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New liquid crystalline cyclohexene and cyclohexane derivatives and compositions based upon them

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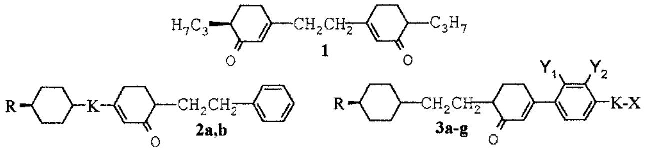
The synthesis and chemical transformations of 3,6-disubstituted cyclohex-2-enones into new liquid crystalline cyclohexene and cyclohexane derivatives are discussed. 3,6-Disubstituted cyclohex-2-enones have been synthesized by the condensation of appropriate 2-bromoethyl ketones or Mannich salts with 2-[2-(*trans*-4-alkylcyclohexyl)ethyl]acetoacetic or 2-[2-(4-substituted phenyl)ethyl]acetoacetic esters.

1. Introduction

The mesomorphic derivatives of *trans*-1-alkyl-4-phenyl(or biphenylyl)cyclohexanes, 1-alkyl-4-phenylcyclohex-1-enes and 1-(*trans*-4-alkylcyclohexyl)-2-phenyl-(or biphenylyl)ethanes are very useful in LC mixtures because they have low melting points and a low viscosity of their smectic or nematic phases [1–5]; this allows them to be used to prepare LC compositions with a very wide temperature range of the nematic phase, for example from −40 to 100°C. Unfortunately, the synthetic routes to such compounds are multi-stage and the starting materials (4-alkylcyclohexanones, the Grignard reagents, etc.) are usually difficult to prepare.

We have recently reported that different liquid crystalline derivatives of cyclohexane and cyclohexene can be easily prepared from appropriate 3,6-disubstituted cyclohex-2-enones [6–8]. In continuation of these investigations, and in an attempt to obtain new promising components of liquid crystalline materials for display applications, we have synthesized new 3,6-disubstituted cyclohex-2-enones (**1**; **2a**,**b**; **3a–g**) having a CH_2CH_2 bridge and then the corresponding 1,4-disubstituted cyclohexenes and *trans*-1,4-cyclohexanes. We have investigated their mesomorphic properties and the physical and electro-optical properties of LC compositions based on them; the results are summarized here, emphasizing structure–property relations.

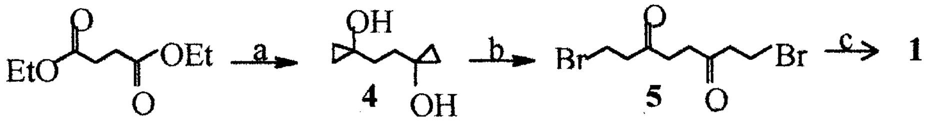


$R = C_2H_5$–C_5H_{11}; Y_1, Y_2 = H, F, OCH_3; K = a bond or a benzene or a cyclohexane ring; X = F, OCH_3, C_3H_7.

2. Results and discussion

2.1. *Synthesis*

Bis-1,2-(6-propylcyclohex-2-enone-3-yl)ethane (**1**) has been synthesized by the interaction of bis-2-bromoethyl ketone (**5**) with 2-propylacetoacetic ester in the presence of potassium hydroxide (see scheme 1). Unfortunately, unlike the condensation of *trans*-4-alkylcyclohexyl-2-bromoethyl ketone with 2-alkylacetoacetic esters [9], this reaction does not proceed well in the required direction and leads to the formation of the ketone (**1**) in low yield (about 10%).



Scheme 1. a. 2.5 eq. C_2H_5MgBr, 15 mol % $Ti(Oi\text{-}C_3H_7)_4$, ether; b. Br_2, CH_3OH/H_2O; c. $CH_3COCH(C_3H_7)COOC_2H_5$, 6 KOH, dioxane.

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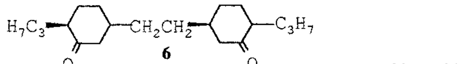
3-Substituted 6-[2-(4-substituted phenyl)ethyl]cyclohex-2-enones (**2a**,**b**) and 3-[2-(*trans*-4-alkylcyclohexyl)ethyl]-6-arylcyclohex-2-enones (**3a–g**) have been prepared in yields of 50–70% by the condensation of 2-[2-(*trans*-4-alkylcyclohexyl)ethyl]acetoacetic or 2-(2-phenylethyl)acetoacetic esters with the appropriate Mannich salts or *trans*-4-alkylcyclohexyl-2-bromoethyl ketones under the same conditions [6–9] (see table 1).

