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SYNTHESIS OF HEXA-ALKYLOXYTRIPHENYLENES USING $FeCl_3$ SUPPORTED ON ALUMINA

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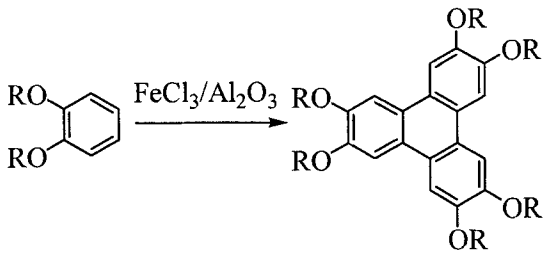
Abstract: Several symmetrical and unsymmetrical hexa-alkyloxytriphenylenes have been synthesised in good yield from diakyloxy benzenes and terphenyl derivatives using $FeCl_3$ supported on alumina.

Hexa-alkyloxytriphenylenes are arguably the most important class of discotic liquid crystal, principally due to their burgeoning application as quasi-one-dimensional conductors[1] and photoconducting devices.[2] At the present time, the most important synthetic route to these fascinating systems involves the use of $FeCl_3$ to catalyse the trimerisation of dialkyloxy benzenes[3] or cyclisations of dialkyloxy benzenes and terphenyl derivatives.[4] These synthetic methodologies usually involve the Lewis acid being dissolved in an organic solvent, to which the triphenylene precursors and a

catalytic amount of concentrated sulfuric acid are added. Although this technique usually affords the triphenylenes in good yield, the reaction and work-up procedure is a little laborious, requiring use of environmentally hazardous organic solvents and mineral acids.

In this publication we report a convenient, high yielding and environmentally friendly method of performing the trimerisation of dialkyloxy benzenes and the cyclisation of dialkyloxy benzenes with terphenyl derivatives, using $FeCl_3$ supported on acidic Al_2O_3. The synthesis of derivatives **6** - **10** was readily accomplished by dropwise addition of the dialkyloxy benzene precursor to the alumina/$FeCl_3$ catalyst (**Scheme 1**). The subsequent reaction was very exotherimic, and the colour of the resulting solid changed from brown to a blue/purple colour. Tlc evidence indicated the reaction was essentially complete after approximately 15 min, however, the reaction was left overnight before work-up. The purification was simply achieved by filtration of the solid through a short plug of silica gel, eluting with toluene. The filtrate was concentrated under *vacuo*, to yield the pure derivative in better yields than those reported for the solution technique.[3]

In endeavours to determine whether this methodology could be applied to the synthesis of unsymmetrical derivatives, we attempted the synthesis of compound **12** using a mixture of veratrole and compound **3** (2 mole



1 R = CH_3
2 R = $(CH_2)_4CH_3$
3 R = $(CH_2)_5CH_3$
4 R = $(CH_2)_6CH_3$
5 R = $(CH_2)_7CH_3$

6 R = CH_3 (89%)
7 R = $(CH_2)_4CH_3$ (86%)
8 R = $(CH_2)_5CH_3$ (88%)
9 R = $(CH_2)_6CH_3$ (87%)
10 R = $(CH_2)_7CH_3$ (82%)

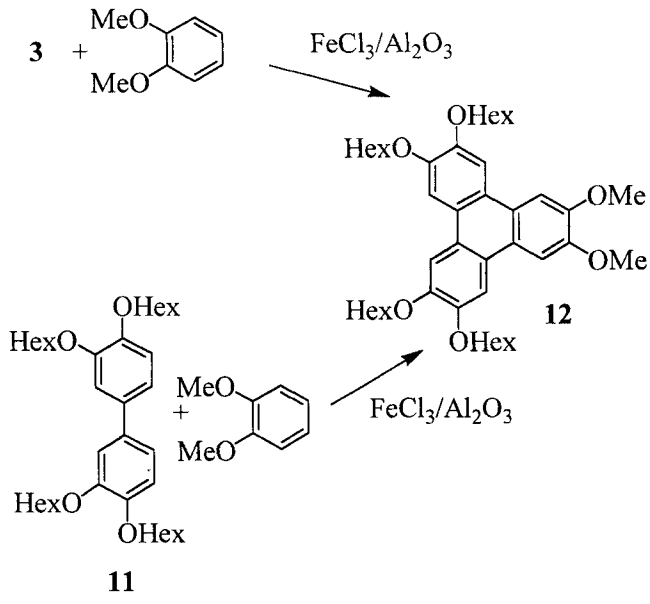
Scheme 1

equivalents) or 3,3',4,4'dihexyloxybenzene **11**[4] (1 mole equivalent). Both of the supported reagent routes were slightly more effective in producing derivative **12** than the solution routes, resulting in yields of 30 % and 70 %, respectively.[3,4]

In conclusion, we have established the conditions whereby both symmetrical and unsymmetrical triphenylenes can be synthesised cleanly and in good yield using $FeCl_3$ supported on alumina.

Experimental Section

Preparation of $FeCl_3$-alumina: To a well stirred solution of $FeCl_3$ (5 g, 31 mmol) in CH_2Cl_2 (20 mL), acidic Al_2O_3 (Brockmann grade 1) (1g) was added and the subsequent mixture was stirred for 10 min at 25°C. The solvent was removed under *vacuo*, and the residual olive green/brown solid



Scheme 2

residue was dried under high vacuum for 20 min., to afford the bench-stable supported reagent.

General cyclisation procedure:

*Synthesis of 2,3,6,7,10,11-hexahexyloxytriphenylene (**8**).*

To the alumina catalyst (1 g) in a 2 cm test tube was added compound **3** (1 g, 3.6 mmol) dropwise over 1 min. An extremely exothermic reaction then took place, affording a purple/blue solid. After 12 hours the solid was transferred to a short column containing silica gel (2cm X 10 cm) and the column was then eluted with toluene. The solvent was evaporated

under reduced pressure to afford the pure product. Yield 88 %, mpt = 96 - 97 °C (lit.[3] 97 °C).

Calculated for $C_{54}H_{84}O_6$: C, 78.26; H, 10.14;

Found: C, 78.33; H, 9.99 %

H NMR ($CDCl_3$/ TMS): 7.82 (s, 6H), 4.23 (t, 12H), 1.94 (m, 12H), 1.41-1.56 (m, 36H),

0.93 (t, 18H)

MS (FAB): m/z = 828 (M^+)

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3. Yields quoted for solution method are: compound **6** = 86%, compound **7** = 73% compound **12** = 22%. Boden, N.; R. C. Borner, Bushby, R. J.; Cammidge, A. N.; Jesudason, M.V. *Liquid Crystals*, **1993**, *15*, 851.

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