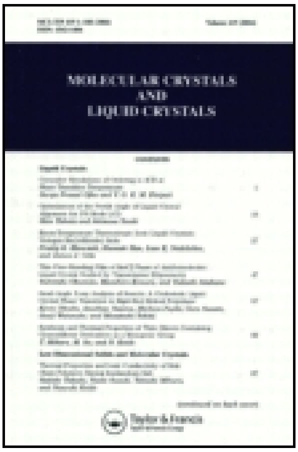

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Some Developments in the Synthesis of Liquid Crystal Materials

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Some Developments in the Synthesis of Liquid Crystal Materials†

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Advances in fields such as the applications, the physics, or the theory of liquid crystals depend very critically upon the organic chemist and his role in synthesising materials that, at the one extreme, are novel and imaginative enough to exhibit new and challenging phases or sequences of phase behaviour, or at the other extreme, have preselected molecular structures tuned to make some new application possible or to test some theory.

A conference lecture of this kind provides a convenient opportunity to stress the importance of the organic chemist's role and to illustrate how his artistry is brought to bear in solving a range of materials problems.

Several areas of progress are reviewed and used to illustrate how the development of new synthetic methods and reagents is enhancing the chemist's ability to respond to the needs of the liquid crystal community for highly pure compounds of growing structural complexity that have increasingly exacting physical properties and are frequently, today, also chiral and totally optically pure.

One particularly important area is highlighted. This refers to developments in cross-coupling reactions, whereby routes to complex linear structures have been perfected and allow small manageable units, e.g., benzene derivatives in which substituents destined to be lateral groups are pre-positioned, to be used as the synthetic precursors that are then linked together in a convergent manner by palladium-catalysed processes and under conditions that are tolerant of many functional groups that may be wanted in the finished molecules.

By such and other means, many mesogenic compounds that could only have been synthesised a few years ago by impossibly low yield processes, are now readily and economically available for study or applications.

1. CHIRAL MATERIALS

Work in this field has been much stimulated by recent needs for ferroelectric and electroclinic materials. The chiral centre has often been introduced into mesogenic molecules in the form of common, naturally accessible end groups such as 2-

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†Presented at the 13th International Liquid Crystal Conference, Vancouver, 1990.

methylbutyl, 3-methylpentyl, 4-methylhexyl, 2-octyl, or terpenoid ester functions, or by the use of core chiral units such as lactates or mandelates. Relative exhaustion of these easy approaches has since led to the use of readily synthesised chiral functions such as those in:

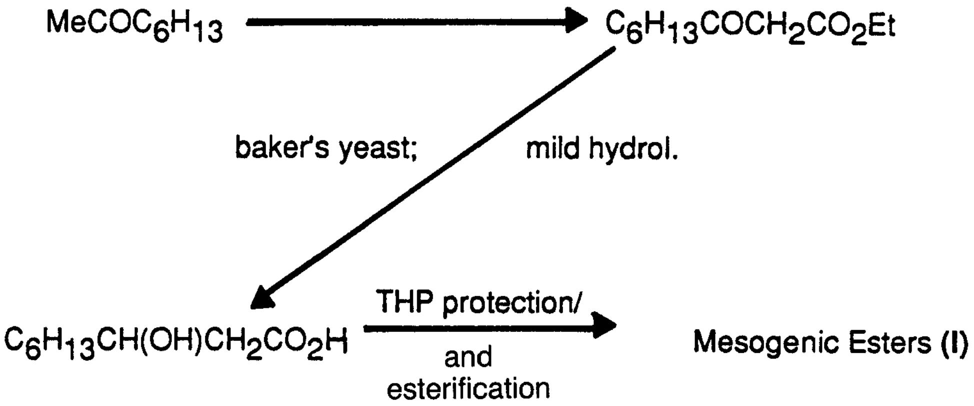
2-Chloropropyl esters	—$COOCH_2CHClMe$
Cyanohydrin esters	—$COOCH(CN)R$
Cyano- and chloro-alkanoates	—$OOCCR_1R_2(CN\text{ or }Cl)$

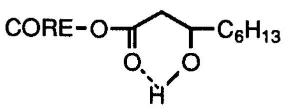
or the newer:

Fluoroalkyl compounds	—$(CH_2)_2CHFC_6H_{13}$
Compounds with substituted 2-hydroxypropyl groups	—$CH_2CHMeO(Me\text{ or }COR)$
Fluoroalkyl esters[1]	—$COOCHFR$
2-Fluoroalkanoates[2]	—$OOCCHFR$

Future developments must however depend upon methods for separation of optical enantiomers or new stereoselective synthetic routes for the production of novel chiral materials for the LC field. Happily, there is much activity amongst chemists in the field of stereospecific synthetic methods, and application to LC materials should yield interesting new systems. This is aready occurring, and three cases may be quoted.

(a) **Use of a natural yeast** to effect chiral reduction of a ketone

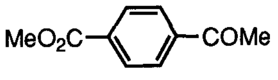




(I)

Some of these esters[3] of (R)-3-hydroxynonanoic acid, wherein the chiral centre is part of a ring formed by intramolecular hydrogen bonding, exhibit S_C phases with ferroelectric properties.

(b) **Use of synthetic chiral reducing agents.** For example, reduction of **(II)** with BH_3 in the presence of Corey's chiral catalyst,[4] followed by propylation of the -OH group and hydrolysis of the ester function yields[5] (R)-**(III)** with an 89% ee and reduction of **(IV)** with H_2/100 atm/room temp.