Subsequent hydrogenation of the cyclohex-2-enones (**1–3**) in the presence of 5 or 10% of palladium on charcoal and potassium hydroxide in isopropanol or THF/isopropanol/methanol mixtures leads to the appropriate *trans*-2,5-disubstituted cyclohexanones (**6–8**) in yields of 70–80% (see table 2). It should be noted that 5% palladium on charcoal is preferable for the reduction of the difluoroderivatives (**3b**,**e**). In the presence of 10% palladium on carbon the replacement of fluorine by hydrogen partially occurs.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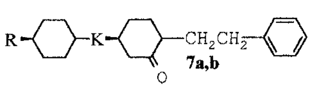
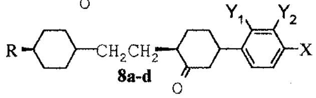
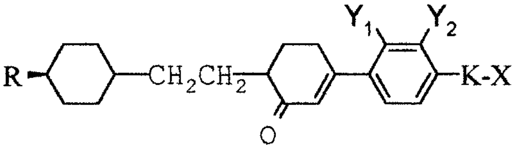

7a,b


8a-d

$R = C_2H_5$–C_5H_{11}; Y_1, Y_2 = H, F, OCH_3; K = a bond, or a benzene, or a cyclohexane ring; X = F, OCH_3, C_3H_7.

The *trans*-2,5-disubstituted cyclohexanones (**6–8**) are prospective intermediates for the synthesis of other LC compounds, for example, *trans*-1,4-disubstituted cyclohexanes, which are formed by Wolf–Kishner reduction

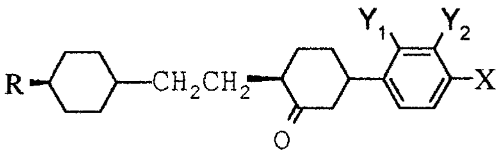
Table 1. Yields and transition temperatures of 3,6-disubstituted cyclohex-2-enones **3a–g**: () denote monotropic phases and I–N temperatures.



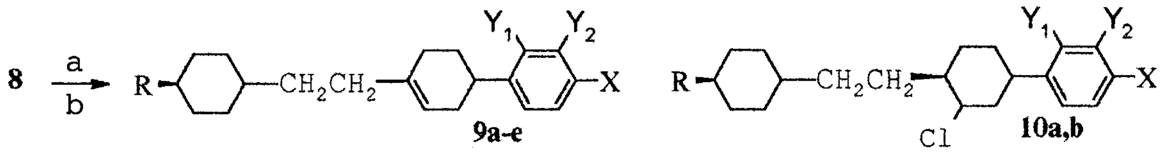
							Transition temperature/°C						
Compound	R	Y_1	Y_2	K^a	X	Yield/%	Cr		Sm		N		I
3a	C_3H_7	H	H	—	F	61	•	87	—		•	101	•
3b	C_4H_9	H	F	—	F	49	•	(89)	—		(•)	92	•
3c	C_4H_9	F	H	—	OCH_3	64	•	76	—		•	126	•
3d	C_5H_{11}	H	H	—	F	58	•	85	—		•	109	•
3e	C_5H_{11}	H	F	—	F	58	•	(84)	—		(•)	97	•
3f	C_4H_9	H	H	C	C_3H_7	47	•	<20	•	243	•	252	•
3g	C_5H_{11}	H	H	C	C_3H_7	61	•	<20	•	248	—		•

[a] C = cyclohexane ring.

Table 2. Yields and transition temperatures of *trans*-2,5-disubstituted cyclohexanones **8a–d**.



						Transition temperature/°C				
Compound	R	Y_1	Y_2	X	Yield/%	Cr		N		I
8a	C_3H_7	H	H	F	79	•	73	•	119	•
8b	C_5H_{11}	H	H	F	74	•	83	•	124	•
8c	C_4H_9	H	F	F	69	•	63	•	101	•
8d	C_5H_{11}	F	H	OCH_3	82	•	65	•	137	•

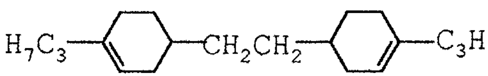


Scheme 2. $R = C_2H_5–C_5H_{11}$; Y_1, Y_2 = H, F, OCH_3; X = F, OCH_3, C_3H_7; a. $NaBH_4$; b. $POCl_3$, Py.

of the ketones. However, the most interesting direction for further chemical transformations of the *trans*-2,5-disubstituted cyclohexanones (**6–8**), especially of the ketones (**8**), is their reduction with sodium borohydride and then the dehydration or the interaction of the alcohols formed with $POCl_3$ in the presence of pyridine (see scheme 2), leading to the corresponding 1,4-disubstituted cyclohex-1-enes (**9a–e**) and 2,5-disubstituted chloro-cyclohexanes (**10a**,**b**), which form the nematic phase at low temperatures and over wide temperature ranges (see tables 3, 4).

