# Oxidative trimerization of *o*-dialkoxybenzenes to hexaalkoxytriphenylenes: molybdenum(V) chloride as a novel reagent

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**Symmetrically substituted hexaalkoxytriphenylenes are obtained from *o*-dialkoxybenzenes by oxidative trimerization with $MoCl_5$ in high yields; oxidative coupling of a 3,3′,4,4′-tetraalkoxybiphenyl and 1,2-dialkoxybenzenes yields unsymmetrically substituted derivatives of triphenylene and a direct coupling of a 3,3′,4,4′-tetraalkoxybiphenyl with alkoxyphenol produces the monofunctionalized triphenylenes.**

Hexasubstituted triphenylenes are the most widely synthesized and studied discotic mesogens.[1] Recently, these materials have been discussed as potential candidates for opto-electronic devices.[2,3] Several research groups are currently working on the synthesis of symmetrical, unsymmetrical and functionalized triphenylene discotic liquid crystals.[4–9] Here we report the synthesis of a variety of triphenylene derivatives using a novel reagent, molybdenum(V) chloride.

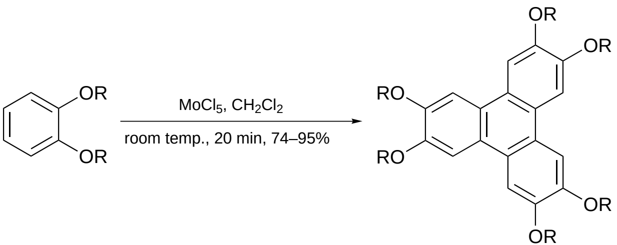
Synthesis of hexamethoxytriphenylene has been achieved previously by oxidative trimerisation of 1,2-dimethoxybenzene (veratrol) in $H_2SO_4$ using chloranil or iron chloride as oxidant.[10] The trimerization involves three consecutive Scholl reactions but surprisingly under normal Scholl conditions using aluminium chloride and nitrobenzene this does not work well.[10e] Triphenylene derivatives show mesomorphism only when the six peripheral alkoxy chains have a minimum of four carbon atoms, *i.e.* butoxy chains. The trimerization using chloranil is limited to the preparation of hexamethoxytriphenylene only and with higher homologues like 1,2-dihexyloxybenzene it gives only a poor yield of hexahexyloxytriphenylene with many side products.[4g] To prepare these long chain derivatives, the methyl groups of hexamethoxytriphenylene are dealkylated by $BBr_3$ or HBr and the resultant hexaphenol is realkylated with the appropriate alkyl halide to give different hexaalkoxytriphenylene discotics.

Hexamethoxytriphenylene can also be prepared by the cyclic anodic trimerization of dimethoxybenzene and, using a chemical or electrochemical reductive work-up, a moderate yield of the product can be obtained.[11] The method is not limited to dimethoxybenzene but can be extended to other dialkoxybenzenes to form directly hexaalkoxytriphenylene discotics, but this slow reaction is only applicable on a very small scale and, thus, limited in its use.

The use of $FeCl_3$ as oxidant was further explored by the Ringsdorf group, which reported the synthesis of hexahexyloxytriphenylene by the trimerization of 1,2-dihexyloxybenzene in 70% $H_2SO_4$ at 80 °C using iron chloride in 20% yield.[12] A further modification to this process was implemented by the Boden group, who used only a catalytic amount of $H_2SO_4$ (0.3%) in $CH_2Cl_2$ and reported yields of 55–86% for different alkoxytriphenylenes.[4g] Coupling of a tetraalkoxybiphenyl with the appropriate dialkoxybenzene under the same conditions gives unsymmetrical hexaalkoxytriphenylenes in 45–77% yield.[4f]

Well-defined synthesis of unsymmetrical and low degree substituted triphenylenes has been reported recently using organometallic chemistry and $FeCl_3$.[7,8] These sophisticated methods are useful for the preparation of low degree substituted triphenylenes but difficult to apply for a large scale production.

We have discovered that molybdenum(V) chloride is a novel reagent for the oxidative trimerization of 1,2-dialkoxybenzenes to hexaalkoxytriphenylenes in high yield. The reaction occurs under very mild conditions with or without acid catalyst and in a very short time at room temperature (Scheme 1). In a typical reaction, $MoCl_5$ (1.4 g, 0.0051 mol) was added to a solution of 1,2-dibutoxybenzene (1.1 g, 0.005 mol) in 10 ml of dry $CH_2Cl_2$. The reaction mixture was stirred at room temperature for 20 min under anhydrous conditions. It was then poured over cold MeOH (15 ml), diluted with water (20 ml) and extracted with hexane (4 × 20 ml). The combined extracts were washed with water and brine, dried over anhydrous sodium sulfate, the solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel, yielding 1.04 g (95%) of hexabutoxytriphenylene. The product was characterized by its spectral data, phase behaviour and a direct comparison with an authentic sample. Yields of different hexaalkoxytriphenylenes are given in Table 1. As $MoCl_5$ is a 2 $e^-$ oxidant, only *ca.* 1 equiv. of the reagent is required to



