A Quick-and-Easy Route to Unsymmetrically Substituted Derivatives of Triphenylene: Preparation of Polymeric Discotic Liquid Crystals

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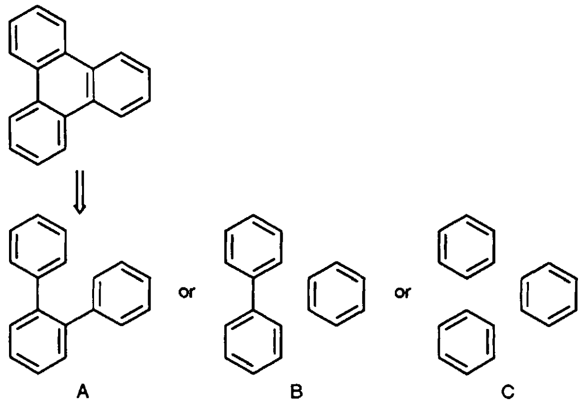
Unsymmetrically substituted triphenylenes can be obtained by the iron(III) chloride mediated oxidative coupling of a 3,3′,4,4′-tetraalkoxybiphenyl with a 1,2-dialkoxybenzene thus opening up a practicable route to polymeric discotic liquid crystals.

The most widely studied discotic liquid crystals[1] are esters and ethers of triphenylene. These materials are particularly interesting because they form an ordered (D_{ho}) columnar mesophase, ideal for one-dimensional energy[2] and electron[3] transport. The development of their applications has, however, been hindered by the difficulties of synthesising sufficiently large quantities of high purity material. Retrosynthetic analysis using one, two, or three bond disconnections suggests that substituted triphenylenes can be assembled from either an *o*-terphenyl [A], from benzene and biphenyl based components [B] or from three benzene derivatives [C] (Scheme 1).

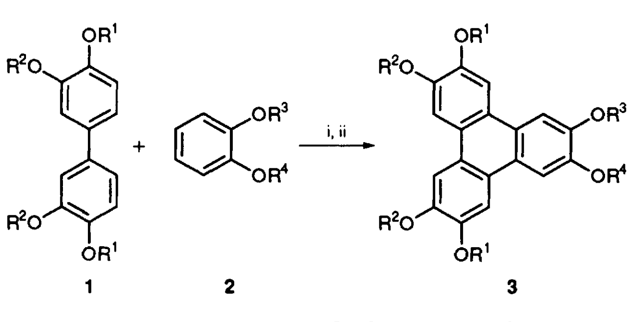
Table 1 Yields for Scheme 2

	R^1	R^2	R^3	R^4	Yield (%)
a	Hx[a]	Hx	Me	Me	65
b	Hx	Me	Hx	Hx	77
c	Me	Hx	Hx	Hx	45
d	Hx	Hx	Me	Ac[b]	45

[a] Hx = hexyl, $Me(CH_2)_5$. [b] The acetate is lost during the reaction/work-up.



Scheme 1



Scheme 2 *Reagents*: i, $FeCl_3/CH_2Cl_2$, ii, MeOH

A variation on route [C] (oxidative trimerisation of a 1,2-dialkoxybenzene[4]) has invariably been used for symmetric low molar mass mesogens. We have recently reported a new procedure in which iron(III) chloride is used as the oxidant in these trimerisation reactions and allows these compounds to be readily produced on a multigram scale.[5] However, it is the polymeric and not the low molar mass mesogens that are likely to lead to applications.[6] The preparation of main-chain and side-chain polymers require routes to monomers which are unsymmetrically substituted on the triphenylene nucleus. However, the lack of regiocontrol inherent in 'benzene' trimerisation strategies [C] means that they cannot be generally used and that an alternative approach is required. An '*o*-terphenyl' based strategy [A] could, in principle, be used but such routes prove relatively laborious.[7] We now report a better, much more general synthesis of triphenylene ethers based on the coupling of tetraalkoxybiphenyls with dialkoxybenzenes, strategy [B], using iron(III) chloride. The reaction appears to be widely applicable and good yields are obtained (Scheme 2). The yields are reported in Table 1.

In a typical procedure iron(III) chloride (6 equiv.) is added to a rapidly stirred mixture of the 1,2-dialkoxybenzene (**2**, 4 equiv.) and the 3,3′,4,4′-tetraalkoxybiphenyl (**1**, 1 equiv.) (prepared by an Ullman coupling of dialkoxyiodobenzenes[8]) in dichloromethane. After 1 h at room temp. the whole reaction mixture is poured carefully onto methanol (reductive work-up) and the resultant solid isolated by filtration and purified by column chromatography.† The major byproduct is the symmetrical trimer of the 1,2-dialkoxybenzene. It is perhaps surprising that under these conditions the cross-coupling reaction leading to the desired product **3** dominates over the known oxidative dimerisation of the biphenyl.[9] The products **3a–d** have been elaborated into polymeric discotic liquid crystals including main-chain polymers in which the triphenylene is linked specifically through the 2,7- or 3,6-positions. This has been achieved by selective removal of the methyls with lithium diphenylphosphide[10] and condensation of the resultant diphenol with an α,ω-dibromide.[8]

This reaction provides the first general, regiospecific synthesis of unsymmetrical hexaalkoxytriphenylenes. It can obviously be extended to cases where up to five of the substituents are different. In particular, it allows structurally homogeneous, discotic liquid-crystalline polymers of this type to be made on a reasonably large scale, enabling their physical properties to be explored.

We thank the SERC for financial support.

Received, 17th September 1993; Com. 3/05619H

Footnote

† For example, a mixture of iron(III) chloride (45 g, 0.279 mol), 3,3′-dihexyloxy-4,4′-dimethoxybiphenyl (8 g, 0.019 mol) and 1,2-dihexyloxybenzene (22.8 g, 0.082 mol) was stirred in dichloromethane (150 ml) for 1 h. The reaction mixture was carefully poured onto methanol (500 ml) and after cooling in ice the resultant precipitate was filtered off and washed with methanol. Column chromatography on silica (benzene eluent) afforded **3c** (6 g, 45%), mp 98 °C (uncorrected). ^1H NMR (300 MHz) δ 0.93 (t, 12H), 1.4–1.6 (m, 24H), 1.95 (m, 8H), 4.10 (s, 6H), 4.24 (m, 8H), 7.81 (s, 4H), 7.85 (s, 2H).

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