Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

LC diketones: synthesis, transformations and mesomorphic properties

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To cite this Article Bezborodov, V. S. , Sasnouski, G. M. and Lapanik, V. I.(2000) 'LC diketones: synthesis, transformations and mesomorphic properties', Liquid Crystals, 27: 7, 935 — 941
To link to this Article: DOI: 10.1080/02678290050043897
URL: http://dx.doi.org/10.1080/02678290050043897

LIQUID CRYSTALS, 2000, VOL. 27, NO. 7, 935–941

LC diketones: synthesis, transformations and mesomorphic properties

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(*Received 27 October 1999; in final form 28 December 1999; accepted 31 January 2000*)

The synthesis and chemical transformations of various diketones into liquid crystalline compounds are discussed. The diketones were prepared by the interaction of cyclohexene with acid chlorides and benzene in the presence of aluminium chloride (Nenitzescu method) or by Friedel Crafts reaction of *trans*-4-alkanoyl-1-phenylcyclohexanes or *trans*-2-alkyl-5-phenylcyclohexanones with acid chlorides, or by the condensation of corresponding Mannich salts with 2-substituted acetoacetates or acetylacetone.

1. Introduction

It has been reported that liquid crystalline ketones, for example 3,6-disubstituted cyclohex-2-enones, are promising intermediates for the preparation of liquid crystalline compounds [1–5]. They can be transformed in high yield into various derivatives of cyclohexane, cyclohexene, phenylcyclohexane or biphenyl [6, 7] which are useful components of liquid crystalline mixtures for display applications. In continuation of the investigations of liquid crystalline ketones and their derivatives [8–10], it was interesting to synthesize new liquid crystalline compounds containing two keto groups and estimate the possibility of their transformation into liquid crystals with optimized features. It should be noted that different reaction possibilities for the keto groups allow transformations to be achieved selectively and give a chance of preparing liquid crystalline compounds with novel combinations of structural fragments of LC molecules.

2. Results and discussion

2.1. *Synthesis*

Taking into account the results of our previous investigations [1–3], we have synthesized diketones **1–6** and investigated their transformations into liquid crystalline compounds.

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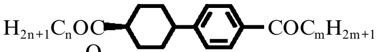

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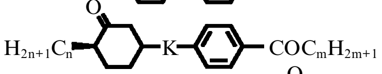

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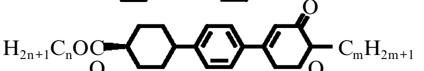

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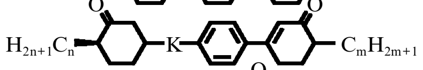

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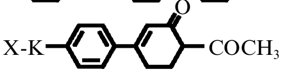

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In the above structures, terminal substituent X is usually hydrogen, alkyl (C_nH_{2n+1}) or alkoxy ($C_nH_{2n+1}O$); K is a single bond or a benzene or cyclohexane ring.

It is well known that the interaction of benzene and cyclohexene with alkanoyl chlorides in the presence of anhydrous aluminium chloride (Nenitzescu method) leads to the corresponding *cis*- and *trans*-4-alkanoylcyclohexylbenzenes [11, 12]. We have found that under some specific conditions this reaction is accompanied by the formation of bis-adducts: 1,4-bis(*trans*-4-alkanoylcyclohexyl)benzenes **1**. Usually the yields of bis-ketones **1** are not high (about 5%), but after the distillation of the main products from the reaction mixture—that is,

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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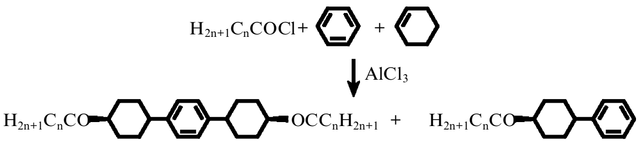
the *trans*-4-alkanoylcyclohexylbenzenes **1′**, the ketones **1** can be very easily isolated by crystallization from the residue (table 1).

