Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Mesomorphic Properties of Some 3,6-Disubstituted Cyclohex-2-Enones

Vladimir Bezborodov [a b c] , Roman Dąbrowski [a b] , Genadź Sasnovski [a] & Jerzy Dziaduszek [b]

[a] Institute of Applied Physics Problems, 220064, Minsk, Belarus

[b] Military University of Technology, 01-489, Warsaw, Poland

[c] Samsung Display Devices Co. Ltd., R&D Center, 575 Shin-Dong, Paldal-Do, Korea, 445-970

Version of record first published: 04 Oct 2006

To cite this article: Vladimir Bezborodov, Roman Dąbrowski, Genadź Sasnovski & Jerzy Dziaduszek (1997): Synthesis and Mesomorphic Properties of Some 3,6-Disubstituted Cyclohex-2-Enones, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 297-304

To link to this article: http://dx.doi.org/10.1080/10587259708039438

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 297–304
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND MESOMORPHIC PROPERTIES OF SOME 3,6-DISUBSTITUTED CYCLOHEX-2-ENONES

VLADIMIR BEZBORODOV (*), ROMAN DĄBROWSKI **),
GENADŹ SASNOVSKI*, JERZY DZIADUSZEK**
* Institute of Applied Physics Problems, 220064, Minsk, Belarus
** Military University of Technology, 01-489 Warsaw, Poland

Abstract The synthesis and mesomorphic properties of several dozen 3,6-disubstituted cyclohex-2-enones are described. The compounds were obtained by the condensation of 4-substituted β-(N,N-dimethylamino)ethylphenyl ketone hydrochlorides (Mannich salts) with 2-alkylacetoacetic esters. The influence of the structure of the reactants, catalysts and solvents on the yield is discussed.

INTRODUCTION

3-Substituted and 3,6-disubstituted cyclohex-2-enones are very promising and convenient reactants for the synthesis of different classes of mesogenes with aliphatic rings (cyclohexane, cyclohexene[1], bicyclohexane[2], or tricyclohexane[3]) and also with aromatic rings[1,4]. They are also intermediates for their laterally substituted derivatives such as 2,5-disubstituted cyclohexanones[5,6,7] and then for difluorocyclohexanes[8] and fluoro-cyclohexenes[9] or 3,6-disubstituted chlorobenzenes.[4] Single enantiomers of some

(*) Present address Samsung Display Devices Co.Ltd., R&DCenter, 575 Shin-Dong, Paldal-Do, Korea 445-970,
**) Author for correspondence

3,6-disubstituted cyclohex-2-enones were separated and used as components of ferroelectric mixtures.[10,11]

Many different methods of preparation of cyclohexenone ring have been described:

- condensation of aldehydes with acetoacetic ester[13,14]
- condensation of benzyl ketones and propiophenones or 1,3-diketones or 1,3-ketoesters or diesters with α or β-unsaturated ketones[15,16,17] or their precursors such as chloropropiophenones
- quaternary salts of the Mannich base (β-(N,N-dialkylamino)ethylketones) in the presence of alkaline catalyst.[9,18-27]
- Nef reaction in which the nitro group in a cyclohexylene ring is transformed to the keto group gives also high yield of cyclohexenones[28].

The method in which Mannich salt is used seems to be the more general and more convenient for the synthesis of cyclohexenone mesogenic structures than the other mentioned methods, because a variety of diverse Mannich salts may easily be prepared with rather good yield from aromatic as well as from aliphatic methyl ketones[29].

We have tested the condensation of Mannich salts with 2-substituted acetoacetates (substituted with alkyl, alkylcyclohexylethyl, alkylphenylethyl). More than hundred mesogenic structures have been prepared with satisfactory yields.

RESULTS AND DISCUSSION

Condensation of β-N,N-dimethylaminopropiophenones hydrochlorides with α-substituted acetoacetates

Abdullah reported that β-dimethylaminopropiophenone undergoes a Michael type condensation (scheme 1) with acetoacetic acid esters in presence of sodium ethoxide.[18] Novello as the condensing agent used potassium t-butoxide in benzene, t-butyl alcohol or dioxane since it gave higher yield of the cyclized product 5 and in some instances minimized loss of the carboethoxy group.[19] Baiocchi[22,23] used KOH in butyl alcohol and Walker proposed also benzyltrimethylamonium hydroxide as the condensing agent in the reaction of benzylacetates with methyl vinyl ketones[15].