Cyclohexanones (**7**) are also prospective intermediates for the synthesis of liquid crystalline compounds with promising properties. By the modification of these ketones using acetylation and subsequent transformation of the acetyl derivatives (**11**) according to scheme 3, we prepared the cyclohexenes (**13a**,**b**), which are characterized by low temperature formation of mesophases with wide temperature ranges (see table 5).

Bisketone (**6**), unlike the ketones (**7**, **8**), cannot be successfully used as an intermediate for the preparation of components of liquid crystalline materials for display application, because both the bis-cyclohex-2-enone (**1**) and the bis-cyclohexene (**14**) or other possible products of the modification of the bisketone (**6**) are formed in low yield.



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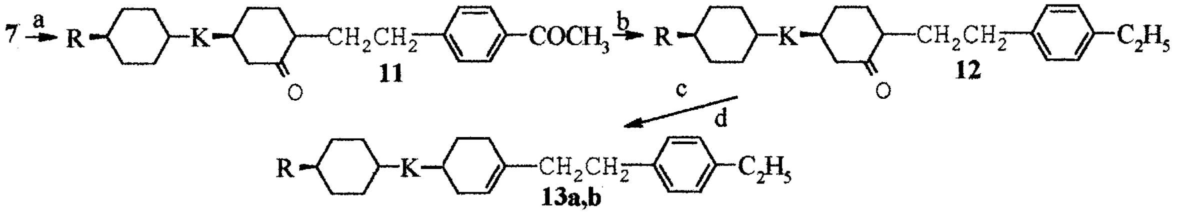
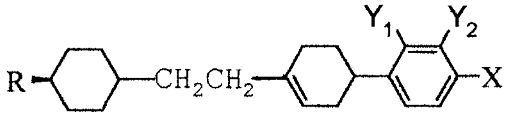
The proton NMR spectra (δ, ppm) of the 3,6-disubstituted cyclohex-2-enones (**1–3**) showed that the multiplet at 5.81–5.85 or 6.25–6.41 belongs to the proton located at the double bond of the cyclohexenone fragment. The signals at 2.20–3.22 in the proton NMR spectra of the saturated ketones (**6–8**) correspond to the protons in the cyclohexanone fragment. The multiplet at 5.45–5.69



Scheme 3. $R = C_2H_5–C_5H_{11}$; K = a bond, or a benzene ring; a. CH_3COCl, $2AlCl_3$, methylene chloride; b. H_2, 10% Pd/C; c. $NaBH_4$; d. TsOH.

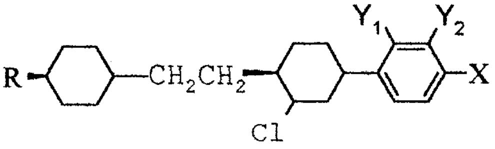
Table 3. Yields and transition temperatures of 1,4-disubstituted cyclohex-1-enes **9a–e**.



							Transition temperature/°C						
Compound	R	Y_1	Y_2	K[a]	X	Yield/%	Cr		Sm		N		I
9a	C_3H_7	H	H	—	F	38	•	27	—		•	78	•
9b	C_4H_9	H	F	—	F	44	•	<0	—		•	59	•
9c	C_4H_9	F	H	—	OCH_3	41	•	<0	—		•	90	•
9d	C_5H_{11}	H	H	—	F	39	•	25	—		•	72	•
9e	C_4H_9	H	H	C	C_3H_7	61	•	<0	•	197	•	215	•

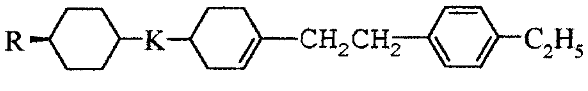
[a] C = cyclohexane ring.

Table 4. Yields and transition temperatures of 2,5-disubstituted 1-chlorocyclohexanes **10a**,**b**.