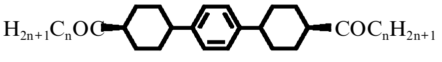


(1) **(1«)**

n = 1-4

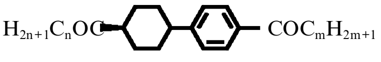
The Friedel-Crafts acylation of *trans*-4-alkanoylcyclohexylbenzenes **1′** and *trans*-2-alkyl-5-phenylcyclohexanones, which were obtained by catalytic hydrogenation of the corresponding 3,6-disubstituted cyclohex-2-enones in a basic medium [13], leads to dicarbonyl compounds **2** and **3** in moderate to good yields (50–80%) (tables 2 and 3). However, some isomerization always occurred in the acylation process and we observed that in most cases the resulting *trans*-diketones **3** contained about 5% of the corresponding *cis*-isomer.

Table 1. Yields and transition temperatures of 1,4-bis-(*trans*-4-alkanoylcyclohexyl)benzenes **1**.



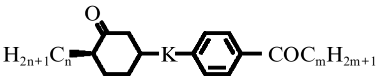
		Transition temperature/°C					
n	Yield/%	Cr		SmB	N		I
1	6	•		—	—	190	•
2	5	•	165	—	•	178	•
3	5	•	172	•	—	180	•
4	9	•	169	•	—	183	•

Table 2. Yields and transition temperatures of *trans*-4-alkanoylcyclohexyl-4′-alkanoylbenzenes **2**.



n	*m*	Yield/%	m.p./°C.
1	1	54	83
2	1	48	78
1	2	57	68
1	4	45	77
1	7	53	66
1	8	56	64
1	9	51	71

Table 3. Yields and transition temperatures of *trans*-2,5-disubstituted cyclohexanones **3**.



				Transition temperatures/°C						
n	*m*	K[a]	Yield/%	Cr		Sm		N		I
10	1	—	62	•		—		—	73	•
10	6	—	56	•	52	•		—	91	•
3	1	C	54	•	112	—		•	187	•
3	2	C	56	•	91	—		•	205	•
3	4	C	52	•	98	—		•	194	•
3	5	C	57	•	103	—		•	186	•
3	6	C	51	•	88	•	117	•	182	•
3	7	C	50	•	90	•	121	•	176	•
5	1	B	62	•	100	•	111	•	189	•
5	1	C	80	•	106	—		•	192	•
5	2	C	76	•	77	—		•	217	•
5	4	C	58	•	70	•	74	•	197	•
5	5	C	62	•	92	•	108	•	186	•
5[b]	6	B	50	—		•		—	195	•
8	1	B	60	•	110	—		•	189	•
8[c]	3	B	55	—		•	179	•	191	•
8[d]	6	B	56	•	47	•		—	196	•

[a] C = cyclohexane, B = benzene.

[b] SmX 169 SmC 176 SmA 195 I (°C).

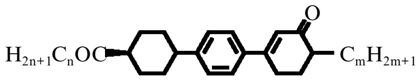
[c] SmX 134 SmC 150 SmA 179 N 191 I (°C).

[d] Cr 47 SmB 148 SmC 184 SmA 196 I (°C).

The dicarbonyl compounds **4** and **5** (tables 4 and 5) were synthesized by the condensation of 2-alkylacetoacetic esters with Mannich salts (prepared from the corresponding 4-substituted acetophenones **2** and **3** ($m = 1$) in the usual way by treating them with dimethylamine hydrochloride and paraformaldehyde in basic media [1].

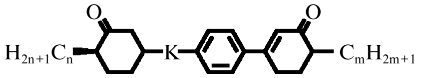
The same reaction conditions were used for the preparation of 3-aryl-6-acetylcyclohex-2-enones **6** (table 6) from the corresponding Mannich salts and acetylacetone.

Table 4. Yields and transition temperatures of 3,6-disubstituted cyclohex-2-enones **4**.