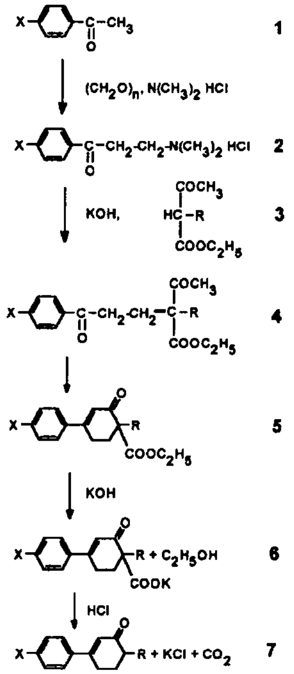


FIGURE 1 Route of the synthesis of cyclohexen-1-ones.

We found that 3-arylcyclohex-2-ones (R=H) and 3-aryl-6-alkylcyclohex-2-ones (R= alkyl, alkylcyclohexylethyl, alkylphenylethyl) are formed in one pot procedure from **2** and **3** with the yield approaching to 70-80% in the presence of potassium hydroxide under refluxing in isopropyl alcohol, dioxane or diglyme. The refluxing in benzene or toluene gives worse results.

The necessary time to finish the condensation (formation of compound **5**, and its hydrolysis and the elimination of carboxylic group in **6**) is usually few hours. The use of β-N,N-dimethylaminopropiophenones **2** gives higher yields of the compounds **7** than the use of other Mannich salts prepared from higher boiling amines such as diethylamine, piperidine or morpholine. The Mannich salts were prepared from different acetophenones (4-alkyl, 4-alkylphenyl, 4-alkoxyphenyl, 4-alkylcyclohexylacetophenones) using standard procedure[29] from dimethylamine hydrochloride and paraformaldehyde. Isolated yields of Mannich salts as a crystalline solid was 70-80%. KOH is more effective as an alkaline condensing agent in comparison to NaOH, K_2CO_3, or alcoholates (ethoxide, propoxide, t-butoxide). The presence of small amounts of benzyltrimethyl ammonium chloride or similar tetraalkylamonium salt sometimes increases yields, but usually it is not necessary to use it. The influence of the different conditions of carrying the condensation reaction is discussed in more details in our parallel work referring to *trans*-4-(4-alkylphenyl)cyclohexyl β-(N,N-dimethylamino)ethyl ketones[2].

The general condensation procedure which was used for the preparation of the different mesogenic structures containing the 3,6-disubstituted cyclohex-2-enone ring was the following. The nearly equimolar amounts of the Mannich salt **2** and acetoacetic ester **3** in the presence of three molar excess of KOH were refluxed in dioxane for 5 hours. The compounds obtained from 2-alkylacetoacetates according the above procedure are listed in Table I and the ones obtained from 2-(4-alkylphenylethyl) or 2-(*trans*-4-alkylcyclohexylethyl)acetoacetates in Table II.

In this general procedure the yields was better than 50% for the most cases and spans over the variety of mesogenic structures. It seems that the yield may be increased in individual cases by the prolongation of the reaction time. Sometimes it is possible to improve the yield by additional dilution of the mixture with water and further short boiling.

Mesomorphic properties

3,6-Disubstituted cyclohex-2-enones show a strong smectogenic character, but the smectic polymorphism is rather poor. Compounds with different structures having two, three and four rings usually have only the smectic A phase in a broad temperature range. The smectic B phase was observed additionally below the smectic A phase in some four ring compounds (Table II, compound 7 No 11,12,14,15) and a nematic phase in some structures containing a cyclohexane ring (Table I, compound 7 No 42, 43, 44, 45, 46, 47, 49, 50, 53, 55; Table II, compound 7 No 10, 11.

3,6-Disubstituted two ring cyclohex-2-enones with two alkyl terminal substitutents and compounds with one alkyl and the other alkoxy substitutent differ in mesogenic properties. While the fist ones are only monotropic liquid crystals the second ones have clearing points above one hundred centigrades. The difference in the clearing points between these two groups is about 80 °C or higher.