						Transition temperature/°C				
Compound	*R*	Y_1	Y_2	*X*	Yield/%	Cr		N		I
10a	C_4H_9	F	H	OCH_3	37	●	63	●	128	●
10b	C_4H_9	H	F	F	33	●	<0	●	57	●

Table 5. Yields and transition temperatures of 1,4-disubstituted cyclohex-1-enes **13a**,**b**.



				Transition temperature/°C				
Compound	*R*	K^a	Yield/%	Cr		Sm		I
13a	C_3H_7	—	42	●	<0	●	74	●
13b	C_5H_{11}	B	54	●	68	●	188	●

[a] B = benzene ring.

in the spectra of the cyclohexene derivatives (**9**, **13**, **14**) belongs to the protons located at the double bond of the cyclohexene fragment. In the proton NMR spectra of the *cis*-2-[2-(*trans*-4-butylcyclohexyl)ethyl]-*trans*-5-aryl-1-*r*-chlorocyclohexanes (**10a**,**b**) the doublet signal at 4.47, with a spin–spin constant interaction of 2.5 Hz of the proton located at the first carbon atom of the cyclohexane ring, confirms the axial position of the chloro substituent in the ring.

2.2. *Mesomorphic properties*

The phase transition temperatures of the 3,6-disubstituted cyclohex-2-enones (**3a–g**) are listed in table 1. As can be seen, the cyclohexenones (**3a–e**) containing fluoro substituents and the methoxy group in the benzene ring form only monotropic or thermotropic nematic phases in the temperature range 76–126°C. The introduction of an additional cyclohexane ring and the alkyl group in the benzene ring results in the appearance of the smectic phase over wide temperature ranges (see compounds (**3f**,**g**) in table 1). Unlike the ketones (**3a–g**), the ketones (**1**, **2**) are non-mesomorphic or are characterized by the formation of a smectic phase in a narrow temperature range. Similar phase transition changes are also observed for the saturated ketones (**6–8**). It should be noted that the *trans*-2,5-disubstituted ketones (**8a–d**) (see table 2) form the nematic phase at lower temperatures and over wider temperature ranges than the unsaturated analogues (**3a–d**). The replacement of the cyclohexanone fragment by cyclohexene or chlorocyclohexane rings leads to a sharp decrease in the temperature of formation and a broadening of the temperature range of the smectic or nematic phases for the corresponding cyclohexenes (**9a–e**, **13**), and chlorocyclohexanes (**10a**,**b**) (see tables 3–5). This can be explained by a weakening of the anisotropy of the intermolecular interactions on passing from the cyclohex-2-enone and cyclohexanone to the chlorocyclohexane and cyclohexene derivatives; this is the result of reducing the perpendicular dipole moment and the distortion, especially for the cyclohexene derivatives (**9**), of the rod shape of molecules (see the figure).

Investigations of the electro-optic and dynamic parameters of LC mixtures containing the cyclohexene derivatives synthesized (**9a–e**, **13**) have shown that these compounds are promising components of materials for 240° twist STN displays, multiplexed 2nd minimum TN displays and active matrix addressed displays. These, like fluorocyclohexene derivatives [10], allow the threshold voltage and the steepness parameter of the voltage–contrast curve to be decreased, and also to verify the