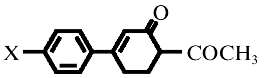
			Transition temperatures/°C				
n	*m*	Yield/%	Cr		SmA		I
2	3	32	•	101	•	156	•
2	5	35	•	104	•	162	•

Table 5. Yields and transition temperatures of *trans*-2,5-disubstituted cyclohexanones **5**.



			Transition temperatures/°C				
n	*m*	Yield/%	Cr		SmA		I
4	2	25	•	91	•	179	•
4	5	30	•	118	•	225	•

Table 6. Yields and transition temperatures 3-aryl-6-acetyl-cyclohex-2-enones **6**.



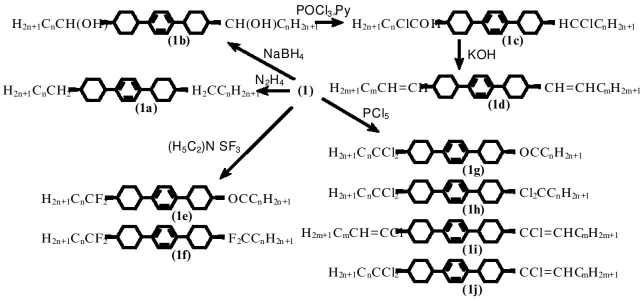
		Transition temperatures/°C				
X	Yield/%	Cr		SmA		I
H	37	•		—	96	•
CH_3	39	•		—	93	•
C_2H_5	42	•		—	78	•
C_5H_{11}	34	•		—	66	•
C_6H_{13}	40	•		—	51	•
CH_3O	30	•		—	103	•
C_2H_5O[a]	48	•			86	•
C_4H_9O[b]	38	•			79	•
$C_3H_7C_6H_{10}$	27	•	99	•	156	•

[a] Monotropic SmA at 67°C.

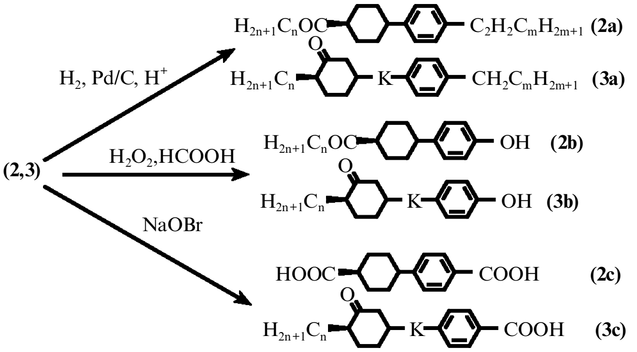
[b] Monotropic SmA at 77°C.

2.2. *Chemical transformations*

We have shown that diketones **1** can be easily converted into the corresponding liquid crystalline 1,4-bis(*trans*-4-alkylcyclohexyl)benzenes **1a** by Wolff–Kishner reduction. The reduction of ketones **1** by sodium borohydride gives the alcohols **1b**, which in a boiling mixture of pyridine and phosphorus oxychloride can be transformed into the corresponding dichlorides **1c**. Our attempts to dehydrate alcohols **1b** in boiling toluene in the presence of *p*-toluenesulphonic acid were unsuccessful. The reaction proceeds very slowly and does not allow preparation of the corresponding 1,4-bis(*trans*-4-alkenyl-1-cyclohexyl)benzenes **1d** in high yield. For the synthesis of these unsaturated compounds we dehydrohalogenated the dichlorides **1c** in the presence of potassium hydroxide. The interaction of the ketones **1** with DAST (diethylaminosulphur trifluoride) or phosphorous pentachloride leads to the formation of mixtures of *gem*-difluorides **1e** and **1f** or *gem*-dichlorides **1g** and **1h** and the corresponding vinyl chlorides **1i** and **1j**.