TABLE 1 Yield [%] and phase transition temperatures [°C] of compounds 7.

No	X	R	Yield	Cr		S_A		N	I
1	H	C_2H_5	44	*	33	-		-	*
2	H	C_5H_{11}	64	*	liquid	-		-	*
3	HO	C_3H_7	35	*	128	-		-	*
4	HO	C_5H_{11}	29	*	98	-		-	*
5	F	C_5H_{11}	70	*	liquid	-		-	*
6	Br	C_5H_{11}	57	*	liquid	-		-	*
7	CH_3	C_4H_9	58	*	48	-		-	*
8	C_2H_5	C_4H_9	52	*	36	*	(21)	-	*
9	C_5H_{11}	C_4H_9	51	*	75	-		-	*
10	C_5H_{11}	C_5H_{11}	56	*	90	-		-	*
11	C_6H_{13}	C_3H_7	47	*	31	*	34	-	*
12	CF_3O	C_5H_{11}	42	*	37	-		-	*
13	3,4-CH_3O	C_4H_9	62	*	65	-		-	*
14	2-F, 4-CH_3O	C_5H_{11}	57	*	48	-		-	*
15	C_2H_5O	CH_3	53	*	62	-		-	*
16	C_2H_5O	C_3H_7	62	*	56	*	67	-	*
17	C_2H_5O	$CH_2CH{=}CH_2$	53	*	71	-		-	*
18	C_2H_5O	C_4H_9	54	*	55	*	79	-	*
19	C_2H_5O	C_5H_{11}	50	*	70	*	86	-	*
20	C_3H_7O	C_5H_{11}	47	*	58	*	94	-	*
21	C_4H_9O	CH_3	42	*	71	-		-	*
22	C_4H_9O	C_3H_7	64	*	67	*	97	-	*
23	C_4H_9O	C_4H_9	59	*	67	*	96	-	*
24	C_4H_9O	C_5H_{11}	48	*	41	*	109	-	*
25	$C_5H_{11}O$	C_3H_7	72	*	55	*	96	-	*
26	$C_5H_{11}O$	C_5H_{11}	67	*	53	*	110	-	*
27	$C_6H_{13}O$	C_5H_{11}	73	*	56	*	109	-	*
28	$C_9H_{19}O$	C_5H_{11}	71	*	59	*	109	-	*
29	$C_{10}H_{21}O$	C_5H_{11}	58	*	60	*	113	-	*
30	C_6H_5	C_3H_7	65	*	119	*	(104)	-	*

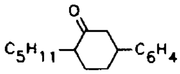
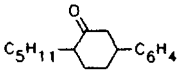
31	C_6H_5	C_4H_9	62	*	110	*	116	-		*
32	C_6H_5	C_5H_{11}	59	*	101	*	120	-		*
33	$F-C_6H_4-$	C_5H_{11}	55	*	89	*	114	*	141	*
34	$Br-C_6H_4-$	C_5H_{11}	50	*	91	*	114	*	219	*
35	$CH_3-C_6H_4-$	C_5H_{11}	51	*	117	*	179	-		*
36	$C_2H_5-C_6H_4-$	C_5H_{11}	47	*	83	*	171	-		*
37	$C_2H_5-C_6H_4-$	C_6H_{13}	50	*	94	*	191	-		*
38	$C_5H_{11}-C_6H_4-$	C_2H_5	54	*	93	•	157	-		*
39	$C_2H_5O-C_6H_4-$	C_3H_7	47	*	118	*	204	-		*
40	4-CH_3O, 3F-$C_6H_3C_6H_{10}$	C_5H_{11}	51	*	84	*	176	-		•
41	C_6H_5- OCH_2CH_2	C_5H_{11}	48	*	(54)	*		-	66	*
42	$C_3H_7C_6H_{10}CH_2CH_2$	C_5H_{11}	66	*	71	*	133	*	139	*
43	$C_2H_5-C_6H_{10}$	C_3H_7	70	*	69	*	84	*	121	*
44	$C_2H_5-C_6H_{10}$	C_5H_{11}	75	*	77.5	*	127	*	133.5	*
45	$C_3H_7-C_6H_{10}$	C_3H_7	77	*	76	*	102	*	150	*
46	$C_3H_7.C_6H_{10}$	C_4H_9	53	*	57	*	125	•	149	*
47	$C_3H_7-C_6H_{10}$	$CH_2CH=CH_2$	50	*	84	-		•	102	*
48	$C_2H_5CO-C_6H_{10}$	C_5H_{11}	34	*	104	*	162	-		*
49	$C_3H_7-C_6H_{10}$	C_5H_{11}	47	*	77	*	149	*	157	*
50	$C_4H_9-C_6H_{10}$	C_5H_{11}	62	*	91	*	143	*	185	*
51	$C_3H_7-C_6H_{10}$	C_6H_{13}	57	*	83	*	152	-		*
52	$C_5H_{11}-C_6H_{10}$	C_2H_5	54	*	87	*	121	-		*
53	$C_5H_{11}-C_6H_{10}$	C_4H_9	46	*	66	*	144	*	153	*
54	$C_5H_{11}-C_6H_{10}$	C_5H_{11}	53	*	58	*	149	-		*
55	$C_4H_9-C_6H_{10}-CH_2CH_2$	C_2H_5	47	•	66	-		*	104	*
56	4-C_5H_{11}-3-CH_3-C_6H_9-C_6H_4	C_5H_{11}	52	*	65	*	234	-		*
57		C_2H_5	29	*	91	*	179	-		*
58		C_5H_{11}	33	*	118	*	225	-		*