**1a–d**

**2a–d**

**a** R = Bu
**b** R = $C_6H_{13}$
**c** R = $C_{10}H_{21}$
**d** R = Me

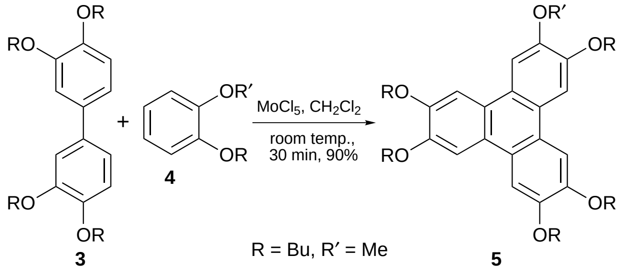
**Scheme 1**

**Table 1** Preparation of triphenylene derivatives using $MoCl_5$ in $CH_2Cl_2$ solution

| Starting Material | $H_2SO_4$ (%) | Product | Yield (%) |
|---|---|---|---|
| **1a** | 0.0 | **2a** | 95 |
| **1a** | 0.2 | **2a** | 92 |
| **1a** | 0.5 | **2a** + **7** | 78 + 5 |
| **1a** | 1.0 | **2a** + **7** | 41 + 25 |
| **1b** | 0.0 | **2b** | 94 |
| **1b** | 0.2 | **2b** | 90 |
| **1c** | 0.0 | **2c** | 80 |
| **1c** | 0.2 | **2c** | 78 |
| **1d** | 0.0 | **2d** | 74 |
| **1d** | 0.2 | **2d** | 74 |
| **3** + **4** | 0.0 | **5** | 90 |
| **3** + **4** | 0.2 | **5** | 75 |
| **3** + **6** | 0.0 | **7** | 44 |
| **3** + **6** | 0.2 | **7** | 47 |

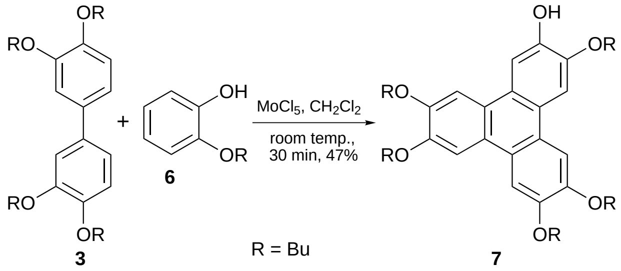
perform the reaction. The best yields of hexaalkoxytriphenylenes were obtained without using any acid and gave better yields than any of the known methods. We have also observed that on increasing the amount of $H_2SO_4$, partial dealkylation of hexaalkoxytriphenylenes occurs and variable amounts of monohydroxypentaalkoxytriphenylene can be isolated (Table 1). The work-up of the reaction is very simple; in most cases, on pouring the reaction mixture over MeOH, a white precipitate forms which can be filtered and recrystallized. Otherwise, addition of water followed by extraction with hexane gives a colourless product.

Synthesis of unsymmetrical and monofunctionalized triphenylenes was achieved by coupling a 3,3′,4,4′-tetraalkoxybiphenyl and appropriate 1,2-dialkoxybenzenes (Scheme 2) under similar reaction conditions. Thus, when 3,3′,4,4′-tetrabutoxybiphenyl **3**, prepared by classical Ullman coupling of dialkoxymonoiodobenzene, was coupled with 2-butoxyanisole **4**, 2-methoxy-3,6,7,10,11-butoxytriphenylene **5** was formed in 90% yield. Symmetrical and nonsymmetrical trimers of 1,2-dialkoxybenzenes were the two side products in this reaction.



**Scheme 2**

Monofunctionalized triphenylene, an extremely important precursor for the synthesis of discotic dimers, oligomers and polymers, can be prepared by direct coupling of a 3,3′,4,4′-tetraalkoxybiphenyl and monoalkoxyphenol. Thus, oxidative coupling of 3,3′,4,4′-tetrabutoxybiphenyl **3** and 2-butoxyphenol **6** using $MoCl_5$ under similar reaction conditions yielded 2-hydroxy-3,6,7,10,11-butoxytriphenylene **7** in 47% yield (Scheme 3).



**Scheme 3**

The potential of this new reagent is currently under investigation for the synthesis of different symmetrical, unsymmetrical and functionalized triphenylenes. The effects of different solvents, acids and concentrations are also under investigation and the results will be published in due course.

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## Footnote and References

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