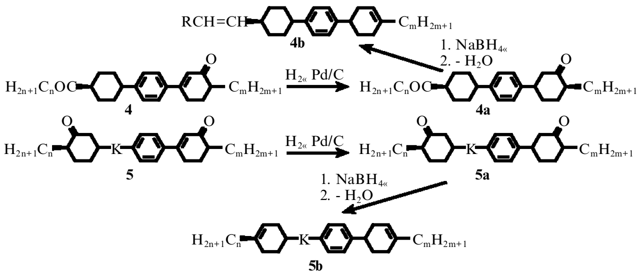


In contrast to the 1,4-bis(*trans*-4-alkanoylcyclohexyl)-benzenes **1**, dicarbonyl compounds **2** and **3** have different reaction possibilities for the keto groups, allowing selective transformations and the preparation of the promising intermediates **2a–2c** and **3a–3c**. The catalytic hydrogenation of the diketones **2** and **3** in the presence of palladium on carbon results in *trans*-4-alkanoyl-1-(4-alkylphenyl)-cyclohexanes **2a** and corresponding disubstituted cyclohexanones **3a**. The Baeyer–Villiger oxidation of these ketones gives the phenols **2b** and **3b**, while hypobromide oxidation of the ketones yields diacids **2c** and corresponding 4-substituted benzoic acids **3c**.



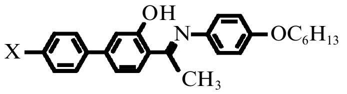
trans-4-Alkanoyl-1-(4-alkylphenyl)cyclohexanes **2a**, disubstituted cyclohexanones **3a** and cyclohexanones prepared by the alkylation of the phenols **3b** with alkyl bromides or iodides in the presence of bases, were efficiently used for the synthesis of different LC derivatives and laterally substituted derivatives of cyclohexane and dicyclohexane, cyclohexene and cyclohexenylcyclohexane [6, 7]. The phenols **2b** and **3b** and some of their derivatives, the diacids **2c**, the 4-substituted benzoic acids **3c** and the *trans*-4-arylcyclohexanecarboxylic acids prepared by the alkylation of *trans*-1-acetyl-4-(4-hydroxyphenyl)cyclohexanes **2b** followed by hypobromide oxidation of the corresponding alkoxy derivatives, are prospective intermediates for the synthesis of various LC esters, especially of the ferroelectric and antiferroelectric types [14].

The diketones **4** and **5** can be successfully used for the preparation of the liquid crystalline compounds **4b** and **5b** containing two double bonds in the molecule. The interaction of the unsaturated and saturated ketones **4** and **5** and **4a** and **5a** with methyl magnium iodide, DAST or phosphorous pentachloride gives, as in the case of diketones **1**, mixtures of products.



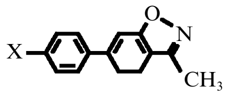
The same results have been obtained in reactions of 3-aryl-6-acetylcyclohex-2-enones **6** with methyl magnium iodide, DAST or phosphorous pentachloride. These ketones, through the influence of bromine, are easily aromatized to 4-(4-substituted phenyl)-2-hydroxyacetophenones **6a**, which are intermediates for the synthesis of the corresponding Schiff's bases **6h** (table 7) or azomethines **6i** and their metal complexes **6j**. The catalytic reduction of the ketones **6** in the presence of palladium on carbon resulted in the formation of *trans*-5-(4-substituted phenyl)-2-acetylcyclohexanones **6c**, and interaction with sodium borohydride, in the formation of 4-substituted 4′-ethylbiphenyls **6b**. The reaction of 6-acetylcyclohex-2-enones **6** with hydroxylamine hydrochloride in boiling alcohol gives dihydrobenzisoxazoles **6e** in 70–80% yield (table 8), and the condensation of 2-substituted acetoacetic esters with Mannich salts prepared from diketones **6**, using paraformaldehyde and dimethylamine hydrochloride gives yields of 20–30% of dicyclohex-2-enones **6d** (table 9), which can be modified into different liquid crystalline compounds or other compounds of practical interest.

Table 7. Yields and transition temperatures of Schiff's bases **6h**.