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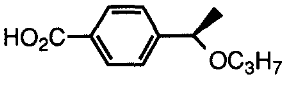

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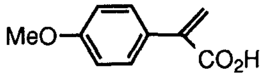

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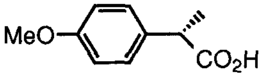


(V)

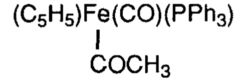
in the presence[6] of Ru[(R-) or (S-) bis(diarylphosphino)-1,1′-binaphthyl] $(OCOMe)_2$ gives, e.g., (S)-**(V)** with a 92% ee. Acids **(III)** and **(V)** were elaborated into LC materials, but Ps values were only about the same as those for ArOCHMeR or $ArCO_2CHMeR$ systems.

(c) **Approaches using chiral IRON ACYLS.** For the LC field, the significance of the work of S. G. Davies *et al.*[7] at Oxford in effecting reactions with a very high stereoselectivity using iron acyl complexes has been recognised by Toyne at Hull University where possibilities are being explored.

Davies's work has centred on the use of the iron acyl auxiliary **(VI)** which may be converted into iron acyl complexes, e.g., **(VII)**. These complexes are available commercially (BP Chemicals, UK) in both chiral forms and as the racemate.

$[(C_5H_5)Fe(CO)(PPh_3)]$

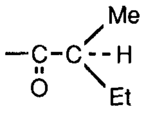
(VI)



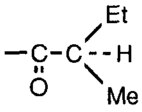
$$\underset{\displaystyle COCH_3}{(C_5H_5)\underset{|}{Fe}(CO)(PPh_3)}$$

(VII)

The acyl complexes are configurationally stable and unaffected by air, and so are easy to handle/store. The significant point is that the acyl function gives all common reactions of the group, e.g., enolate alkylations, aldol condensations, Michael additions etc., but with a very high stereoselectivity (better than 3000:1). For example, treatment of the acetyl complex (—$COCH_3$) with BuLi followed by Mel gives —$COCH_2Me$, which on treatment with (i) BuLi, (ii) Etl gives **(VIII)** in an optically pure state. Use of the other enantiomeric acetyl complex or reversal of the Mel/Etl sequence above gives the other enantiomer **(IX)**.

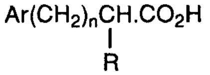


(VIII)



(IX)

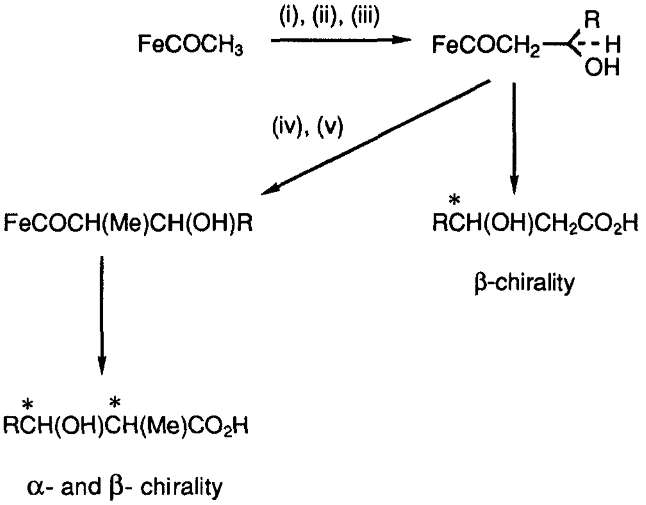
The chiral auxiliary can then be removed by use of Br_2, I_2, Ce^{IV} or Fe^{III} in the presence of water, alcohols or amines giving carboxylic acids, esters or amides respectively. Acids such as (**X**), of obvious relevance to the LC field, can therefore be made with chosen chirality and high optical purity.



$$\underset{\displaystyle R}{\mathrm{Ar(CH_2)_nCH.CO_2H}}$$

(X)

Significantly too, the sequence of transformations in Scheme 1 can be effected *via* a diethylaluminium enolate and aldol condensation, generating first β-chirality, followed if desired by alkylation, so generating additional α-chirality.



(i) BuLi; (ii) Et_2AlCl; (iii) RCHO; (iv) BuLi; (v) MeI

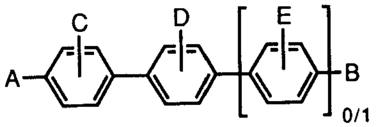
Scheme 1

Chiral sulphoxides[8] and chiral liquid crystalline sulphoxides[9] may also be made more readily accessible, since enantiomerically pure sulphoxides can also be obtained[7] using chiral iron acyls.

2. PALLADIUM CATALYSED COUPLING PROCESSES

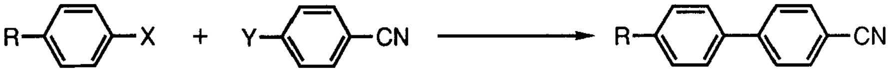
Perhaps the most significant influence upon the facile synthesis of LC materials has arisen through the application of Pd-catalysed coupling processes for linking together aryl groups (sp^2-sp^2) and also for other types of carbon-carbon coupling (sp^2-sp, sp^2-sp^3, sp^3-sp^3).

