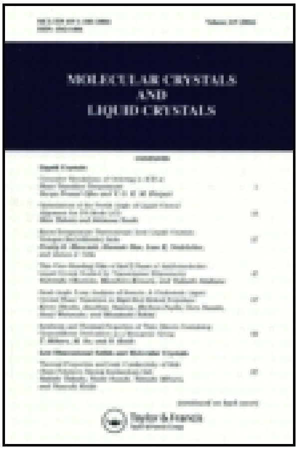

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A New Pathway for the Synthesis of Liquid Crystalline Bicyclohexanes

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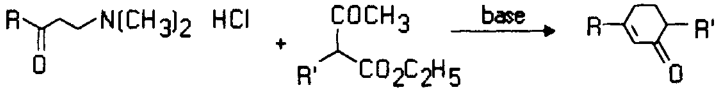
We have proposed and realised a new synthetic approach for the preparation of liquid crystalline dicyclohexyl derivatives. Recently discovered reaction of Grignard reagents with esters leading to 1-substituted cyclopropanoles in the presence of tetraisopropoxytitanium was used as a key stage. Starting from ethyl trans-4-alkylcyclohexancarboxylates the corresponding 6-(4-alkylcyclohexyl)-3-alkylcyclohex-2-en-1-ones have been prepared. Their catalytic hydrogenation in the base media gave mainly saturated trans,trans-ketones which are liquid crystalline and can be used also as a promising intermediate products for the preparation of different kinds of other LC compounds containing bicyclohexane moiety.

Keywords: synthesis of liquid crystals; intermediates for liquid crystals; dicyclohexyl derivatives

INTRODUCTION

The liquid crystalline compounds containing trans,trans-dicyclohexyl moiety are very useful in LC mixtures because of their low viscosity and low birefringence[1-3]. The synthesis of these compounds was generally realised according to schemes which provide for catalytic cross-coupling reaction as a key stage or using of 4-(trans-4-alkylcyclohexyl) cyclohexanone as a main intermediate.

Earlier we have worked out the «condensation approach» for the synthesis of poly ring liquid crystalline compounds which provides for the Michael type condensation of Mannich salts with 2-substituted acetoacetic esters leading to intermediate 3,6-disubstituted cyclohex-2-en-1-ones (I) (R = aryl or trans-4-arylcyclohexyl, R' = alkyl) as a key stage[4,5].



(I)

A wide variety of LC compounds including three ring ones possessing trans,trans-dicyclohexyl moiety[6] have been prepared this way. But our attempts to prepare two ring compounds (I) (when R = trans-4-alkylcyclohexyl, R' = alkyl) were not enough successful. The needed Mannich salt is not easily available. First of all the yield of the corresponding methyl trans-4-alkylcyclohexyl ketone prepared from the tarns-4-alkylcyclohexane-carboxylic acid and malonic ester was not very good (about 55-60%). Moreover the Mannich salt from this ketone was not crystalline and it was very difficult to purify it. It should be noted also that the yield of Mannich salt was not better than 50%.

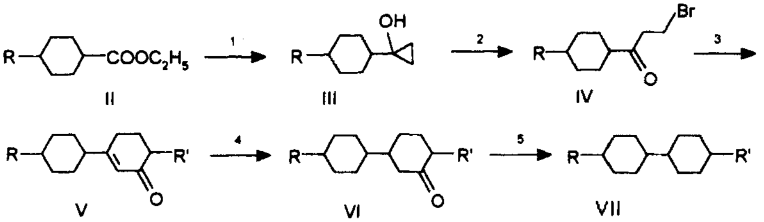
Here we propose the «cyclopropanol approach» for the synthesis of such systems. Instead of Mannich salt the corresponding β-bromoethyl 4-alkylcyclohexyl ketone was used in the condensation with 2-substituted acetoacetic ester in the same conditions.

RESULTS AND DISCUSSION

We have used recently discovered reaction of Grignard reagents with esters in the presence of tetraisopropoxytitanium which leads to the corresponding 1-substituted cyclopropanols with high yields (more than 90%)[7]. These compounds are convenient intermediates for the further transformation into β-bromoketones which can be used as the precursors of vinylketone instead of Mannich salt in condensation with 2-substituted acetoacetic esters.

The main advantage of this method is the high yield on each stage which it was more than 90% (before condensation stage).

Cyclohexenones (V) were prepared starting from ethyl ester of trans-4-alkylcyclohexanecarboxylic acids (II) as follows.



1. 2.5 eq. C_2H_5MgBr; 15 mol.% $Ti(Oi\text{-}C_3H_7)_4$; ether;
2. Br_2; CH_3OH/H_2O;
3. $R'CH(COCH_3)COOC_2H_5$; 3 eq. KOH; dioxane;
4. H_2; Pd/C; KOH; ethanol;
5. N_2H_4; KOH; diethylene glycol;

The yields of ketones (V) were 65-70% (after three stages).

Prepared 3,6-disubstituted cyclohexenones (V) were used for the synthesis of LC compounds having trans,trans-dicyclohexyl moiety. First of all 3-(trans-4-alkylcyclohexyl)-6-alkylcyclohex-2-en-1-ones (V) have been catalytically hydrogenated in ethanol over palladium on char coal in the presence of potassium hydroxide[8]. This method provides the formation of trans,trans-isomer as a main product.

This way prepared trans,trans-2,5-disubstituted cyclohexanones (VI) are liquid crystalline (table). They have been used also in Wolf-

Kizhner reaction to prepare the corresponding trans,trans-4,4'-dialkyldicyclohexyls (VII) described earlier[2]. The usual procedure has been applied.