		Transition temperatures/°C				
X	Yield/%	Cr		N		I
C_2H_5	54	•	165	•	194	•
C_2H_5O	47	•	187	•	233	•
C_4H_9O	62	•	157	•	211	•

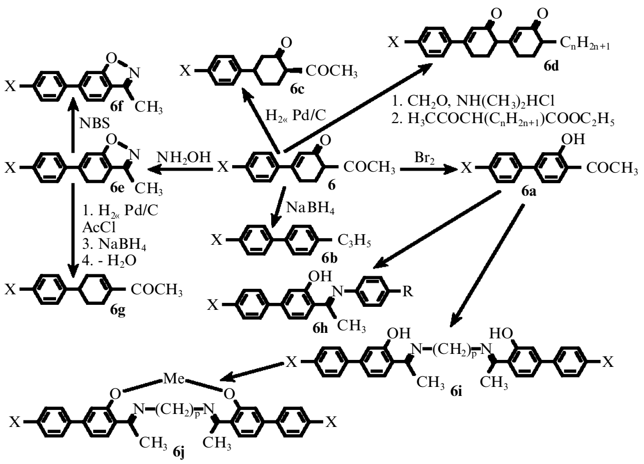
Table 8. Yields and transition temperatures of dihydrobenzisoxazoles **6e**.



		Transition temperatures/°C				
X	Yield/%	Cr		N		I
H	53	•		—	105	•
C_2H_5	56	•		—	84	•
C_6H_{13}	49	•		—	63	•
C_2H_5O	61[a]	•			120	•
C_4H_9O	59[b]	•			94	•

[a] Monotropic nematic at 75°C.

[b] Monotropic nematic at 86°C.

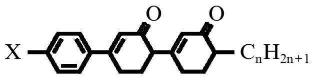


The proton NMR spectra (*δ*, ppm) of the diketones **4–6** showed that a multiplet at 6.35–6.45 belongs to the protons located at the double bond of the cyclohexenone fragment. The signals of the alkanoylcyclohexane and alkylcylohexanone fragments of compounds **1–3** are observed in the NMR spectra at 1.30–2.56. It was found that the singlet and multiplet signals at 5.42 and 5.60 in the proton NMR spectra of compounds **1d** and **5b** also belong to the protons located at the double bond of the alkenyl tail and cyclohexene fragment.

2.2. *Mesomorphic properties*

The compounds **1** exhibit liquid crystalline properties—mainly a high temperature smectic LC phase is present. The phase transition temperatures of the 1,4-bis-(*trans*-4-alkanoylcyclohexyl)benzenes **1** are listed in table 1. As can be seen, the acetyl compounds **1** are not mesomorphic, but increasing the tail lengths results in the

Table 9. Yields and transition temperatures of dicyclohex-2-enones **6d**.



			Transition temperatures/°C						
X	*n*	Yield/%	Cr		Sm		N		I
C_2H_5O	5	26	•	92	•	130	•	154	•
C_2H_5O	2	20	•	91	•		—	112	•
$C_3H_7C_6H_{10}$	5	24	•	153	•		—	194	•

appearance of nematic or smectic B phases. A comparison of the mesomorphic properties of the diketones **3** (table 3) and corresponding 2,5-disubstituted cyclohexanones [8] with the same terminal chain length shows that replacement of the alkyl or alkoxy groups with an alkanoyl fragment in the 4-position of the benzene ring depresses the smectic phase and enhances the range of the nematic phase. For example, introducing an acetyl fragment, instead of ethyl or methoxy groups, expands the nematic phase range to 78°C. Enhancement of the nematic phase is especially evident for the diketones **3** containing the bicyclohexyl moiety for which the nematic temperature range exceeds 100°C. The diketone **3** ($n = 5$, $m = 4$) has a nematic phase range of 123°C whereas the corresponding alkyl substituted ketone—*trans*-1-(4-pentylphenyl)-4-(*trans*-4-pentylcyclohexyl)cyclohexane prepared from **3** by catalytic hydrogenation—does not form a nematic phase (Cr 30 SmX 191 I). It is also interesting to note the existence of SmC phases for the diketones **3** having longer alkanoyl fragments. The diketones **4–6** (tables 4–6) form only smectic A phases, the temperature range of which depends on the length of the molecules.