Considering first aryl-aryl coupling in the context of a typical biphenyl or terphenyl with A/B end groups and lateral substituents required to tune physical parameters.



The LINEAR APPROACH to the synthesis starting with biphenyl, $n = 0$ (terphenyl, $n = 1$) precursors is long and often impossible except say in simple cases such as the preparation of a 4-alkyl-4′-cyanobiphenyl-three steps: (i) 4′-acylation of 4-bromobiphenyl, (ii) reduction of the carbonyl group, (iii) cyanation of the bromo-substituent.

The CONVERGENT APPROACH to the synthesis might be through the direct linkage of the two rings as shown in Scheme 2.



Scheme 2

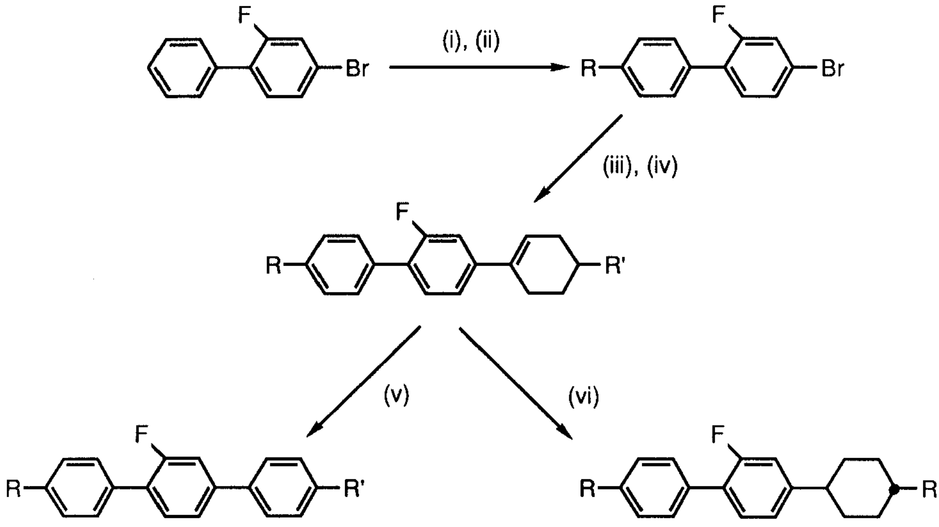
Although this may not be an economically viable route to an alkylcyanobiphenyl, this approach offers great advantages with more complex biphenyls/terphenyls, often making them synthetically available when impossible to make by the linear approach.

Earlier Methods for Aryl-Aryl Coupling

(a) The procedure shown in Scheme 3 is long and its scope is limited by the availability of the precursor biphenyl and cyclohexanone.

(b) Nickel-Phosphine Catalysed Grignard Coupling

For example, a coupling between compounds (**XI**) and (**XII**) may be achieved in the presence of $Ni(Ph_2P(CH_2)_3PPh_2)Cl_2$/THF. Yields are not high and purification problems are not made easier by the occurrence of some homocoupling (<10%) giving the quaterphenyl.



(i) acylation; (ii) reduction;

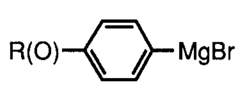
(iii) Mg, 4-alkylcyclohexanone;

(iv) dehydration;

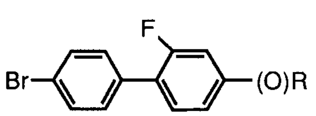
(v) aromatisation;

(vi) H_2, epimerisation

Scheme 3



(XI)



(XII)

None the less, this procedure was used[10] to obtain a range of laterally monofluorinated terphenyls with terminal alkyl and/or alkoxy groups and first revealed the interesting LC properties of such materials.

(c) Attempts to use coupling between ArZnBr and aryl bromides using $Pd(PPh_3)_2Cl_2$/DIBAL—H were not successful. Intractable mixtures and the occurrence of homocoupling made it impossible to obtain pure products.

By contrast, the Pd catalysed sp^2-sp^2 cross coupling process using:

BORONIC ACIDS:

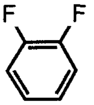
$$ArB(OH)_2 + Ar'Br/I \rightarrow Ar{-}Ar'$$

a procedure first reported by Miyaura *et al.*[11] is a highly effective procedure. The boronic acids are made as shown below:

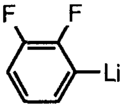
$$ArBr/I{-}(i), (ii), (iii) \rightarrow ArB(OH)_2$$

$$(i)\ Mg/THF;\ (ii)\ (i\text{-}PrO)_3B/THF/-78°C;\ (iii)\ 10\%\ HCl$$

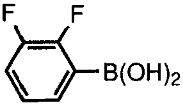
but a further crucial point, first appreciated by Toyne, is that lithiation can be achieved *ortho* to a ring fluorine (BuLi, THF. $< -60°C$), so enabling the transformation of, for example compound (**XIII**) into the boronic acid (**XV**)—by steps (ii) and (iii) above—*via* the lithio-derivative (**XIV**).



