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

# Present and Future of the Liquid Crystals Chemistry

V. Bezborodov [a c] & R. Dabrowski [b]
[a] Institute of Applied Physical 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-Gu, Suwon City, Kyungki-Do, Korea, 442-390

Version of record first published: 04 Oct 2006

To cite this article: V. Bezborodov & R. Dabrowski (1997): Present and Future of the Liquid Crystals Chemistry, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 1-18

To link to this article: http://dx.doi.org/10.1080/10587259708041967

*Mol. Cryst. Liq. Cryst.*, 1997, Vol. 299, pp. 1–18
Reprints available directly from the publisher
Photocopying permitted by license only

# PRESENT AND FUTURE OF THE LIQUID CRYSTALS CHEMISTRY

VLADIMIR BEZBORODOV*
Institute of Applied Physical Problems, 220064, Minsk, Belarus

ROMAN DABROWSKI
Military University of Technology, 01-489, Warsaw, Poland

* Present address: Samsung Display Devices Co.Ltd., R&D Center, 575,
Shin-Dong, Paldal-Gu, Suwon City, Kyungki-Do, Korea, 442-390.

Abstract This paper presents a review of well-known synthetic methods and technological aspects of the preparation of liquid crystals and describes new strategies and tactics in the liquid crystals chemistry

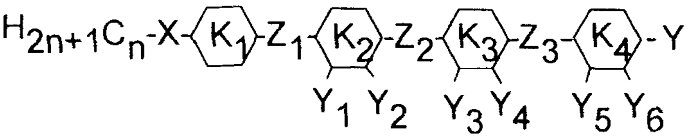
## INTRODUCTION

The exploration of liquid crystals is still a challenge since the rapid development of liquid crystal display technology demands new liquid crystal materials which possess as wide of range of properties as possible.

Most methods for the synthesis of new liquid crystals that have been developed during the past decades are usually tactical devices that are created for the improvement of a particular strategy. Seldom are methods devised that lead to new general strategic solutions for the synthesis of complicated molecules. Even more rarely do new methods provide entirely new types of molecules. It is the intention of this discussion to review well-known methods for the synthesis of liquid crystals and to develop new strategies and tactics in liquid crystal chemistry.

## DISCUSSION

The structures of liquid crystalline compounds can be expressed by the following general formula:



$H_{2n+1}C_n$-X-(K$_1$)-$Z_1$-(K$_2$)-$Z_2$-(K$_3$)-$Z_3$-(K$_4$)-Y; $Y_1$ $Y_2$ $Y_3$ $Y_4$ $Y_5$ $Y_6$

where for :

**a) nonchiral nematic and smectic LC compounds**

n = 1 - 10; X = O, single bond, S, NH, etc;

$K_{1-4}$ = benzene, cyclohexane, cyclohexene, heterocyclic fragments (N, O, S, B and Si containing cycles);

$Z_{1-3}$ = COO, single bond, CH=CH, $CH_2CH_2$, $OCH_2$, C≡C, etc;

$Y_{1-6}$ = H, Cl, F, CN, etc;

Y = alkyl, alkoxy radicals, F, Cl, CN, NCS, $CF_3$, $OCF_3$, $OCHF_2$, $OCF_2Cl$.

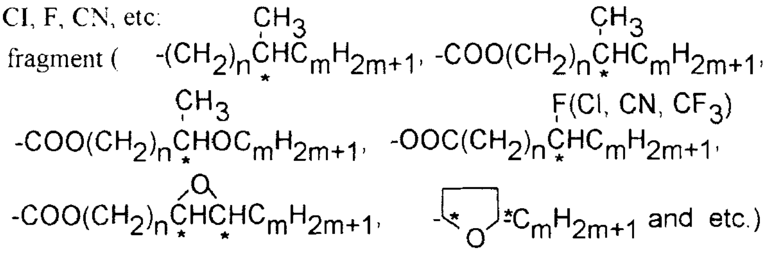
**b) Chiral nematic and smectic (FLC and AFLC) compounds**

n = 6 - 12; X = O, single bond;

$K_{1-4}$ = benzene, cyclohexane, cyclohexene, heterocyclic fragments (N, O, S and B containing cycles);

$Z_{1-3}$ = COO, single bond, CH≡CH, $CH_2CH_2$, $OCH_2$, etc;

$Y_{1-6}$ = H, Cl, F, CN, etc:



Y = chiral fragment ( $-(CH_2)_n\underset{*}{\overset{CH_3}{C}}HC_mH_{2m+1}$, $-COO(CH_2)_n\underset{*}{\overset{CH_3}{C}}HC_mH_{2m+1}$, $-COO(CH_2)_n\underset{*}{\overset{CH_3}{C}}HOC_mH_{2m+1}$, $-OOC(CH_2)_n\underset{*}{\overset{F(Cl,\ CN,\ CF_3)}{C}}HC_mH_{2m+1}$, $-COO(CH_2)_n\underset{*}{C}H\overset{O}{\phantom{x}}\underset{*}{C}HC_mH_{2m+1}$, $-\overset{*}{\square}_{O}{}^{*}C_mH_{2m+1}$ and etc.)

**c) Lyotropic LC compounds**

n = 6 - 12; X = O, single bond;

$K_{1-4}$ = benzene, cyclohexane, cyclohexene, heterocyclic fragments;

$Z_{1-3}$ = COO, single bond, CH≡CH, N=N, $CH_2CH_2$, etc;

$Y_{1-6}$ = H, Cl, F, CN, etc.

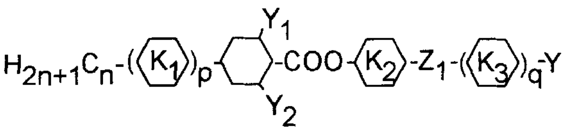
Y = $(CH_2)_nCOOH$, $(CH_2)_nCOONa(K)$, $(CH_2)_n\overset{+}{N}H(CH_3)_2Cl^-$

**d) monomers for LC polymers**

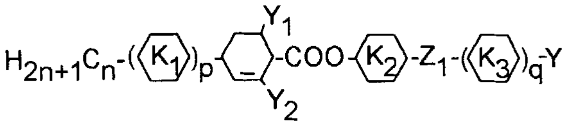
$n = 0$; $X$ = CH=CHCOO, CH=C(CH$_3$)COO, BrCH(CH$_2$)$_n$
HOCH(CH$_2$)$_n$, CH=CH(CH$_2$)$_n$;
$K_{1\text{-}4}$ = benzene, cyclohexane, cyclohexene, heterocyclic fragments;
$Z_{1\text{-}3}$ = COO, single bond, CH$_2$CH$_2$, OCH$_2$, etc;
$Y_{1\text{-}6}$ = H, Cl, F, CN, etc;
$Y$ = alkyl, alkoxy radicals, F, Cl, CN, NCS, CF$_3$, OCF$_3$, etc.