The products of the modification of 1,4-bis-(*trans*-4-alkanoylcyclohexyl)benzenes **1**—1,4-bis(*trans*-4-alk-1-enylcyclohexyl)benzenes—form the nematic phase at high temperature and over a fairly narrow temperature range. For example, the temperature range of the nematic phase of 1,4-bis(*trans*-4-prop-1-enylcyclohexyl)benzene is 132–152°C. The products of modification of 6-acetylcyclohex-2-enones **6**, the Schiff's bases **6h**, are also characterized by high temperature nematic phases (table 7). Monotropic nematic phases only are observed for the dihydrobenzisoxazoles **6e** (table 8); the dicyclohex-2-enones **6d** give both nematic and smectic phases (table 9).

3. Experimental

A very large number of compounds has been prepared and we simply confirm that their structures are consistent with analytical data obtained from methods including IR, ^{1}H NMR and mass spectroscopy. Phase transition temperatures were measured using a Linkam heating stage in conjunction with a polarizing PZO microscope and also a Setaram DSC 92.

3.1. *1,4-Bis(trans-4-propionylcyclohexyl)benzene (1)*

A mixture of 82 g (1 mol) of cyclohexene and 92.5 g (1 mol) of propionyl chloride was added dropwise during 3 h to a stirred mixture of 146.6 g (1.1 mol) of anhydrous aluminium chloride in 500 ml of benzene, keeping the temperature of the mixture at 40–50°C. The mixture was then stirred for a further 1 h and decomposed with the cold dilute hydrochloric acid. The benzene layer was separated and washed with water. After removing solvent, the main product, 4-propionylcyclohexylbenzene, was distilled giving 127.4 g (yield 59%). To the residue after distillation, isopropyl alcohol (100 ml) was added and the mixture was cooled in a refrigerator overnight. The 1,4-bis(*trans*-4-propionylcyclohexyl)benzene was filtered off and recrystallized from isopropyl alcohol; yield 17.7 g (5%).

A similar procedure gave the other compounds **1** presented in table 1.

3.2. *trans-5-(4-Acetylphenyl)-2-decylcyclohexanone (3)*

To a solution of 15.7 g (0.05 mol) of *trans*-5-phenyl-2-decylcyclohexanone in 50 ml of methylene chloride was added the complex prepared from 4.7 g (0.06 mol) of acetyl chloride and 14.7 g (0.11 mol) of anhydrous aluminium chloride preliminarily cooled to 0°C. The reaction mixture was kept at room temperature overnight and then poured into a mixture of hydrochloric acid and ice. After the usual work-up, the product was crystallized from ethanol (the content of *trans*-isomer was 95.1%); yield 11 g (62%), m.p. 73°C.

A similar procedure gave the other compounds **2**, **3** presented in tables 2 and 3.

3.3. *3-Phenyl-6-acetylcyclohex-2-enone (6)*

A mixture of 42.7 g (0.2 mol) of 3-dimethylaminopropanoylbenzene hydrochloride, 21 g (0.21 mol) of acetylacetone and 39.2 g (0.7 mol) of potassium hydroxide in

300 ml of dioxan was heated at reflux during 5 h with stirring. After cooling to room temperature, 600 ml of 10% aqueous sulfuric acid was added and the product was extracted into benzene. The organic layer was washed with water, dried over anhydrous magnesium sulphate and filtered through a layer of aluminium oxide. The residue obtained after the solvent had been removed was recrystallized from ethanol. The yield was 15 g (35%), m.p. 96°C.

Similar methods gave the other compounds **4–6**, **6d** presented in the tables 4–6 and 9.

3.4. *1,4-Bis(trans-4-pentylcyclohexyl)benzene* ***1a***

1,4-Bis(*trans*-4-valerylcyclohexyl)benzene **1** 8.2 g (0.02 mol) was reduced with 5 ml of 85% hydrazine hydrate and 4.5 g of potassium hydroxide in 50 ml of diethylene glycol according to the usual Wolff–Kishner procedure. The yield of product was 4.1 g (54%); Cr 49 SmB 195°C I.