(XIII)

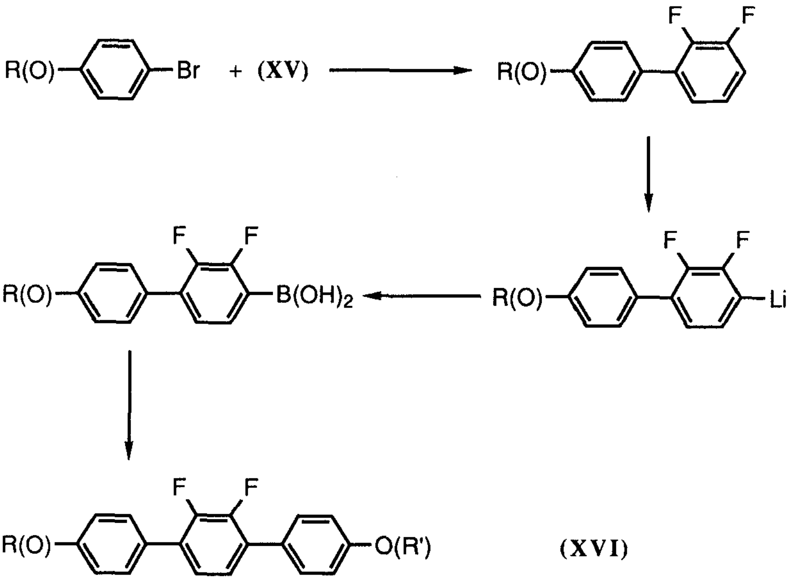


(XIV)

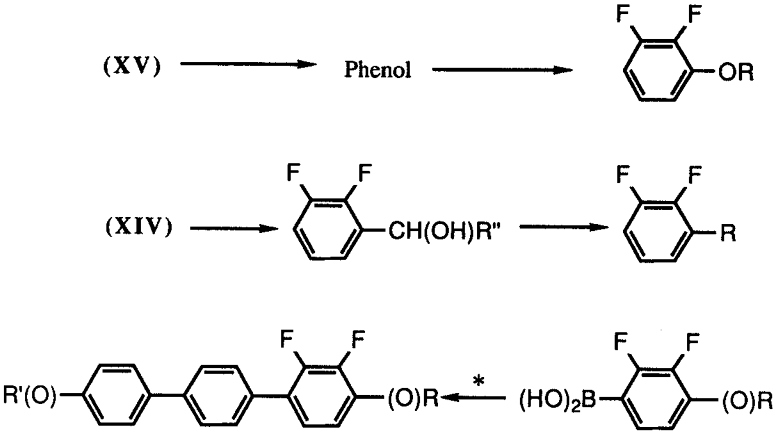


(XV)

These procedures can make available a wide range of difluoroterphenyls (**XVI**; **XVII**) with terminal alkyl and/or alkoxy end groups[12] as shown below.



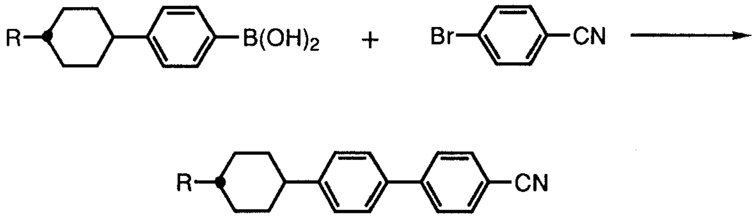
(XVI)



(XVII)

* using appropriate bromobiphenyl

It is clear that these processes have immense scope for adaptation/extension and for making available a host of di, tri- and poly-substituted biphenyls/terphenyls, e.g.,



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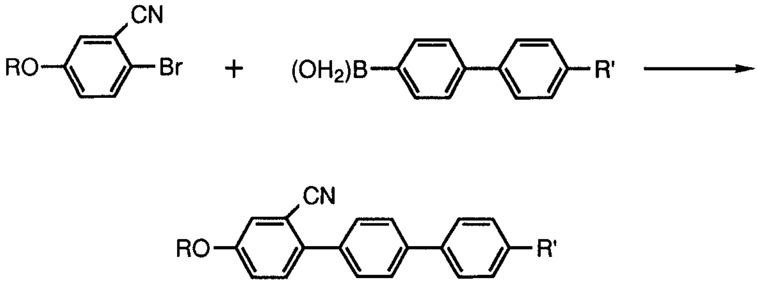


Important points now to be emphasised are the following:

(a) boronic acids are air and moisture stable, can be made in large quantities, and have a good shelf-storage capability;

(b) they need not be purified, but this is recommended unless hydrodeboronation (—$B(OH)_2$ to —H) is a problem;

(c) substituent restrictions are only those imposed by prevention of interference in Grignard or lithio-formation.

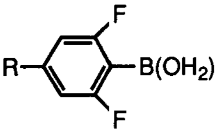
THE COUPLING PROCEDURE

$$ArB(OH)_2 + Ar'\text{-}LG \rightarrow Ar\text{-}Ar'$$

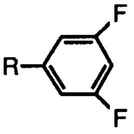
Where LG = Leaving Group = I, Br or OTf(Triflate)

The conditions originally reported are for a heteregeneous procedure—$Pd(PPh_3)_4$/benzene/EtOH/2M-Na_2CO_3/boil/24 hr—but recently Huth *et al.*[13] have developed homogeneous conditions using dimethoxyethane as the organic solvent, thereby bettering the yields from 70–75% to about 80%. The process is clean, NO homocoupling occurs, products are readily purified by crystallisation and many functional groups are tolerated.

The only problem concerns hydrodeboronation, particularly in the case of **(XVIII)** with which yields are bad (0–10%); homocoupling occurs and significant amounts of (**XIX**) can be isolated.