TABLE 2 Yield [%] and phase transition temperatures [°C] of compounds 7.

No	X	R	Yield	Cr		S_B		S_A		N		I
1	CH_3	$CH_2CH_2C_6H_5$	56	*	89	-		-		-		*
2	F	$CH_2CH_2C_6H_5$	18	*	126	-		-		-		•
3	4-CH_3O, 3-F	$CH_2CH_2C_6H_5$	44	•	98	-		-		-		*
4	4-CH_3O, 2-F	$CH_2CH_2C_6H_5$	20	*	78	-		-		-		•
5	C_2H_5O	$CH_2CH_2C_6H_5$	57	*	94	-		•	(78)	-	(78)	*
6	3,4-F	$CH_2CH_2C_6H_{10}C_4H_9$	67	*	91.5	-		-		•	(89)^a	*
7	3,4-F	$CH_2CH_2C_6H_{10}C_5H_{11}$	52	*	96.5	-		-		•	(84)^a	•
8	4-CH_3O, 2-F	$CH_2CH_2C_6H_{10}C_4H_9$		*	76	-		-		•	126^a	•
9	$C_3H_7C_6H_{10}$	$CH_2CH_2C_6H_5$	43	*	117	-		*	170	-		•
10	$C_3H_7C_6H_{10}$	$CH_2CH_2C_6H_4OC_2H_5$	36	*	121	-		•	172	*	193	•
11	$C_3H_7C_6H_{10}$	$CH_2CH_2C_6H_{10}C_4H_9$	63	*	<20	*	174	•	243	•	252	•
12	$C_3H_7C_6H_{10}$	$CH_2CH_2C_6H_{10}C_5H_{11}$	48	•	<20	*	175	•	248^a	-		•
13	$C_5H_{11}C_6H_{10}$	$CH_2CH_2C_6H_4C_3H_7$	48	*	143	-		*	204	-		*
14	$C_3H_7C_6H_{10}CH_2CH_2$	$CH_2CH_2C_6H_{10}C_4H_9$	61	*	<20	*	161	*	222^a	-		*
15	$C_4H_9C_6H_{10}CH_2CH_2$	$CH_2CH_2C_6H_{10}C_4H_9$	59	*	71	*	187	*	226^a	-		*

a - phase transition temperature from Ref. 4.

It is well known for many homologous series that alkoxy compounds have higher stability of mesophases than alkyl compounds, but the observed differences are not as big as in this cases. For example, differences in clearing points between 4,4'-dialkylbiphenyls and 4-alkyl-4'-alkoxybiphenyls or between 4-(4-alkylcyclohexyl)alkylbenzenes and 4-(4-alkylcyclohexyl)alkoxybenzenes are 30-50 °C[31].