3.5. *1,4-Bis[trans-4-(1-hydroxypropyl)cyclohexyl]-benzene* ***1b***

A mixture of 14.2 g (0.04 mol) of 1,4-bis(*trans*-4-propionylcyclohexyl)benzene, 1.5 g (0.04 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% aqueous hydrochloric acid and organic matter was extracted into ether. The ethereal extract was washed with water and dried over anhydrous magnesium sulphate. The solvent was removed in vacuum and the product crystallized from heptane. The yield was 10.3 g (72%); m.p. 172°C.

3.6. *1,4-Bis[trans-4-(1-chloropropyl)cyclohexyl]-benzene* ***1c***

The alcohol **1b** (3.6 g 0.01 mol) was dissolved in 15 ml of pyridine and 1 ml of phosphorus oxychloride added. The reaction mixture was heated at reflux for 5 h and then poured into water. The product was extracted with ether and the ether layer washed with water. After removing the ether, the residue was dissolved in hexane and filtered through a short column of silica gel. After removing the solvent, the product was purified by recrystallization from isopropyl alcohol. The yield was 2.4 g (62%); m.p. 134°C.

3.7. *1,4-Bis[trans-4-(prop-1-enyl)cyclohexyl]benzene* ***1d***

A stirred mixture of 3.9 g (0.01 mol) of the dichloride **1c** and potassium hydroxide 5.6 g (0.1 mol) in 50 ml of ethylene glycol was heated at reflux for 5 h and then poured into water. The product was extracted into ether and washed with water. After removing the ether, the residue was dissolved in hexane and filtered through a short column of silica gel. After removing the solvent the product was purified by recrystallization from isopropyl alcohol. The yield was 1.9 g (58%); Cr 132.5 N 152°C I.

3.8. *3-Methyl-4,5-dihydro-6-(4-ethoxyphenyl)-1,2-benzisoxazole* ***6e***

A mixture of 25.8 g (0.1 mol) of 3-(4-ethoxyphenyl)-6-acetylcyclohex-2-enone **6**, 8.3 g (0.12 mol) of hydroxylamine hydrochloride and 13.8 g (0.1 mol) of K_2CO_3 was boiled in 40 ml of isopropyl alcohol for 5 h and then poured into water. The product was extracted into ether and washed with water. After removing the ether, the residue was crystallized from isopropyl alcohol. The yield was 15.5 g (61%); m.p. 120°C.

A similar procedure gave the other compounds **6e** presented in table 8.

3.9. *4-Ethoxy-3′-hydroxy-4′-acetylbiphenyl* ***6a***

A mixture of 25.8 g (0.1 mol) of 3-(4-ethoxyphenyl)-6-acetylcyclohex-2-enone (**6**) and 17.6 g (0.11 mol) of bromine was boiled for 2 h in 40 ml of CCl_4, then cooled and ether added. The mixture was washed with water and the organic layer dried over anhydrous magnesium sulphate. After removing the solvents the residue was crystallised from toluene. The yield was 12.3 g (48%), m.p. 123°C.

3.10. *N-[1-Ethylid-1′-ene-2-hydroxy-4-(4-ethoxylphenyl)phenyl]-4-hexyloxyaniline* ***6h***

A mixture of 5.1 g (0.02 mol) of 4-ethoxy-3′-hydroxy-4′-acetylbiphenyl **6a** and 3.8 g (0.02 mol) of 4-hexyloxyaniline was boiled for 6 h in 70 ml of isopropyl alcohol and then cooled. The crystals were filtered off and recrystallized from isopropyl alcohol. The yield was 4.6 g (54%), temperature range of nematic phase 187–233°C.

A similar method gave the other compounds **6h** presented in the table 7 and the compounds **6i**.

4. Conclusion

The results presented demonstrate that diketones with different reaction possibilities for the keto groups allow selective transformations to be made and open the door to the preparation of new liquid crystalline compounds with novel combinations of the structural fragments of LC molecules.

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