In the general formula, the cyclic fragments can be five- or seven-membered rings, naphthalene or decalene rings and the bridge fragments can be azomethine, azoxy or other groups.

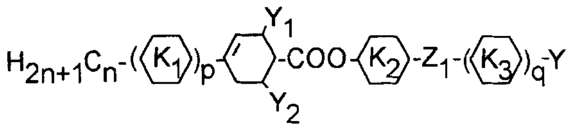
From these compounds, the esters of trans-4-alkylcyclohexancarboxylic acids (1, $p = 0$, $Y_1$, $Y_2$ = H) [1-3] are very simple to prepare since the starting acids may be prepared in one step by catalytic reduction of the corresponding 4-alkylbenzoic acids. However, these esters, as well as the aryl or trans-4-substituted cyclohexyl esters of trans-4-arylcyclohexancarboxylic (1, $p = 1$, $K_1$= benzene, $Y_1$, $Y_2$ = H) [4,5], trans-4-(trans-4-alkylcyclohexyl)cyclohexancarboxylic (1, $p = 1$, $K_1$= cyclohexane, $Y_1$, $Y_2$ = H) [6,7], trans-4-alkyl-2-methyl(2,6-dimethyl)cyclohexancarboxylic (1, $p = 0$, $Y_1$, $Y_2$ = H, CH$_3$) [8,9], 4-alkylcyclohex-2-(3)enecarboxylic (2,3) [10,11] or other substituted cyclohexane or cyclohexenecarboxylic acids [12,13] are usually characterized by higher viscosity in the nematic phase making them less useful as components in liquid crystal mixtures than the corresponding derivatives of phenylcyclohexane or biphenylcyclohexane [14-18] without COO bridge fragment.



(1)



(2)



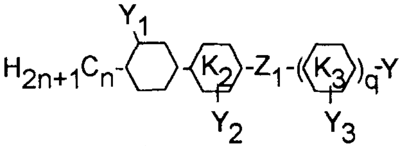
(3)

$n = 2$-$7$; $K_1, K_2, K_3$ = benzene or cyclohexane;
Y = alkyl, alkoxy radicals, F, Cl, CN, NCS, $CF_3$,
$OCF_3$, $OCHF_2$, $OCF_2Cl$;
$Y_1$, $Y_2$ = H, $CH_3$; $p,q = 0,1$; $Z_1$ = single bond or
bridge fragment.

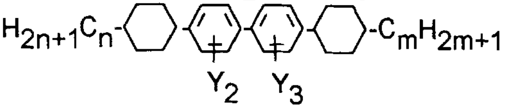
It has been shown that the most useful liquid crystalline (LC) compounds for display applications [14,15] - derivatives of phenylcyclohexane can be prepared by using the Nenitzescu method, Grignard reaction or cross-coupling reaction between alkylchlorides and 1-chloro-4-benzene-1-cyclohexene [16-18]. According to the Nenitzescu method, the reaction of aliphatic acid chlorides with cyclohexene or methylcyclohexene and benzene in the presence of anhydrous aluminum chloride gives a mixture of cis- and trans-1-alkanoyl-4-phenylcyclohexanes or cis- and trans-1-alkanoyl-2-methyl-4-phenylcyclohexanes in yields of 60 - 70%. The pure trans-isomers in the form of 4-alkanoylcyclohexylacetophenones or alkylcyclohexyl acetophenones can be easily separated. These ketones are very promising intermediates for the preparation of different kinds of LC compounds, such as trans-1-alkyl-4-(4-isothiocyanatophenyl)-cyclohexanes and trans-1-alkyl-(4-cyanophenyl)cyclohexanes which are the most useful components of liquid crystal mixtures.

It has been found that the Nenitzescu and Grignard reactions are not so effective for the preparation of the three- and more ring liquid crystals and for those containing lateral substitutents other than a methyl group on cyclohexane, or benzene rings, or with the $CH_2CH_2$ bridge between cyclohexane and benzene rings. Three- and four-ring liquid crystals, which are very important components of wide temperature liquid crystal materials can be prepared using a Grignard [19,20], a cross-coupling [21-23], or Friedel-Crafts reactions [24]. However, a number of problems with these methods make it difficult to prepare derivatives of cyclohexylbiphenyl (4) and 4,4'-dicyclohexylbiphenyl (5) in high yield and without formation of by-products than can be difficult to remove from the product. Grignard reagents are difficult to prepare from 4-bromo-1-(trans-4-alkylcyclohexyl)benzenes and 4-bromo-4-substituted biphenyls. The synthesis of 4-(4-substituted phenyl)cyclohexanones and 4-(trans-4-substituted cyclohexyl)cyclohexanones from the corresponding 4-substituted benzylmethylketones [26], 4-substituted benzylcyanides [25], ethylene ketal of 1,4-cyclohexanedione [27,28], or from the adducts of the condensation of 2-chloro(ethoxy, formyloxy, trimethylsilyloxy)-1,3-butadienes with 4-substituted styrenes [29,30] all are long and produce low yields.

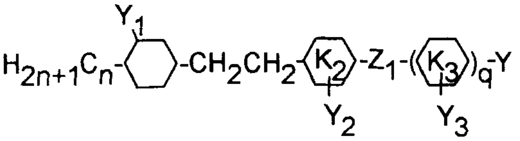
It should be noted that the nonselective reduction of phenylene fragments of different derivatives of biphenyl and bibenzyl using the Berch method has shown that this method can not be used for the preparation of the liquid crystalline derivatives of cyclohexenylbenzene, cyclohexylbenzene, 1-cyclohexenyl-2-phenylethane or 1-cyclohexyl-2-phenylethane [31]. Usually, the liquid crystalline derivatives of 1-cyclohexyl-2-phenylethane, or 1-cyclohexyl-2-biphenylethane (6) are synthesized using a not so simple Friedel-Crafts acylation of the corresponding aromatic compounds by trans-4-alkylcyclohexylacetyl chlorides and than conversion of the ketones in several steps to the product [32].