It is rather unexpected properties because cyclohex-2-enone derivatives posses the carbonyl group in the lateral position of molecules. Usually the lateral substitutent decreases the clearing point of the compounds but not in this case. The reason for this is not understood for us yet. Perhaps it results from a convenient dipol-dipol intermolecular interaction or from the convenient geometrical shape of molecules.

This work was supported by the Polish Committee for Scientific Research under grant No 3P405 003 07 and the European Community under grant CIPACT 940157.

REFERENCES

1. V. Bezborodov, R. Dąbrowski, and J. Dziaduszek, SPIE, 2372, 242 (1995).
2. G. Sasnowski, V. Bezborodov, R. Dąbrowski, and J. Dziaduszek, paper presented at the same conference.
3. W. Sucrow and H. Wolter, Chem.Ber., 119, 387 (1986).
4. V. Bezborodov, R. Dąbrowski, J. Dziaduszek, K. Czupryński, and Z. Raszewski, Liq.Cryst., 20, 1 (1996).
5. V. Bezborodov, G. Sasnowski, R. Dąbrowski, J. Dziaduszek, J. Schirmer, and P. Kohns, Liq.Cryst., (1996) in press.
6. Y. Hataaki, Jap. Pat., 63203634 (1988); Chem.A., 110:75026m.
7. Y. Hataaki and K. Koichi, Jap. Pat., 62185036 (1987); Chem.A., 108:131286a.
8. M. Hird, K. J. Toyne, A. J. Slaney, J. W. Goodby, and G. W. Gray, J.Chem.Soc., Perkin Trans.2, 2337 (1993).
9. Reiffenrath and H. Plach, Ger.Pat., 4427266 (1995).
10. R. Brettle, D. A. Dunmur, L. D. Farrand, N. J. Hindley, and Ch. M. Marson, Chem.Lett., 1663 (1993).
11. R. Brettle, D. A. Dunmur, L. D. Farrand, and Ch. M. Marson, J.Chem.Soc., Chem.Commun., 2305 (1994).
12. W. Sucrow, D. Fiedel, E. Poetsch, and G. Radecker, Ger.Pat., 3827675 (1989).
13. W. T. Smith and D. S. P. Eftax, J.Org.Chem., 21, 174 (1956).
14. G. V. Krysthal, V. V. Kulganek, V. F. Kucherov, and L. A. Yanovskaya, Synthesis, 107 (1979).
15. G. N. Walker, J.Am.Chem.Soc., 77, 3664 (1955).
16. J. Golonge and J. P. Kehlstadt, Bull.Chem.Soc.(Fr), 504 (1955).
17. F. C. Novello and M. E. Christy, J.Am.Chem.Soc., 75, 5431 (1953).
18. S. M. Abdullah, J.Ind.Chem.Soc., 12, 62 (1935).
19. F. C. Novello, M. E. Christy, and J. M. Sprague, J.Am.Chem.Soc., 75, 1330 (1953).
20. R. N. Lacey, J.Chem.Soc., 1625 (1960).
21. R. M. Dodson and P. Sollman, J.Am.Chem.Soc., 73, 4197 (1951).
22. L. Baiocchi, Bull.Chim.Farm., 107, 762 (1968).
23. G. Palazzo and L. Baiocchi, Tetrahedron Lett., 4739 (1968).
24. M. W. Partrigde, H. J. Vipond, J. Urwin, and J. S. Nicholson, Brit.Pat., 1265800 (1972).
25. E. C. du Feu, F. J. McQuillin, and R. Robinson, J.Chem.Soc., 53 (1937).
26. A. M. Dounes, N. S. Gill, and F. Lions, J.Am.Chem.Soc., 72, 3464 (1950).
27. A. M. Dounes, N. S. Gill and F. Lions, Aust.J.Sci., 10, 147 (1948).
28. W. C. Wildman, R. B. Wildman, W. T. Norton, and J. B. Fine, J.Am.Chem.Soc., 75, 1912 (1953).
29. F. F. Blicke, in Organic Reactions, edited by J. Wiley and Sons (New York, 1947), Vol. I, 303.
30. B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith, and A. R. Tatchell, Vogel's Textbook of Practical Organic Chemistry (Longman Group Limited, London, 1978), Chap. IV, 147.
31. V.Vill, Landolt-Börnstein, Liquid Crystals, edited by J.Thiem (Springer Verlag, 1992), Chap. 7a.