(XVIII)



(XIX)

With just one fluorine, the smaller problem of hydrodeboronation is eliminated by use of a 10–20% excess of the boronic acid, whereon yields return to 70–75%.

The coupling process can be extended to alkenyl boronic acids (again sp^2-sp^2 coupling), but NOT to alkynyl boronic acids (sp-sp^2).

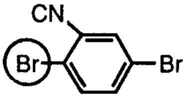
SELECTIVITY is an important factor[14] when more than one leaving group exists in a molecule: the order is then

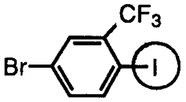
$$I > OTf > Br$$

but where these do not exist as pairs within a molecule, we find:

$$Br > OTf$$

For example, with a boronic acid $ArB(OH)_2$, the coupling sites in the molecules shown below are ringed, but of course in the products Ar—Ar′—Br, the remaining —Br is open to a second coupling. An excess of boronic acid should not therefore be used, or the triaryl, Ar—Ar′—Ar will be formed. None the less, yields up to 60% can be obtained for Ar—Ar′—Br. If in a crucial case, better yields are needed,





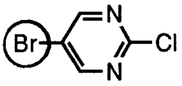
the following procedure using a triflate is recommended.

$$ArB(OH)_2 + 4\text{-}BrC_6H_4OMe \rightarrow ArC_6H_4OMe \rightarrow ArC_6H_4OH \rightarrow$$

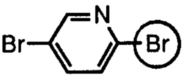
$$ArC_6H_4OTf \rightarrow ArC_6H_4Ar'$$

Note: Triflates, $ArOSO_2CF_3$ are made from the phenol ArOH by treatment with either (a) $(CF_3SO_2)_2O/Py/0°C$ or (b) $PhN(SO_2CF_3)_2/CH_2Cl_2/Et_3N/-78°C$ following literature procedures.

Reiffenrath *et al.*[15] at Merck, Darmstadt have also established useful selective couplings for heterocyclic systems, the coupling sites in **(XX)** and **(XXI)** again being ringed.



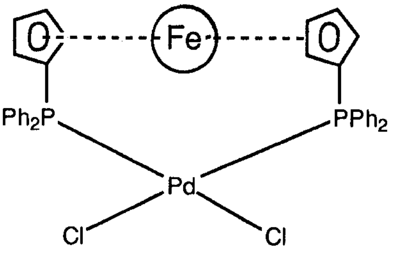
(XX)



(XXI)

OTHER CARBON-CARBON COUPLINGS

Up to now, only sp^2-sp^2 couplings (for Ar—Ar′ or Ar—CH=CHR) have been considered, using $(Pd(PPh_3)_4$ as the catalyst. For sp^2-sp^3 carbon-carbon couplings, elimination dominates (through metal abstraction) and prevents coupling. This would possibly be avoided by a faster transmetalation step and a ferrocene catalyst **(XXII)** first provided by Hayashi *et al.*[16] may meet this requirement.



(XXII)

The catalyst, dichloro-[1,1′-bis(diphenylphosphino)ferrocene] palladium II, abbreviated to $PdCl_2(dppf)$, has not apparently been tried with aryl boronic acids (only with catechol boranes[17]), but does avoid β-elimination in sp^3-sp^3 processes such as:

$$\text{s-Bu—MgBr or —ZnBr} + BrC_6H_5 \rightarrow \text{s-Bu—}C_6H_5$$

and has been applied by Castle and Widdowson[18] to sp^3-sp^3 couplings, e.g.,

$$Ph(CH_2)_3MgBr + C_6H_{13}I \rightarrow Ph(CH_2)_8CH_3\ (91\%)$$

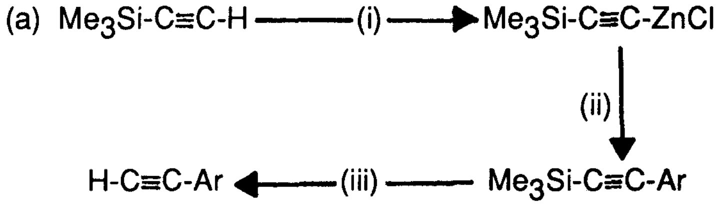
using $PdCl_2(dppf)$ reduced with DIBAL/THF.

Finally, it is mentioned that aryl triflates have been used[19] with organostannanes (R_3SnR') and $Pd(PPh_3)_4$ to obtain Ar—R′ (aryl-aryl, aryl-alkenyl, aryl-alkynyl and aryl-alkyl, i.e., sp^2-sp^2, sp^2-sp and sp^2-sp^3) couplings, but aryl-allyl is not effective (see however Reference 20, and Reference 21 is also relevant).