(4)



(5)



(6)

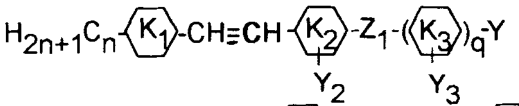
n,m = 2-7; $K_2$,$K_3$ = benzene or cyclohexane;

$Y_1$= H, $CH_3$; $Y_2$,$Y_3$ = H, F,CI,$CH_3$; q = 0,1;

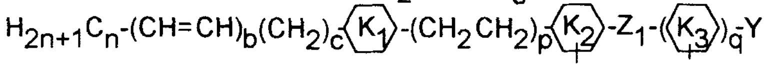
Y = alkyl, alkoxy radicals, F, CI, CN, NCS, $CF_3$, $OCF_3$, $OCHF_2$,$OCF_2CI$, or additionally some cyclic fragments with alkyl or alkoxy radicals, or the polar groups;

$Z_1$ = single bond or bridge fragment.

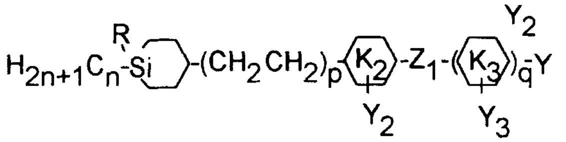
The same problems (difficulty in preparing the starting materials) are also characteristics of the preparation of the following liquid crystals: tolanes (7) [33,34]; derivatives of alkenylcyclohexane (8) containing a double bond in different positions of an alkenyl tail [35-37]; compounds containing a ring silicon atom (9) [38-40] having a lower crystal to nematic transition temperature than the corresponding liquid crystalline derivatives of cyclohexane; and some heterocyclic compounds, having a very high positive dielectric anisotropy, such as the derivatives of 1,3,2-dioxaborinane (10) [41-43].



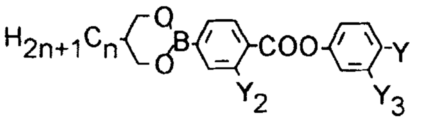
(7)



(8)



(9)



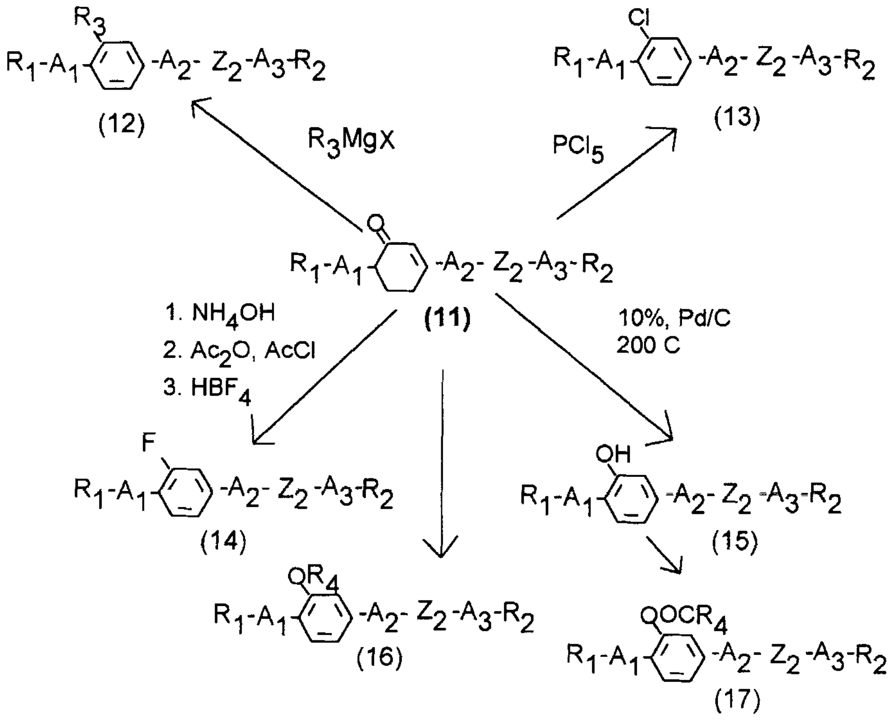
(10)

$n =$ 0-10; $K_1,K_2,K_3$ = benzene or cyclohexane;
$R = H, CH_3$; $Y_2,Y_3 = H, F, Cl, CH_3$; $b = 1$; $c, p, q = 0$ or 1;
Y = alkyl, alkoxy radicals, F, Cl, CN, NCS, $CF_3$, $OCF_3$, $OCHF_2$, $OCF_2Cl$;
$Z_1$ = single bond or a bridge fragment.

