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

3-(2-Cyanoethyl)-6-aryl- or 6-(*trans*-4-alkylcyclohexyl)cyclohex-2-enones: synthesis, transformations and mesomorphic properties

V. S. Bezborodov; G. M. Sasnouski; V. I. Lapanik

To cite this Article Bezborodov, V. S. , Sasnouski, G. M. and Lapanik, V. I.(2001) '3-(2-Cyanoethyl)-6-aryl- or 6-(*trans*-4-alkylcyclohexyl)cyclohex-2-enones: synthesis, transformations and mesomorphic properties', Liquid Crystals, 28: 6, 897 — 900

To link to this Article: DOI: 10.1080/02678290110039129

URL: http://dx.doi.org/10.1080/02678290110039129

LIQUID CRYSTALS, 2001, VOL. 28, NO. 6, 897–900

3-(2-Cyanoethyl)-6-aryl- or 6-(*trans*-4-alkylcyclohexyl)-cyclohex-2-enones: synthesis, transformations and mesomorphic properties

V. S. BEZBORODOV* G. M. SASNOUSKI and V. I. LAPANIK
Institute of Applied Physics Problems, 220064 Minsk, Belarus

(*Received 16 November 2000; accepted 18 December 2000*)

The synthesis and chemical transformations of 3-(2-cyanoethyl)-6-aryl- or 6-(*trans*-4-alkylcyclohexyl)cyclohex-2-enones into nematic and smectic liquid crystalline compounds are discussed. These 3,6-disubstituted cyclohex-2-enones were prepared by the condensation of appropriate Mannich salts or *trans*-4-alkylcyclohexyl 2-bromoethyl ketones with ethyl 2-(2-cyanoethyl)acetoacetate.

1. Introduction

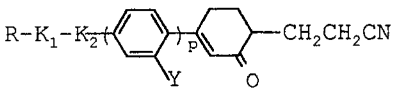
It has been reported that 3,6-disubstituted cyclohex-2-enones [1–5] are promising intermediates for the preparation of various mesomorphic derivatives of cyclohexane, cyclohexene, phenylcyclohexane or biphenyl [6, 7], which are in turn useful components for liquid crystalline mixtures for display applications. In continuation of these investigations of liquid crystalline 3,6-disubstituted cyclohex-2-enones containing a functional group in the terminal position, it was interesting to examine possible transformations of these compounds into liquid crystal materials with optimized features. It should be noted that different reaction possibilities for the functional group and the cyclohexenone fragment allow transformations to be achieved selectively and give the opportunity of preparing liquid crystalline compounds with novel combinations of the structural fragments of LC molecules.

In this paper, using the example of 3-(2-cyanoethyl)-6-aryl- or 6-(*trans*-4-alkylcyclohexyl)cyclohex-2-enones we show how both nematic and smectic liquid crystalline compounds can be prepared by transformations of the cyclohexenone fragment and the functional group.

2. Results and discussion

2.1. *Synthesis*

Liquid crystalline 3-(2-cyanoethyl)-6-aryl- or 6-(*trans*-4-alkylcyclohexyl)cyclohex-2-enones (**1a–f**) were prepared by Michael condensation of appropriate Mannich salts or *trans*-4-alkylcyclohexyl 2-bromoethyl ketones with ethyl 2-(2-cyanoethyl)acetoacetate in the presence of potassium hydroxide in boiling dioxan in yields of 50–80% [8] (see table 1).


(**1 a-f**)

$R = C_3H_7$–C_5H_{11}, CH_3O; K_1, K_2 = bond, or a benzene, or cyclohexane ring; $p = 0$ or 1; Y = H or F.

The hydrogenation (see scheme 1) of the 3,6-disubstituted cyclohexenones (**1c**,**d**) in the presence of 10% palladium on carbon leads to the corresponding *trans*-2,5-disubstituted cyclohexanones (**2c**,**d**) in yields 75–80%. *trans*-2,5-Disubstituted cyclohexanones are prospective intermediates for the synthesis of liquid crystalline *trans*-1,4-disubstituted cyclohexanes. However, as our investigations have shown, the most interesting direction for further chemical transformations of *trans*-2-(2-cyanoethyl)-5-aryl- or 5-(*trans*-4-alkylcyclohexyl)cyclohexanones (**1c**,**d**) is their interaction with sodium borohydride or with diethylaminosulphur trifluoride (DAST), as a result of which the corresponding alcohols (**3c**,**d**) or *gem*-difluoro derivatives (**4c**,**d**) are formed. The alcohols (**3c**,**d**) and difluoro derivatives (**4c**,**d**) can be converted into 1,4-disubstituted cyclohex-1-enes and/or 2,5-disubstituted 1-fluorocyclohex-1-enes (**5c**,**d** and **6c**,**d**), which are characterized by low temperature formation of mesophases with a wide temperature range. They are therefore promising components of LC mixtures for TN and STN Displays.