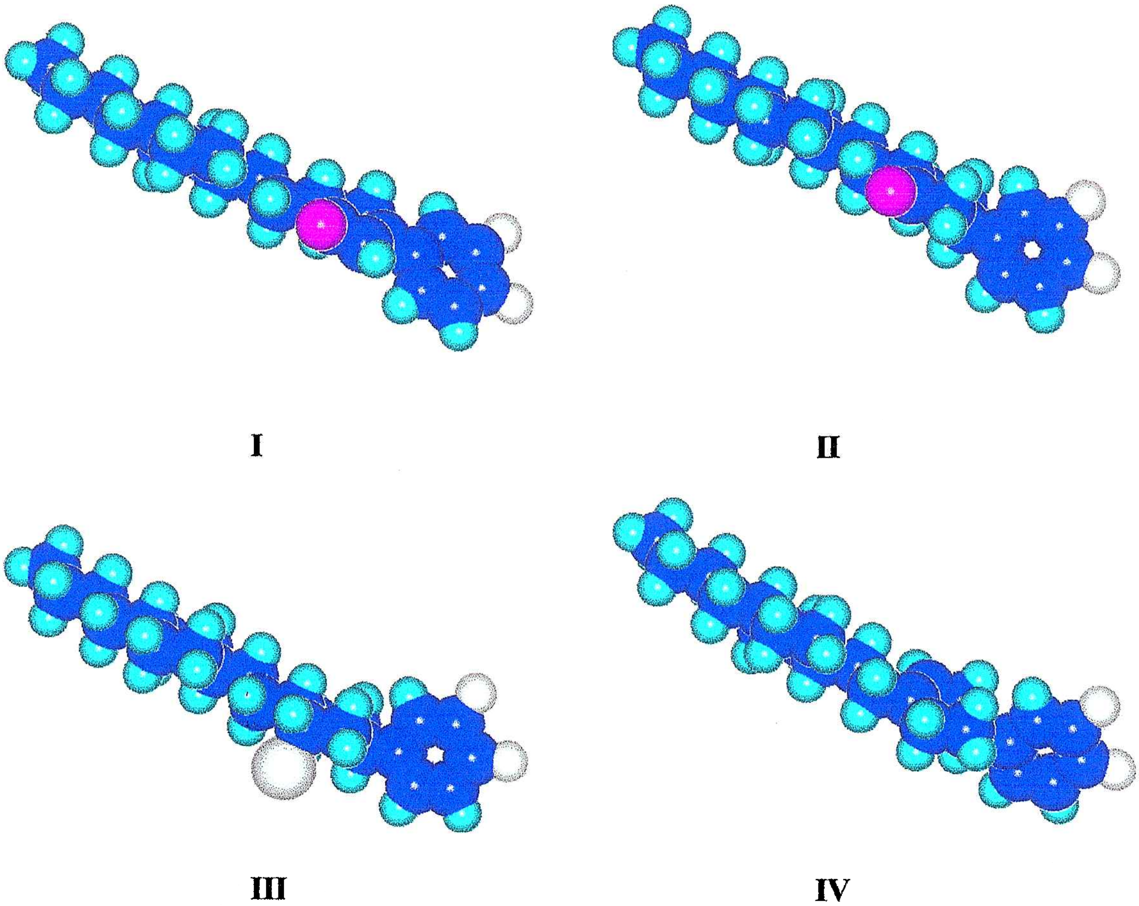


Figure. Molecular models: **I** cyclohex-2-enone **3b**; **II** cyclohexanone **8c**; **III** chlorocyclohexane **10b**; **IV** cyclohexene **9a**.

optical anisotropy of the nematic mixtures without significant changes in other parameters (see table 6). Using the cyclohexene derivatives we have prepared LC compositions with good dynamic parameters for high level multiplexed 2nd minimum TN displays and active matrix addressed displays. For 240° twist STN displays we have developed new mixtures which are characterized by a wide temperature range of the nematic phase ($-40°\mathrm{C} - +100°\mathrm{C}$), a low temperature dependence of the threshold voltage and a small sharpness parameter ($P = 0.03 - 0.022$).

3. Experimental

Confirmation of the structures of all intermediates and final products was obtained by GC/MS mass spectrometry (HP 5972) and ^{1}H NMR spectroscopy. The purity of the compounds was checked using a HP 5890 capillary gas chromatograph fitted with an Hl column.

Phase transition temperatures were measured using a Linkam heating stage in conjunction with a polarizing PZO microscope and also by differential scanning calorimetry (Setaram DSC 92).

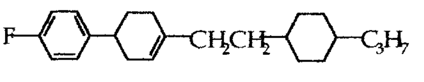
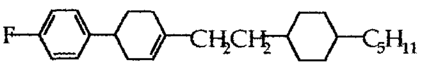
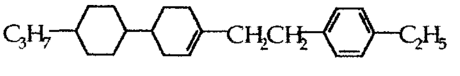
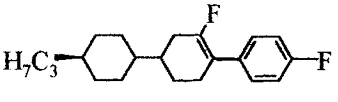
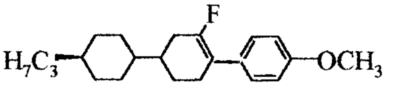
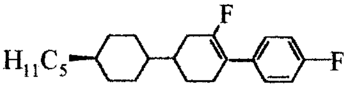
The measurements of the electro-optic parameters of the mixtures were performed at room temperature using twisted nematic cells with 6 μm spacers and a polyamide layer to obtain homogeneously oriented samples.