Carbon-carbon couplings have been nicely reviewed by Poetsch[22] and sp^2-sp couplings using alkynyl-ZnBr systems have been employed extensively recently in the LC field[23], i.e.,

$$R—C{\equiv}C—ZnCl + Ar'Br \qquad R—C{\equiv}C—Ar'$$

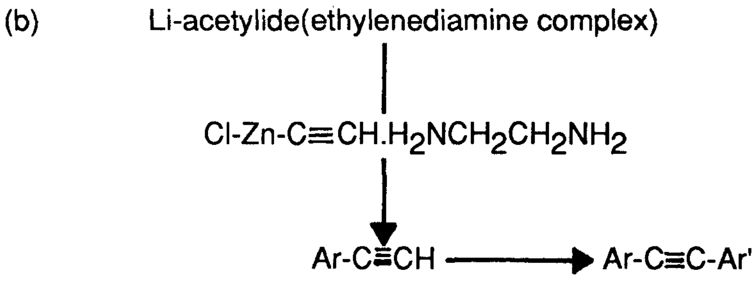
using the procedure originated by King and Negishi.[24] This may be used for both terminal and internal alkynes, e.g.,



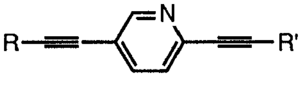
(i) BuLi/THF; $ZnCl_2$/THF

(ii) ArBr/I with $Pd(PPh_3)_4$/THF(room temp for I, boil for Br)

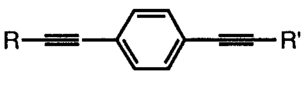
(iii) Deprotection



Triflates too can be used and in selective processes, selection is 100% (I > TfO > Br). Materials such as (**XXIII**) and (**XXIV**) are therefore made readily in two step processes, (**XXIII**) using 2,5-dibromopyridine and (**XXIV**) using 4-bromo-iodobenzene or the triflate of 4-iodophenol.



(XXIII)



(XXIV)

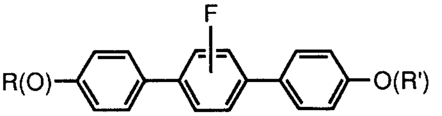
It should be noted that these reactions provide a convenient method of replacing an aromatic —OH by -alkyl (—OH to —OTf to —C≡C-alkyl to —CH_2CH_2-Alkyl) and triflates have recently provided chemists with two further useful synthetic flexibilities:

$$ArCN \leftarrow (i)—Ar—OTf—(ii) \rightarrow ArH$$

(i) $KCN/Ni(PPh_3)_4/60°C/MeCN$[25]
(ii) $Pd(OCOCH_3)_2/Et_3N/Ph_3P/HCO_2H$[26] (removal of —OH from ring)

3. SYNTHESIS AND PHYSICAL PARAMETERS

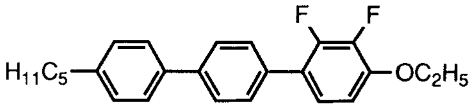
From what has gone before, it will be evident that newly developed synthetic methods have made available a wealth of novel materials, many with desirable physical parameters for applications. Sometimes the physical parameter spin-off is quite adventitious. For example, the monofluoroterphenyls (**XXV**) were first made in a quest for high $T_{N\text{-}I}$ materials with suppressed-(lateral fluoro)-ordered smectic tendencies. As a bonus however, appropriate homologues also showed useful S_C properties. The S_C materials had low m.p.s, the desirable S_C, S_A, N, I sequence, and low viscosity, and when doped with chiral cyanohydrin esters provided good mixtures for fast-switching ferroelectric displays. Their limitations lay in persistent underlying ordered smectics at low temperatures and their only weakly negative or even weakly positive dielectric anisotropies.

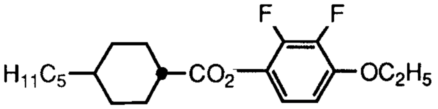


(XXV)

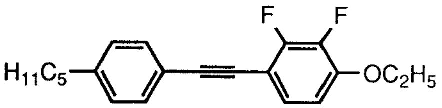
A solution to this problem was provided through the new Pd-catalysed boronic acid coupling routes discussed earlier, since difluoroterphenyls (**XVI** and **XVII**) should have more negative $\Delta\varepsilon$ values. Additionally, they had similar LC thermal stabilities and phases, low m.p.s, and ordered smectics were eliminated. As demonstrated by colleagues at RSRE, Malvern, they provided excellent ferroelectric hosts for displays. Thus, a ternary mixture of dialkyldifluoroterphenyls doped with 10 wt% of a chiral cyanohydrin ester had K-S_C at 15.5°C, a Ps of 30nC cm^{-2}, a tilt angle θ of 21.5° and a switching time, $\tau(10\ V\ cm^{-1})$ of 3 μs.

Whilst 2,3- and 2′,3′-difluoroterphenyls with two terminal *alkyl* chains have Δε values of around −1.7 to −1.9, it emerged that materials such as that with the first structure below:





-4.6



-4.4

i.e., with a 2,3-difluoro-4-*alkoxy*phenyl group, have much more negative Δε values, e.g., −4.2 for the example given, and the use of this moiety is now known[27] to provide a good means of achieving strongly negative Δε values in a wide range of materials—see the two examples above—a means much superior to other ways of enlarging negative dielectric anisotropies, particularly when maintaining a low viscosity is important. This is illustrated by data from Weber *et al.*[27] given in Table I.