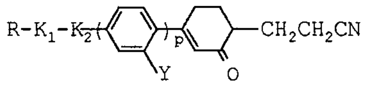
The interaction of the 3,6-disubstituted cyclohexenones (**1d**,**e**) with sodium borohydride or phosphorus pentachloride resulted in the formation of the aromatized

---

*Author for correspondence; e-mail: bezb@pfp.bsu.unibel.by

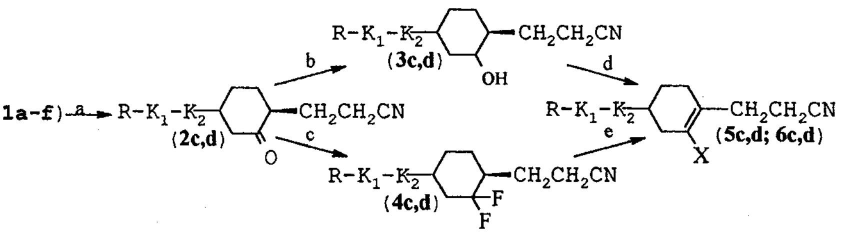
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110039129

Table 1. Yields and transition temperatures of 3,6-disubstituted cyclohexenones **1**.



Compound	*R*	K_1[a]	K_2[a]	*Y*	*p*	Yield/%	Transition temperatures/°C				
							Cr		N		I
1a	H_3CO	—	—	H	1	45	●	89	—		●
1b	H_3CO	—	—	F	1	34	●	66	—		●
1c	H_9C_4	C	—	—	0	55	●	34	—		●
1d	$H_{11}C_5$	B	—	H	1	63	●	103	●	164	●
1e	$H_{11}C_5$	C	—	H	1	68	●	89	●	147	●
1f	$H_{11}C_5$	B	C	—	0	51	●	94	—		●

[a] C = cyclohexane ring, B = benzene ring.

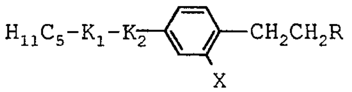


Scheme 1. $R = C_4H_9$, C_5H_{11}; K_1, K_2 = benzene or cyclohexane rings; X = H or F. a. H_2, Pd/C, KOH; b. $NaBH_4$, iso-propanol; c. DAST, benzene; d. $POCl_3$, Py; e. KOH; ethylene glycol.

products (**7d**,**e**), see table 2. These substituted biphenyls and terphenyls can be successfully used for the preparation of ferroelectric liquid crystalline compounds. The hydrolysis of the cyano group using potassium hydroxide in boiling ethylene glycol (see scheme 2) gives 60–70% yields of the corresponding acids (**8d**,**e**) which with chiral alcohols or phenols give the esters (**9a–e**), forming smectic C* phases at low temperature (see table 2).

The proton NMR spectra (δ, ppm) of the 3,6-disubstituted cyclohex-2-enones **1a–f** showed that the multiplets at 5.83 or 6.46 belong to the protons located at the double bond of the cyclohexenone fragment. Two triplets at 2.39–2.35 or 3.01–3.02 in the proton NMR spectra of the saturated ketones **2c**,**d** correspond to signals from protons in the cyclohexanone fragment. The signals from the cyclohexane fragment of the

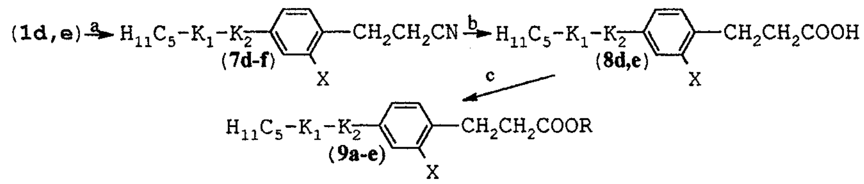
Table 2. Yields and transition temperatures of compounds **7d–f** and **9a–e**.