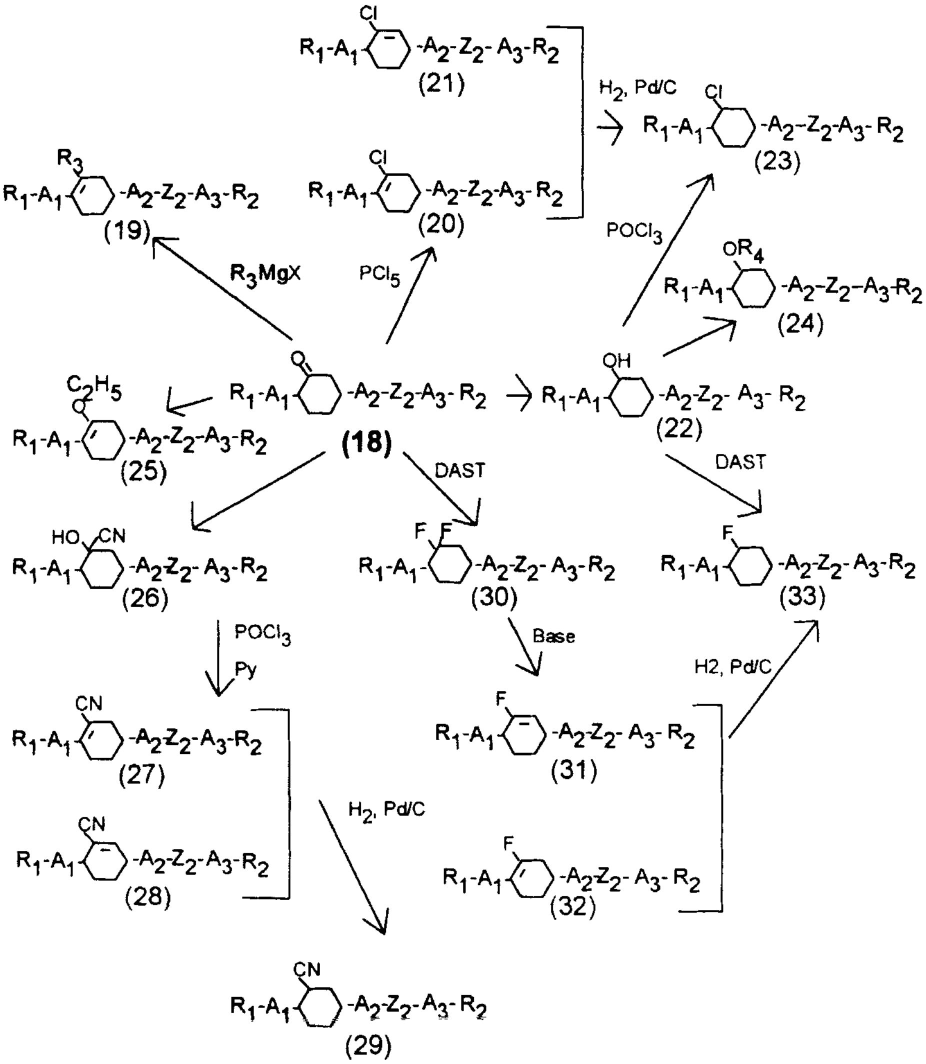
Taking into account that the cyclohexenones can be used as intermediates for the preparation of the corresponding LC derivatives of cyclohexane [44-47] and other liquid crystals [48], we proposed to use non-mesomorphic or mesomorphic 3,6-(2,5)-disustituted cyclohex-2-enones (11) and other analogous cyclic ketones as the main intermediates for the preparation of different types of liquid crystalline compounds [48]. Using these ketones, it is possible, in a few steps to synthesize the following compounds:

1. Different benzene derivatives without lateral substituents (12, $R_3$ = H) or containing lateral fluoro (14) or chloro (13) atoms, alkyl (12, $R_3$ = alkyl radical) or alkoxy (16) tails, hydroxy (15) or alkanoyloxy (17) fragments (see Scheme 1).

2. Different cyclohexanones (12), and after their modification, different LC derivatives of cyclohexene or cyclohexane without lateral substituents (19, $R_3$ = H) or containing lateral gem-difluoro (30), fluoro (31,32,33) or chloro (20, 21,23) atoms, alkyl (19, $R_3$ = alkyl radical) or alkoxy (24,25) tails, cyano (27, 28, 29) group or alkanoyloxy fragment (24) (see Scheme 2).

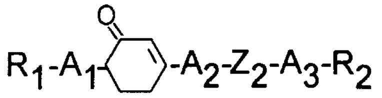


Scheme 1


(18)
(19)
(20)
(21)
(22)
(23)
(24)
(25)
(26)
(27)
(28)
(29)
(30)
(31)
(32)
(33)
R3MgX
PCl5
H2, Pd/C
POCl3
DAST
DAST
POCl3
Py
Base
H2, Pd/C
H2, Pd/C

Scheme 2
2

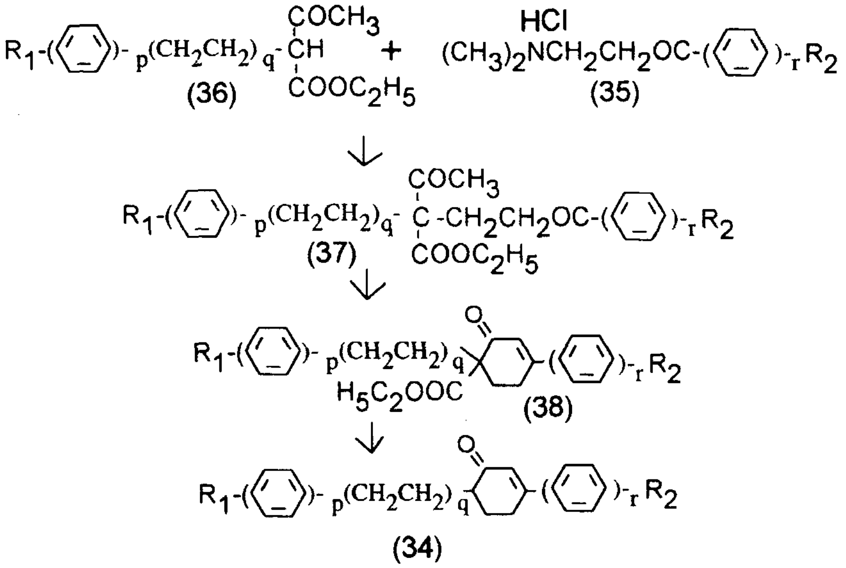
The liquid crystalline 3,6-disubstituted cyclohex-2-enones (11) can be expressed by the following formula:


(11)

wherein $R_1$ is alkyl radical or alkylalkoxy radical; the terminal group $R_2$ is hydrogen or a alkyl, alkoxy radicals, or halogen atoms, other group without or with additional cyclic fragment; $A_1$, $A_2$, $A_3$ are single bond or benzene, or cyclohexane rings without or with bridge fragment.

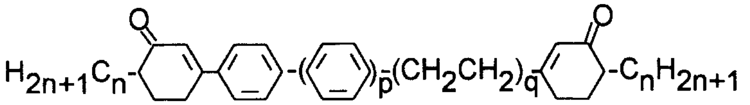
It is known that these substituted cyclohex-2-enones can be prepared by the condensation of aromatic aldehydes with acetoacetic ester or acetylacetone, by the interaction of some derivatives of cinnamic aldehyde or benzilidene acetone with acetoacetic ester, malonic ester or with acetyl acetone [49-52] or by the Michael's connection of vinylalkyl(aryl)ketones to some derivatives of benzylmethyl ketone or acetoacetyc ester to acetylacetone, and followed by cyclization in the presence of a base [54-58]. Other methods are the condensation of the derivatives of acetophenone and vinylalkylketones in the presence of the strong bases ($Bu^tOK$), or with the replacment of the nitro group on the ring by a ketogroup using the Nef's method [59]. These methods allow for the preparation of the different cyclohexenones in high yield from the simple starting materials and in only a few steps.