The intermediates, 3,6-disubstituted cyclohex-2-enones (**1–3**) and the products of their hydrogenation—*trans*-2,5-disubstituted cyclohexanones (**6–8**)—were prepared according to published methods [6–9, 11].

3.1. *trans-5-(trans-4-Propylcyclohexyl)-2-[2-(4-acetylphenyl)ethyl]cyclohexanone (**11**)*

trans-5-(*trans*-4-Propylcyclohexyl)-2-(2-phenylethyl)-cyclohexanone (**2a**) (41 mmol) in 50 ml of dry methylene chloride was slowly added to the complex prepared from acetyl chloride (45 mmol) and anhydrous aluminium chloride (86 mmol) in 100 ml of the same solvent. The temperature was not allowed to exceed 10–15°C. The reaction mixture was stirred during 2 h at 15–20°C and then decomposed with cold diluted hydrochloric acid. The organic layer was separated, washed with water and then dried over anhydrous magnesium sulphate. After removing solvent, the residue was dissolved in ethanol,

Table 6. Physical and electro-optical parameters of the LC compositions[a].

Compound	V_{10}/V	V_{90}/V	P^{c}	Δn	τ_{on}/ms	τ_{off}/ms	Cell gap/μm	T/°C (N-I)
Base mixture[b]	1.72	2.47	0.472	0.1177	16	44	5.82	+ 58.2
	1.76	2.45	0.395	0.1140	18	49	5.78	+ 60.5
	1.72	2.43	0.407	0.1140	19	50	5.77	+ 61.4
	1.85	2.60	0.411	—	19	57	5.82	+ 61.8
	1.80	2.51	0.391	0.1150	16	54	5.86	+ 67.6
	1.87	2.65	0.419	0.1164	15	43	5.86	+ 73.6
	1.79	2.49	0.390	0.1119	16	52	5.88	+ 68

[a] LC mixtures consist of 90% of the base mixture and 10% of the compound.

[b] Base mixture: 4′-pentyl-4-cyanobiphenyl, 20%; 4-(*trans*-4-pentylcyclohexyl)benzonitrile 20%; 4-ethoxyphenylester of *trans*-4-butylcyclohexane-1-carboxylic acid, 30%; 4-butoxyphenylester of *trans*-4-butylcyclohexane-1-carboxylic acid, 30%.

[c] Sharpness parameter.

boiled for 30 min with 1 g of charcoal and then, after filtering, twice recrystallized from ethanol; the yield was 54%. Transitions temperatures: Cr 88 N 170 I (°C).

3.2. *trans-5-(trans-4-Propylcyclohexyl)-2-[2-(4-ethylphenyl)ethyl]cyclohexanone (**12**)*

A solution of *trans*-5-(*trans*-4-propylcyclohexyl)-2-[2-(4-acetylphenyl)ethyl]cyclohexanone (5 g) in 50 ml of acetic acid and THF (1/1 v/v) was hydrogenated at normal pressure in the presence of 0.5 g of 10% palladium on carbon at 30–40°C with vigorous stirring until hydrogen was no longer absorbed. The catalyst was separated by filtration and the solvent removed by distillation under reduced pressure. The residue was crystallized from ethanol; the yield was 88%. Transitions temperatures: r.t. SmB 162 I (°C).

3.3. *4-(trans-4-Propylcyclohexyl)-1-[2-(4-ethylphenyl)ethyl]cyclohex-1-ene (**13a**)*

A mixture of 0.02 mol of *trans*-5-(*trans*-4-propylcyclohexyl)-2-[2-(4-ethylphenyl)ethyl]cyclohexanone (**15**), 0.02 mol of sodium borohydride and isopropyl alcohol (100 ml) was stirred at 50–60°C during 8 h. The reaction mixture was then acidified with 10% hydrochloric acid and the organic layer washed with ether. The ethereal extract was washed with water and dried over anhydrous magnesium sulphate. The solvent was removed *in vacuo* and the alcohol was dissolved in 25 ml of pyridine and 5 ml of phosphorous oxychloride added. The reaction mixture was heated at reflux during 5 h and then poured into water. The product was extracted into ether and washed with water. After removing the ether, the product was isolated by chromatography on silica gel using hexane as eluent and purified additionally, after removing the solvent, by recrystallization from isopropyl alcohol; the yield was 42%. Transitions temperatures: r.t. Sm 74 I (°C).

Similar methods gave the other compounds (**9a–e**; **10a**,**b**; **13a**,**b**) presented in tables 3–5.

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