Compound	K_1[a]	K_2[a]	*X*	*R*	Yield/%	Transition temperatures/°C							
						Cr		SmC		SmA	N		I
7d	B	B	Cl	CN	71	●	105	—		—	●	121	●
7e	C	B	Cl	CN	64	●	88	—		—	●	(82)[b]	●
7f	B	B	H	CN	51	●	201	—		—	●	231	●
9a	B	B	Cl	$COOCH(CH_3)C_4H_9$	74	●	28	●	63.5	●	—	93	●
9b	B	B	Cl	$COOCH(CH_3)C_6H_{13}$	70	●	39	●	52.5	●	—	76	●
9c	B	B	Cl	$COOC_4H_9$	62	●	53	●	66	●	—	107	●
9d	B	B	Cl	$COOCH(CH_3)COOC_2H_5$	65	●	84	—		●	—	103	●
9e	B	B	Cl	$COOC_6H_4OCH(CH_3)C_6H_{13}$	60	●	73	—		●	—	123	●

[a] C = cyclohexane ring, B = benzene ring.

[b] () denotes a monotropic phase.



Scheme 2. X = H, Cl; K_1, K_2 = benzene or cyclohexane rings; R = $CH(CH_3)C_4H_9$, $CH(CH_3)C_6H_{13}$, $CH(CH_3)COOC_2H_5$, C_4H_9, $C_6H_4OCH(CH_3)C_6H_{13}$ a. $NaBH_4$ or PCl_5; b. KOH; ethylene glycol; c. ROH, DCC, DMAP, CH_2Cl_2.

difluoro derivatives **4c**,**d** are observed at 1.47–2.89. The multiplet at 5.64 in the spectra of the cyclohexene derivatives **5c**,**d** belongs to protons located at the double bond of the cyclohexene fragment.

2.2. *Mesomorphic properties*

The phase transition temperatures of the 3,6-disubstituted cyclohex-2-enones **1a–f** are listed in table 1. As can be seen, the two-ring compounds **1a–c** are not mesomorphic. The introduction of an additional ring results in the appearance of the nematic phase in the overall temperature range 89–164°C for **1d**,**e**. *trans*-2-(2-Cyanoethyl)-5-(*trans*-4-pentylcyclohexyl)cyclohexanone (**2c**) has a narrow nematic phase range from 50 to 56°C, whereas *trans*-2-(2-cyanoethyl)-5-(4-pentylbiphenyl-4-yl)cyclohexanone (**2d**) forms smectic A and nematic phases in the temperature range 74–164°C. Unlike the ketone **2c**, 1-(2-cyanoethyl)-4-(*trans*-4-pentylcyclohexyl)cyclohex-1-ene (**5c**) is characterized by the formation of a smectic phase in the temperature range 41–69°C. It should be noted that the same phases were observed for 1-*trans*-(2-cyanoethyl)-4-(*trans*-4-pentylcyclohexyl)cyclohexane [9]. The exchange of the carbonyl group for two fluorines leads to the disappearance of mesomorphic properties for the two-ring compound **4c** and shortening of the temperature ranges of the smectic and nematic phases for the corresponding pentylbiphenyl derivative **4d**. This compound has the following phase transitions: Cr 74 SmA 84 N 164 I (°C).

The introduction of a chlorine coupled with aromatization of the cyclohexenone fragment is also accompanied by shortening of the temperature ranges of the nematic phases of the chlorobiphenyls and terphenyls **7d–f** (see table 2). The esters **9a–e** form smectic C and or A phases in the temperature range 28–123°C.

Investigations of the electro-optic and dynamic parameters of LC mixtures containing 3-(2-cyanoethyl)-6-arylcyclohex-2-enones **1a–c**, 2,5-disubstituted 1,1-difluorocyclohexanes **4c**,**d** and 1,4-disubstituted cyclohex-1-enes **5c**,**d** and **6c**,**d**, have shown that these compounds can be successfully used as components of liquid crystalline mixtures which are characterized by low threshold and saturation voltages in the twisted nematic-effect, by step voltage-contrast characteristics and by low values of switch-on and switch-off times.

3. Experimental

Confirmation of the structures of all intermediates and final products was obtained using GC/MS (mass-spectrometer HP 5972) and ^{1}H NMR spectroscopy. The purity of the compounds was checked using a HP 5890 capillary gas chromatograph fitted with an H1 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 3,6-disubstituted cyclohex-2-enones **1a–f** and the products of their aromatization **7d–f** were prepared according to previously published methods [4, 6, 7].

3.1. *trans-2-(2-Cyanoethyl)-5-(trans-4-butylcyclohexyl)cyclohexanone (**2c**)*

3-(*trans*-4-Butylcyclohexyl)-6-(2-cyanoethyl)cyclohex-2-enone (**1c**) (0.01 mol) in 150 ml of THF containing 0.5 g of potassium hydroxide was hydrogenated with vigorous stirring at room temperature in the presence of 1.0 g of 10% palladium on carbon. The catalyst was separated, and after removing the solvent, the residue was crystallized from isopropanol. The yield was 84%; m.p. 50°C.