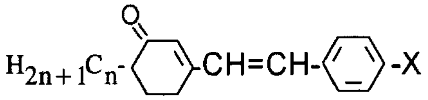
We found that the 3-arylcyclohex-2-enones, 3-aryl-6-alkylcyclohex-2-enones, 3-aryl-6-(2-phenylethyl)cyclohex-2-enones (34) are formed in yields of 70-80% by the condensation of the hydrochlorides of the 4-substituted β-N-dimethylaminopropiophenones (Mannich's salts) (35) with acetoacetic, 2-alkylacetoacetic or 2-(2-phenylethyl)-acetoacetic esters (36) in the presence of potassium carbonate, alkali hydroxide and benzyl trimethylammonium chloride or other phase catalysts in boiling solvents (isopropyl alcohol, diglyme, dioxane) [48, 60-62].

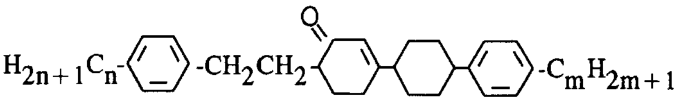


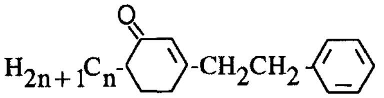
$R_1$ = alkyl, alkoxy radicals; $R_2$ = alkyl, alkoxy radicals
F, Cl, Br, CN, $OCF_3$; p, q, r = 0 or 1.

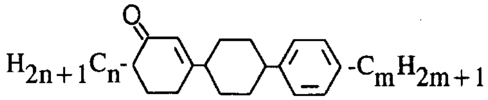
The interaction of the hydrochlorides of 4,1-bis-(4-substituted β-N-dimethylaminopropionyl)benzene, 4,4-bis-(4-substituted β-N-dimethylaminopropionyl)biphenyl and dibenzyl (38), or the hydrochlorides of 4-substituted styryl-β-N-dimethyaminoethylketones (39), the Mannich salts prepared from methylalkylketones, methyl trans-4-alkylcyclohexylketones, methyl(trans-4-phenylcyclohexyl)ketones, methyl-2-arylethylketones (40), or 2-chloro(bromo)ethylaryl(alkyl)ketones (41) with the 2-substituted acetoacetic esters (36), 4-substituted benzylmethylketones (42), esters of α-acetyloxalic, α-glutaric acids and 2-(2-cyanoethyl)acetoacetic ester (43) gives 1,4-bis-(6-alkylcyclohex-2-enonoyl-3)-benzenes, 4,4-bis-(6-alkylcyclohex-2-enonoyl-3)biphenyls and bibenzyls (44), corresponding 3-(4-substituted styryl)-6-alkylcyclohex-2-enones (45), 3-(trans-4-substituted cyclohexyl-1)-6-[2-(4-substituted phenyl)ethyl]cyclohex-2-enones (46), 3-[2-(4-substituted phenyl)ethyl]-6-alkylcyclohex-2-enones (47), 3-(trans-4-substituted cyclohexyl-1)-6-alkylcyclohex-2-enones (48), 3-(trans-4-alkylcyclohexyl-1)-6-(4-substituted phenyl)cyclohex-2-enones (49), 3-(4-substituted phenyl)-6-(4-substituted phenyl)cyclohex-2-enones (50), 3-(4-substituted phenyl)-6-(2-cyanoethyl)cyclohex-2-enones (51), 3-(4-substituted phenyl)-6-carbalkoxymethylcyclohex-2-enones, 3-(4-substituted phenyl)-6-(2-carbalkoxyethyl)cyclohex-2-enones (52) in a yield between 50-80% [48, 60-62].


(44)

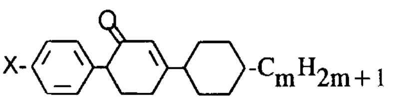

(45)

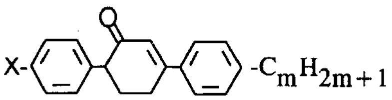

(46


(47)

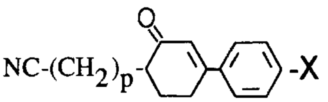

(48)

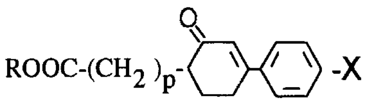
n, m = 1-5; X = H, Cl, $OC_mH_{2m+1}$.


(49)


(50)

X = H, Cl, $OC_nH_{2n+1}$, $OC_nH_{2n+1}$ n, m = 1-5;

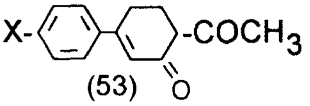

(51)

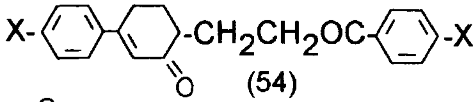

(52)

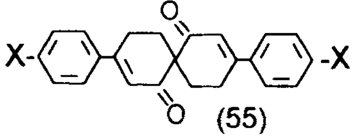
X = H, Cl, $C_mH_{2m+1}$ $OC_mH_{2m+1}$, p = 1, 2; R = H, $CH_3$.

Similar products are also formed from the reaction of hydrochlorides of 4-substituted β-N-dimethylaminopropiophenones (35) with acetylacetone resulting in: 6-aryl-3-acetylcyclohex-2-enones (53), 3-(4-substituted phenyl)-6-[1-(4-substituted phenyl)-

propanoyl-3] cyclohex-2-enones (54) and spirobi-3-(4-substituted phenyl)-6-cyclohex-2-enones (55) [63].