TABLE I

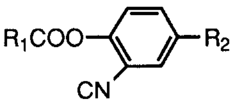
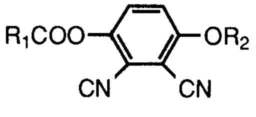
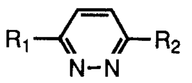
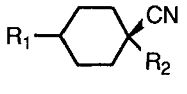
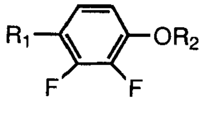
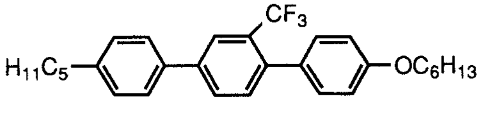
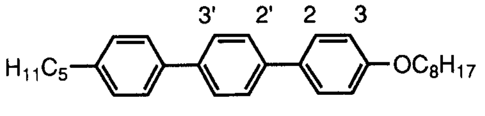
	Δε	Visc (mm^2s^{-1})
	-4	ca 200
	-20	ca 400
	-6	ca 100
	-8	ca 70
	-4	17

Table I shows that whilst other structures may develop strongly negative $\Delta\varepsilon$ values, the 2,3-difluoro-4-alkoxyphenyl unit is the one of choice for obtaining an appreciable negative $\Delta\varepsilon$ combined with really low viscosity.

Although lateral —CN and —CF_3 groups give high viscosities and the materials are strongly smectogenic, it is noted that boronic acid coupling procedures do provide a very facile means for their synthesis. The structure below is an example of one such material (K 32° (S_C 8.0°)I) readily made by the Pd-catalysed boronic acid coupling process, and further data on transition temperatures, $\Delta\varepsilon$ values and viscosity values relating to general structure (**XXVI**) are provided below.





(**XXVI**)

Substituent(s)	Transition Temperatures(°C)	$\Delta\varepsilon$	Viscosity(cP)
3'-CN	K 33.5° S_A 103° I	−1.6	—
2'-CN	K 35° S_C 42° N 78° I	−2.9	—
3-CN	K 62° S_A 160° I	−4.7	10^4
2-F,3-CN	K 100.5° S_A 167° I	−9.5*	5.10^4

*again a 2,3-disubstituted-alkoxy system

4. CHAIN FLUORINATED MATERIALS

Fluorination has a strong role to play in LC chemistry. We have already seen how it can be used to suppress ordered smectic phases, to promote S_C properties, to enhance negative $\Delta\varepsilon$ values, and to depress m.p.s when the mono- or di-fluorination is lateral.

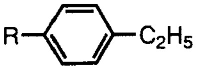
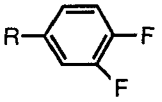
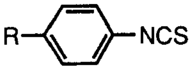
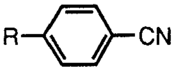
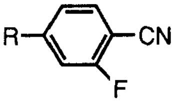
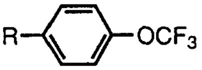
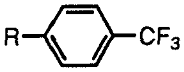
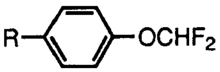
Recent work by the Merck Group at Darmstadt has now shown that the use of fluorinated end chains provides an interesting means of achieving low viscosity values and good positive values of $\Delta\varepsilon$. The end chains are:

$$—OCF_3, —CF_3 \quad \text{and} \quad —OCHF_2$$

Given appropriate benzene precursors carrying these substituents, boronic acid coupling methods or Heck reactions and hydrogenation provide ready routes to mesogenic materials carrying these terminal functions. Table II gives[28] some examples showing that, again where a low viscosity is paramount, materials of very

TABLE II

R- = 

		$\Delta\varepsilon$	Visc (mm^2s^{-1})
		0.4	20
		10.0	31
		10.9	40
(1)		12	90
		20.3	110
(2)		8.9	16
(3)		12.9	32
(4)		9.3	29

(1) K 96 N 219 I

(2) K 43 S_B 128 N 147 I

(3) K 123 N 124.2 I

(4) K 67 S_B 120 N 161.8 I

good positive $\Delta\varepsilon$ are made available, e.g., for active matrix displays.[29] The transition temperatures given in Table II also show that in these three ring mesogens, good N—I transition temperatures are maintained with the fluorinated end groups, although relative to terminal —CN, these temperatures are of course substantially reduced.

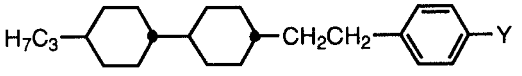
For this reason, two ring analogues of these materials are not liquid crystalline. For example, 4-octyloxybiphenyl with 4'-$OCHF_2$ has K 104° I, and with 4'-CF_3 has K 115° I; virtual $T_{N\text{-}I}$ values for both compounds are estimated at [+20°].

However, appended to suitable cores, the substituents are good, and over a range of core types, the order always appears to be:

$$T_{CI}(°):\quad OCHF_2 > OCF_3 > CF_3$$

$$\text{Viscosity \& } \Delta\varepsilon:\quad CF_3 > OCHF_2 > OCF_3$$

The best compromise is with —$OCHF_2$ which is superior to terminal —F, as shown by the results for the compound **(XXVII)**, for which the appended data are found, i.e., the higher $\Delta\varepsilon$ and T_{CI} values are obtained with —$OCHF_2$



(XXVII)

Y		Vic($mm^2\ s^{-1}$)	T_{CI}(°)
F	6	18	137
$OCHF_2$	7.1	22	154

at the price of only a modest increase in viscosity. Stability of the materials is however open to question in some cases.

5. DISCOTIC SYSTEMS

This review of synthetic developments would hardly be complete without reference to discotic systems, an area of considerable interest, wherein attention has been concentrated up to now on hexasubstituted derivatives of triphenylene and truxene or on copper β-diketonates. Original literature routes to triphenylenes and truxenes are poor, unreliable and generally messy with inbuilt purification problems, and the discotic properties of the copper complexes are complicated by their tendency to give discotic lamellar phases. Availability of good materials has therefore retarded progress in the field.