3.2. *trans-2-(2-Cyanoethyl)-5-(trans-4-butylcyclohexyl)-1,1-difluorocyclohexane (**4c**)*

A mixture of *trans*-2-(2-cyanoethyl)-5-(*trans*-4-butylcyclohexyl)cyclohexanone (**2c**) (0.01 mol) and DAST (0.02 mol) in 100 ml of benzene was heated at reflux during 15 h and, after cooling poured into aqueous KOH. The organic layer was washed with water and dried over anhydrous sodium sulphate. After removing the solvent, the product was isolated by chromatography on silica gel using hexane as eluent. The yield was 43%; m.p. 62°C.

3.3. *trans-2-(2-Cyanoethyl)-5-(trans-4-butylcyclohexyl)cyclohexan-1-ol (**3c**)*

A mixture of *trans*-2-(2-cyanoethyl)-5-(*trans*-4-butylcyclohexyl)cyclohexanone (**2c**) (0.02 mol), sodium borohydride (0.02 mol) 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 the organic layer shaken with 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 hexane and used in the next stage. The yield was 81%; m.p. 47°C.

3.4. *1-(2-Cyanoethyl)-4-(trans-4-butylcyclohexyl)cyclohex-1-ene (**5c**)*

The alcohol **3c** (0.01 mol) was dissolved in 15 ml of pyridine and 1 ml of phosphoros oxychloride was added. The reaction mixture was heated at reflux during 5 h and then poured into water. The product was extracted into ether and the extract 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 64%; m.p. 41°C.

3.5. *4-Pentyl-3″-chloro-4″-(2-carboxyethyl)-p-terphenyl (**8d**)*

A mixture of 4-pentyl-3″-chloro-4″-(2-cyanoethyl)-*p*-terphenyl (**7d**) (0.02 mol), KOH 0.08 mol and 100 ml of ethylene glycol was heated at reflux with vigorous stirring during 10 h. After cooling, the reaction mixture was acidified with 10% aqueous hydrochloric acid; the product was filtered off and used, after drying in the air, in the next stage. The yield was 78%; m.p. 174°C.

3.6. *4-Pentyl-3″-chloro-4″-(2-carbobutoxyethyl)-p-terphenyl (**9c**)*

A mixture of 4-pentyl-3″-chloro-4″-(2-carboxyethyl)-*p*-terphenyl (**8d**) (0.01 mol), butyl alcohol (0.015 mol), dicyclohexylcarbodiimide 0.015 mol and a catalytic amount of *N*,*N*-dimethylamino pyridine in 50 ml methylene chloride was stirred overnight and the mixture filtered through a silica gel layer. After removing the solvent, the product was isolated by chromatography on silica gel using hexane : ethyl acetate (5 : 1) as eluent and purified additionally, after removing volatiles, by recrystallization from isopropyl alcohol. The yield was 62%; m.p. 53°C.

Similar methods gave the other compounds (**9a–e**) presented in table 2.

References

[1] Sucrow, W., and Walter, H., 1986, *Chem. Ber.*, **119,** 387.

[2] Bezborodov, V. S., and Dabrowski, R., 1997, *Mol. Cryst. liq. Cryst.*, **299,** 1.

[3] Bezborodov, V. S., Dabrowski, R., Sasnovski, G., and Dziaduszek, J., 1997, *Mol. Cryst. liq. Cryst.*, **303,** 297.

[4] Bezborodov, V. S., Dabrowski, R., Sasnovski, G., Dziaduszek, J., and Petrov, V. F., 1998, *Liq Cryst.*, **24,** 647.

[5] Brettle, R., Dunmur, D. A., Farrand, L. D., and Marson, C. M., 1996, *J. mater. Chem.*, **6,** 747.

[6] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., and Petrov, V. F., 1997, *Liq Cryst.*, **23,** 69.

[7] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., Czuprinski, K., and Raszewski, Z., 1996, *Liq. Cryst.*, **20,** 1.

[8] Sasnovski, G., Bezborodov, V. S., Dabrowski, R., and Dziaduszek, J., 1999, *Mol. Cryst. liq. Cryst.*, **332,** 227.

[9] Osman, M. A., and Huynh-Ba, T., 1984, *Helv. Chim. Acta*, **67,** 959.