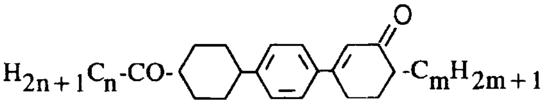

(53)

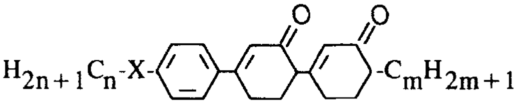

(54)

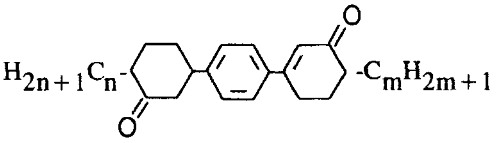

(55)

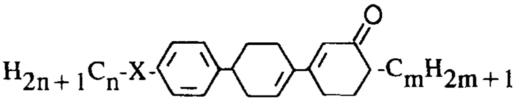
$X = H, Cl, C_mH_{2m+1}\ OC_mH_{2m+1}, C_6H_{10}C_mH_{2m+1}$ , $m = 3\text{-}6$;

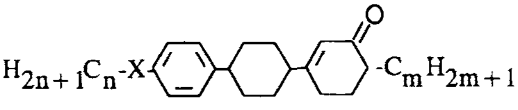
Thus, the obtained results show that the condensation of the Mannich salts (35) or 2-chloro(bromo)ethylaryl(alkyl)ketones (41) with 2-substituted acetoacetic esters (36), 4-substituted methylbenzylketones (42), or with other analogous ketones and β-dicarbonylic compounds leads in a short and simple way to the formation of different mesomorphic cyclohexenones, which can be expressed, for example, by the following general formulas (56-61) [62]:

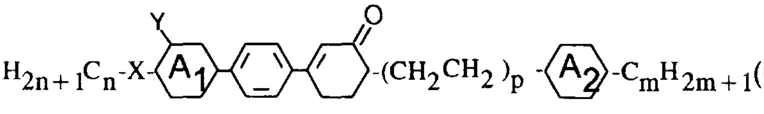

(56)


(57)


(58)


(59)


(60)

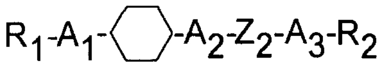

(61)

n, m = 1 -10; $A_1$, $A_2$ = benzene, cyclohexane; p = 0 or 1;
X = single bond, O; Y = H, Cl, F, $CH_3$.

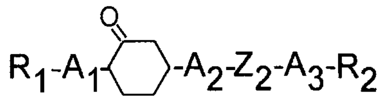
These cyclohexenones can be transformed into both well-known and new liquid crystalline compounds.

Our preliminary investigations have shown that :

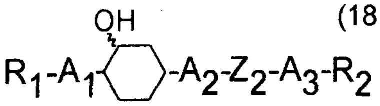
1. Catalytic reduction of the cyclohexenones (11) in the presence of palladium on carbon or other catalysts in basic or acid media leads to the formation in one step to the corresponding LC cyclohexane (62), cyclohexanone (18), or cyclohexanol (22) derivatives of the following formulas [64]:



(62)

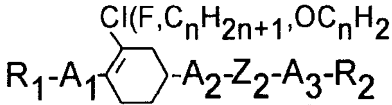


(18)

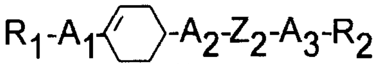


(22)

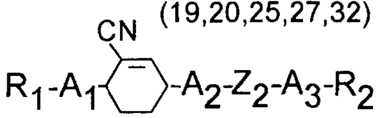
2. The interaction of the cyclohexanones (18) with different reagents results in the LC gem-difluorocyclohexane (30), cyclohexene (19), halogenocyclohexene (21,22,31,32), cyanocyclohexene (27,28) derivatives of the following formulas [48,22] :



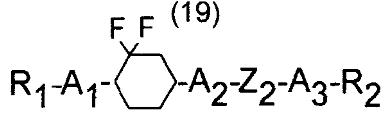
(19,20,25,27,32)



(19)

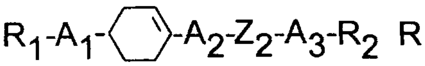


(28)

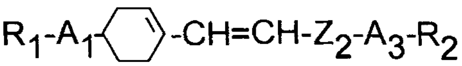


(30)

3. The Wolf - Kishner reaction [65] makes possible the synthesis of the cyclohexene derivatives (63) with various double bond ring positions from the cyclohexenones (11) and the preparation of the styrylcyclohexenes (64) from the styrylcyclohexenones (45). These ketones (45) can be used as the starting compounds for the synthesis of the LC Diels-Alder adducts or LC polymer materials [65].

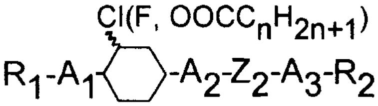


(63)

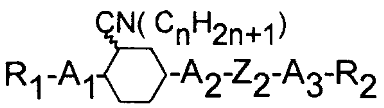


(64)

4. The interaction of the cyclohexanoles (22) with different reagents leads to the formation of the corresponding LC halogencyclohexanes (23,33) or esters (24) [66]. The LC derivatives of cyclohexane containing a lateral cyano group (29) or alkyl tail (19) can be prepared by the catalytic reduction of the corresponding unsaturated compounds (19,27,28).

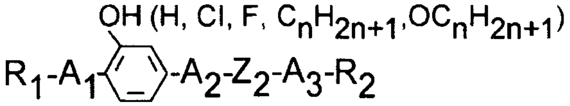


(23,24,33)



(29)

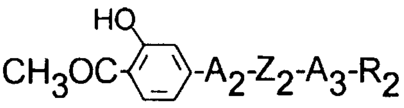
5. The aromatization of the cyclohexenones (11) and their further modification results in polycyclic LC compounds (different derivatives of biphenyl, terphenyl, quaterphenyl and other) containing lateral hydroxy group (15) or alkyl (12), or alkoxy (16), or alkanoyloxy (17), or chloro (13) and fluoro (14) atoms [67,68].



(12-17)

It should be noted that using this process and some additional chemical reactions, it is possible to prepare compounds containing more than one hydroxy group which can be used for the synthesis of the LC polyesters.

4-Substituted 2-hydroxyacetophenones (65) can be used for the preparation of the LC



(65)

azomethines which can form different metal complexes or heterocyclic LC dyes [69].