It should be noted that despite of good yield (60-70%) of hydrocarbons (VII) the ratio of formed trans,trans- and trans,cis-isomers was not enough good (3:2). But after one recrystallization from hexane-ethanol the purity 92% for trans,trans-isomers can be achieved. The additional recrystallization allow to obtain trans,trans-isomers with the purity 98%. The same results we observed earlier in Wolf-Kizhner reduction of three ring ketones which have the similar dicyclohexyl moiety[6].

TABLE. Melting points and phase transfer temperatures for the compounds (V-VII).

No	R	R'	Phase transfer temperatures, °C	Ref
Va	C_4H_9	C_3H_7	Cr 26 I	
Vb	C_4H_9	C_5H_{11}	Cr 25 I	
Vc	C_4H_9	CH_2CH_2CN	Cr 37 I	
Vd	C_3H_7	C_3H_7	Cr 29 I	
VIa	C_4H_9	C_3H_7	Cr 26 S_B 61 N 71 I	
VIb	C_4H_9	C_5H_{11}	Cr -1 S_B 106.5 I	
VIc	C_4H_9	CH_2CH_2CN	Cr 53 S_B (44) N 54.5 I	
VId	C_3H_7	C_3H_7	Cr 46 N 70 I	
VIIa	C_4H_9	C_3H_7	Cr -6 S_B 94 I	[2]
VIIb	C_4H_9	C_5H_{11}	S_B 104 I	
VIIc	C_3H_7	C_3H_7	Cr 63 S_B 80 I	[2]

Any other synthetic transformations of carbonyl group can be applied to convert the ketones (VI) in variety of LC derivatives.

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 Linkam heating stage in conjugation with a polarising PZO microscope and also using a Setaram DSC 92.

1-(Trans-4-butylcyclohexyl)-1-cyclopropanol (IIIa). The Grignard reagent prepared in the usual way from 6.0 g (0.25 mol) of magnesium and 0.25 mol of ethyl bromide was slowly added during 2 h at room temperature to vigorously stirred solution of 0.1 mol of ethyl trans-4-butylcyclohexanecarboxylate and 0.02 mol (20 mol.%) of tetraisopropoxytitanium in 100 ml of dry ether. Reaction mixture having brown colour was then stirred additionally at room temperature during 1 h and decomposed with the cold 10% solution of sulphuric acid. After washing with water and drying over magnesium sulphate the solvent was removed. The prepared this way 1-(trans-4-butylcyclohexyl)-1-cyclopropanol just after removing of the solvent had the purity of about 95% and can be used in next transformation without any additional purification. The yield of cyclopropanol was almost quantitative.

1-(Trans-4-propylcyclohexyl)-1-cyclopropanol (IIIb) was prepared in the same way from ethyl trans-4-propylcyclohexanecarboxylate.

Trans-4-butylcyclohexyl β-bromoethyl ketone (IVa). 1-(Trans-4-butylcyclohexyl)-1-cyclopropanol prepared as described above was dissolved in 100 ml of methanol and approx. 5 ml of water was added. 0.1 Mol of bromine was then added dropwise during 15 min at room temperature. The bromine colour was disappearing continuously. Slightly coloured solution was diluted with water and the product was twice extracted with methylene chloride. The solvent was removed in vacuum and β-bromoketone was then used without additional purification. The yield is more than 90%.

Bromoketone (IV) should be prepared just before the further transformation. When stored it takes dark colour because of some decomposition.

3-(Trans-4-butylcyclohexyl)-6-propylcyclohex-2-en-1-one (Va). The prepared β-bromoketone was mixed with 2-propylacetoacetic ester (0.1 mol) and 0.3 mol of potassium hydroxide in 150 ml of dioxane and resulting mixture was then refluxed under stirring during 5 h. After cooling and treatment with 10% solution of sulphuric acid (evolution of carbon dioxide!) the product was extracted with benzene. After drying and removing of solvent the ketone was crystallised from ethanol. Yield 52% (isolated product); m.p. 36-37°C.

Trans-2-propyl-5-(trans-4-butylcyclohexyl)cyclohexanone (VIa). 0.1 Mol of 3-(trans-4-butylcyclohexyl)-6-propylcyclohex-2-en-1-one solved in 100 ml of ethanol containing potassium hydroxide (0.01 mol) was hydrogenated by gaseous hydrogen in the presence of 0.5 g of 10 weight per cent palladium on carbon at 30-40°C with energetic stirring until hydrogen absorption was stopped. The catalyst was separated by filtration, the alcohol was distilled off and residue was dissolved in benzene. The solution was washed with water and dried over anhydrous magnesium sulphate. After evaporation of the solvent the residue was twice crystallised from ethanol. This way the content of trans,trans-isomer more than 98% was achieved (the initial trans,trans/trans,cis ratio was approx. 10:1). The yield of trans,trans-ketone is 82%.

Trans,trans-4-propyl-4'-butyldicycloxexyl (VIIa). A mixture composed from 0.05 mol of trans-2-propyl-5-(trans-4-butylcyclohexyl) cyclohexane, 7 ml of 85% hydrazine hydrate, 8 g of KOH and 100 ml diethylene glycol was stirred at 100-120°C for 2 h, thereafter the temperature was allowed to reached 195-200°C (2 h) (evolution of nitrogen). The mixture was then cooled and underwent usual treatment. The crude product remaining after the evaporation of the solvent was then twice recrystallised from ethanol-hexane (1:1 v/v). The yield of trans,trans-isomer was about 30%.

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