the product was recrystallized from isopropyl alcohol-hexane mixture. The yields were 60–65%.

4. Conclusions and Perspectives

Thus shown chemical transformations illustrate our approach to be effective and convenient for the synthesis of various liquid crystalline three-ring derivatives possessing 2,3-difluorobenzene moiety and additively chlorine atom or methyl group in the lateral position. Prepared compounds with enough long terminal chains have low melting points, even terphenyl derivatives. They are easily solved in non polar organic solvents (hexane, toluene etc) and are easily mixable with another LC compounds and could be useful as component of the liquid crystalline compositions with negative dielectric anisotropy to adjust their properties.

Acknowledgment

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