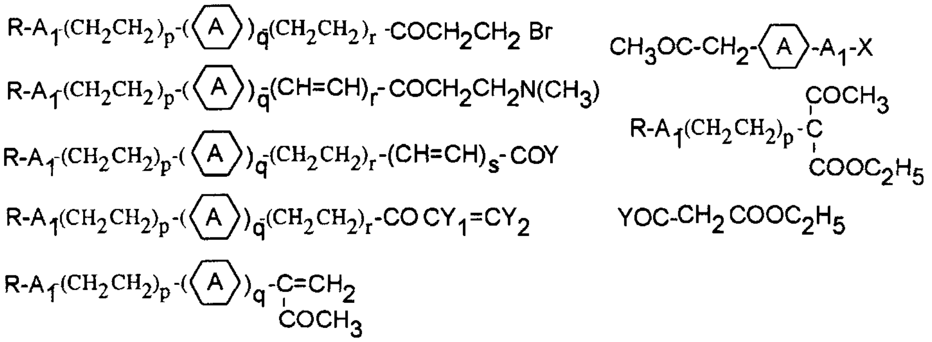
6. Nonchiral and chiral, nematic and smectic LC compounds with low viscosity, positive or negative dielectric anisotropy, wide mesomorphic ranges can be synthesized from the cyclohexenones (34,59-61) depending on the chemical structure of the starting Mannich salts (35, 38-40) and 2-substituted acetoacetic esters (36) or other analogous (42) compounds. Our last results have shown that this technology makes possible the preparation of the LC chiral cyclohexenones with modifications having wide temperature range smectic C phase, for example from 10 to 60-80°C.

7. The Mannich salts containing one and more cyclic fragments can be used for the preparation lyotropic LC materials and Langmuir-Blodgett films [70]. Also it is possible to use the policyclic cyclohexenones containing hydroxy or carboxy fragments for the same purpose.

8. The vinyl ketones, which can be prepared from the corresponding Mannich salts, some cyclohexenones (45) and the products of their transformations (64) containing double bonds in the end fragments or other parts of the molecule can be used for the preparation of the LC polymer materials.

Thus, as investigations have shown [48, 60-69, 71-74] that the cyclohexenones are very promising intermediates for the preparation of different types of liquid crystals.

And additionally, our investigations have shown that the following compounds can be used as starting materials for the preparation of the above mentioned liquid crystals [60-65, 67-69].



R = alkyl radical, halogen atoms; A, $A_1$ = benzene, cyclohexene, cyclohexane; p, q, s = 0,1; $Y_1$ $Y_2$ = H, $CH_3$; Y = alkyl radical.

## CONCLUSION

In this work, both well-known and new synthetic methods for the preparation of liquid crystals have been discussed. These new synthetic methods contribute greatly to the enlargement of our knowledge of the liquid crystal synthesis chemistry.

## REFERENCES

1. D.Demus, H.-J.Deutcher, F.Kuschel, and H.Schubert, DOS No. 24 29 093 (1975),
2. H.-J. Deutcher, B. Laaser, and H.Schubert, J. prakt.Chem., 320, p.1991 (1979),
3. M.A.Osman, Mol.Cryst.Liq.Cryst. 82, p.47, (1982),
4. L.A.Karamysheva, E.I.Kovshev, and M.I.Barnik, Mol.Cryst.Liq.Cryst. 37, p.29,(1976),
5. V.S. Bezborodov, J.Org.Chem (Rus.), 23, p.1268, (1987),
6. R.Eidenschink, J.Krause, L.Pohl, and I.Eichler, in Liquid Crystals, edited by S.Chandrasekhar, p. 515 (1980).
7. J.Krause, R. Eidenschink, L.Pohl, US Pat 4 229 315 (1978),
8. V.S.Bezborodov, and V.I.Lapanik, Liquid Crystals, 11, p.385 (1992),
9. L.A.Karamysheva, K.V.Roitman, I.F.Agafonova, S.I.Torgova, R.Kh.Geyvandov, V.F.Petrov, M.F.Grebyonkin, V.S.Bezborodov, N.P.Andryukhova, and N.A.Bumagin, Mol.Cryst.Liq.Cryst., 191, p.259, (1990),
10. V.S.Bezborodov, V.A.Konovalov, V.I.Lapanik, and A.A.Minko, Liquid Crystals, 4, p.209 (1989),
11. V.S.Bezborodov, V.A.Konovalov, and Yu.L.Ptashnikov, US Pat., 4 605 520 (1986),
12. H.Takatsu, K.Takeuchi, and H.Sato, Mol.Cryst.Liq.Cryst., 112, p.165 (1984),
13. V.S.Bezborodov, V.A.Konovalov, V.I.Lapanik, and Yu.L.Ptashnikov, J.Org.Chem (Rus.), 24, p.615, (1988),
14. V.F. Petrov, SPIE Proc., 2408, p.84 (1995),
15. V.F.Petrov, Liquid Crystals, 19, p.729, (1995),
16. C.D. Nenitzescu, and I.G.Gavat, Lieb. Ann., 519, p,260 (1935),
17. R.Eidenschink, D.Erdmann, J.Krause, L.Pohl, Andew.Chem., 89, p.103 (1977),
18. E.Poetsch, Kontakte (Darmstadt), 2, p,15 (1988),
19. Y.Goto, T.Ogawa, S.Sawada, and S.Sugomori, Mol.Cryst.Liq.Cryst., 209, p.1 (1984),
20. T. Kojima, and S. S.Sugomori, US Pat., 4 548 731 (1983)
21. N.Miyaura, T.Yanagi, and A.Suzuki, Synth.Commun., 11, p.513, (1981)
22. M.Hird, K.J.Toyne, A.J.Slaney, and J.W.Goodby, J.Mater.Chem., 5, p.423 (1995),
23. M.Bremer, Adv.Mater., 7, p. 303 (1995).
24. P. Balkwill, D.Bishop, A.Pearson, and I.Sage, Mol.Cryst.Liq.Cryst., 123, p.1 (1985),
25. E.D.Bergmann, S.Yaroslavsky, H.Weiler-Feilchenfeld, J.Am.Chem.Soc.,