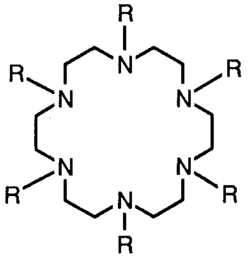
A good, up to date review of discotics has appeared recently,[30] but here we note that Pd-catalysed couplings are again cropping up as a means of providing more accessible and structurally varied discogens. Praefcke *et al.*[31] have used such methods to replace all six bromo-substituents in a hexabromo-benzene or triphenylene with the groups:

$$R{-}C{\equiv}C{-}\quad \text{or} \quad 4{-}R(O){-}C_6H_4{-}C{\equiv}C{-}$$

and more recently still have extended[32] this activity to 1,2,3,5,6,7-hexabromonaphthalene, adding considerably thereby to the range of discotic materials available for study.

It should also be noted that Pd-catalysed boronic acid couplings between appropriate lithio-benzenes and dibromobenzenes, followed by cyclisation, could be used to improve the availability of the older triphenylenes, not only those of a symmetrical, but also those of an unsymmetrical hexasubstituted nature. Such procedures could be important if application areas such as those suggested by the observations of Boden *et al.*[33] that $AlCl_3$-doped triphenylenes behave as p-type semiconductors.

Azamacrocycles were first reported in 1985 by Lehn *et al.*[34] and later by Mertersdorf and Ringsdorf[35] to exhibit discotic phases. The columnar phases are tubular systems. An example is provided by the aza-crown-6 of structure (**XXVIII**) in which



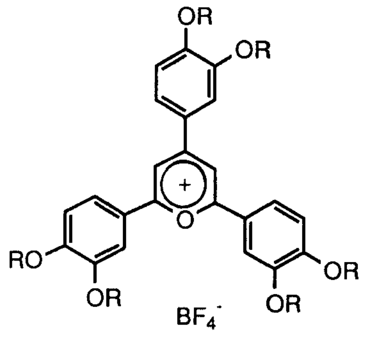
(XXVIII)

the discotic core, 18-ane N6 has groups R = 4—$C_{12}H_{25}O \cdot C_6H_4 \cdot CO$— attached to the nitrogens. Attempts to extend the number of long chain functions by using 3,4,5-trialkoxybenzoyl and 3,5-dialkoxybenzoyl functions resulted only in glasses which were not liquid crystalline when 18-ane N6 and 14-ane N4 were used as cores. Lattermann[36] realised however that more success might be achieved using 3,4-dialkoxybenzoyl groups, and especially with 14-ane N4 he obtained LC phases. Very recently, he has reported[37] very striking results, particularly with 3,4-di-*n*-decyloxybenzoyl functions linked to the nitrogens of 18-ane N6, 12-ane N3 and 9-ane N3. These are summarised below:

18-ane N6 (12 chains)	K 104° D 140° I
12-ane N3 (6 chains)	K 37.5° D 59.5° I-cooling gives a discotic glass, Tg 29.5°
9-ane N3 (6 chains)	K 40° D1 45° D2 67° I-cooling gives a discotic glass, Tg 32.5°.

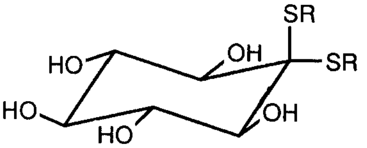
The two mesophases for 9-ane N3 await characterisation, but those for 18-ane N6 and 12-ane N3 are D_{ho} columnar phases.

In this field, a discotic system just reported by Levelut *et al.*[38] is of interest, exhibiting as it does, discotic phases with short alkyl groupos, R = C_2 and C_3. The systems are 2,4,6-triarylpyrylium tetrafluoborates (**XXIX**) and the BF_4^- anion is considered to facilitate mesophase formation by occupying space and exerting a disordering effect between columns, in the same manner as longer alkyl chains in other discotic materials.

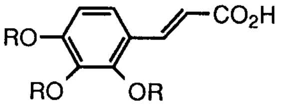


(XXIX)

Also, Praefcke *et al.*, as a development of their work on purely aliphatic disco-systems[39] derived from *scyllo*-inositol, have studied the mesophases (hexagonal and isotropic) formed by double-tailed or peg-shaped molecules[40] which are thioacetals (**XXX**) with R groups = C_2 and C_5—C_9.



(XXX)



(XXXI)

The same group has also reported[41] a novel biaxial nematic system (**XXXI**)-2,3,4-trihexyloxycinnamic acid (dimer). The flat board-like shape of the molecule is thought to be responsible for the formation of the sanidic nematic phase (K 51.2° N_b 59.6° I) and conoscopic, X-ray *and* textural evidence in support of the biaxiality has been obtained.

CONCLUSIONS

It is hoped that this review of some of the developments arising from novel syntheses carried out over the last two years or so emphasises the extent of the chemists' efforts and the advances in fundamental knowledge that have accrued as a consequence. No doubt the review's inclusions and omissions will have pleased some and offended others, but we had to be selective, and in this situation one can but quote Dylan Thomas who wrote "If you cannot please everybody, You may as well not please nobody."

Acknowledgments

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