81, p.2775 (1959),

26 E.C.Horning, M.G.Horning, M.S. Fish, M.W.Rutenberg, J.Am.Chem.Soc., 74, p.773 (1952),

27. S.Matsui, Y.Goto, E.Nakagawa, and S.Sawada, EP, 0 675 187 (1995)

28. M.Petrzilka, and A. Germann, Mol.Cryst.Liq.Cryst., 131, p.327 (1985),

29. A.A.Petrov, J.Gen.Chem. (Rus), 11, p.661 (1941),

30. A.A.Petrov, and I.P.Sopov, J.Gen.Chem. (Rus), 17, p.1295 (1947),

31. L.A.Wiles, Chem.Rew., 56, p.329 (1956).

32. H.Takatsu, K.Takeuchi, and H.Sato, Mol.Cryst.Liq.Cryst., 108, p.157 (1984),

33. H.Takatsu, K.Takeuchi, Y.Tanaka, and M.Sasaki, Mol.Cryst.Liq.Cryst., 141, p.279 (1986),

34. R.Bucheker, G.Marck, and M.Schadt, Mol.Cryst.Liq.Cryst., 260, p.93, (1986),

35. M.Petrzilka, Mol.Cryst.Liq.Cryst., 131, p.109 (1985),

36. M.Schadt, M.Petrzilka, P.R.Gerber, and A.Villiger, Mol.Cryst.Liq.Cryst., 122, p.241 (1985),

37. S.M.Kelly, A.German, and M.Schadt, Liquid Crystals, 16, p. 491 (1994),

38. T.Kinsho, T.Shimizu, T.Ogihara, T.Kaneko, and M.Nakashima, EP 682031 (1995),

39. T.Ogihara, T.Shimizu, T.Kinsho, T.Kaneko, and H.Kurihara, EP 665232 (1995),

40. M.Nakashima, T.Shimizu, T.Ogihara, , T.Kinsho, T.Kaneko, and H.Kurihara, EP 670322 (1995),

41. V.S.Bezborodov, and V.I.Lapanik, Liquid Crystals, 10, p. 803 (1991),

42. V.S.Bezborodov, O.A.Grinkevich, M.F.Grebenkin, V.I.Lapanik, A.A.Minko, V.V.Rzheussky, A.A.Muravsky, V.F.Petrov, and A.V.Ivaschenko, US Pat., 4 853 150 (1989),

43. R.Dabrowski, V.S.Bezborodov, V.I.Lapanik, J.Dziaduszek, and K.Czuprynski, Liquid Crystals, 18, p. 213 (1995),

44. W.Sucrow, and H. Wolter, Chem.Ber., 119, p.387 (1986)

45. S.M.Abdullah, J.Ind.Chem.Soc., 12, p.62 (1935),

46. F.C.Novello, M.E. Christy, and J.M.Sprague, J.Am.Chem.Soc., 75, p.1330 (1952),

47. W.Sucrow, D.Fiedel, E.Poetsch, and G.Radecker, DE 38 27 675 (1989),

48. V. Bezborodov, and R.Dabrowski, SPIE, 2372, p.242 (1994),

49. W.T.Smith, and D.S.P.Eftax, J.Org.Chem., 21, p.174 (1956),

50. G.V.Krystal, V.V.Kulganek, V.F.Kucherov, and L.A.Yanovskaya, Synthesis, p.107, (1979),

51. G.N.Walker, J.Am.Chem.Soc., 77, p.3664 (1955),

52. J.Golonge, and J.P.Kehlstadt, Bull.Chem.Soc. (Fr), p.504 (1955),

53. R.N.Lacey, J.Chem.Soc., p.1625 (1960),

54. R.M.Dodson, and P.Sollman, J.Am.Chem.Soc., 73, p.4197 (1951),

55. G.Palazzo, and L.Baiocchi, Tetrahedron Lett., p. 4739 (1968),

56. M.W.Partrigde, H.J.Vipond, J.Urwin, and J.S.Nicholson, GB 1 265 800 (1972),

57. E.C. du Feu, F.J.McQuillin, and R.Robinson, J.Chem.Soc., p.53 (1937),

58. A.M.Dounes, N.S.Gill, and F.Lions, J.Am.Chem.Soc., 72, p. 3464 (1950),

59. W.C.Wildman, R.B.Wildman, W.T.Norton, and J.B.Fine, J.Am.Chem.Soc., 75, p. 1912 (1953),

60. V.S.Bezborodov, V.A.Konovalov, Yu.L.Ptashnikov, L.A.Karamysheva, K.V.Roitman, and A.V.Ivaschenko, Rus.Pat., 1 793 723 (1986),
61. V.S.Bezborodov, V.A.Konovalov, Yu.L.Ptashnikov, A.A.Minko, L.A.Karamysheva, K.V.Roitman, and A.V.Ivaschenko, Rus.Pat., 1 793 684 (1986),
62. V.S.Bezborodov, R.Dabrowski, D.Trochimiec, J.Dziaduszek, G.Sasnovski, and V.I.Lapanik, Polish Pat., 304 749 (1994),
63. V.S.Bezborodov, and D.V.Silenko, Summer European LCC, Abstracts, Vilnius, 1, p.41 (1991)
64. V.S.Bezborodov, and D.Trochimiec, J.Org.Chem (Rus.), 27, p.1958, (1991),
65. V.S.Bezborodov, The 13th ILCC, Canada, Abstracts, 2,p.468 (1990),
66. J.W.Gooby, K.J.Toyne, M.Hird, and S.J.Lock, PCT Int.Appl., WO 96 00, 710 (1996).
67. V.S.Bezborodov, V.M.Kondratenkov, V.I.Lapanik, and D.A.Trokhimets, Liquid Crystals, 10, p.799 (1991),
68. V.S.Bezborodov, R.Dabrowski, J. Dziaduszek, K.Czuprynski, and Z.Raszewski, Liquid Crystals, 20, p.1 (1996),
69. V.S.Bezborodov, and D.V.Silenko, The 14th ILCC, Italy,Abstracts, 1, p.88 (1992),
70. N.D.Stepina, R.V.Tal'roze, T.L.Lebedeva, L.G.Yanusova, V.S.Bezborodov, Polymer Science, 35, p.184 (1993).
71. Jap.Pat. 62 185 036 (1987), Chem.Abstracts, 108, 131286u (1988),
72. Jap.Pat. 63 203 634 (1987), Chem.Abstracts, 110, 75026m (1989),
73. R.Brettle, D.A.Dunmur, L.D.Farrad, N.J.Hindley, and C.M.Marson, Chem.Lett., p.1663 (1993),
74. R.Brettle, D.A.Dunmur, L.D.Farrad, and C.M.Marson, J.Mater.Chem., 6, p.747 (1996).

## ACKNOWLEDGEMENTS

We would like to thank V.F.Petrov (Samsung Electronics Co., Ltd) for very helpful discussions.