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Preliminary communication

Vanadium oxytrichloride, a novel reagent for the oxidative trimerization of *o*-dialkoxybenzenes to hexaalkoxytriphenylenes

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Triphenylene derivatives with six peripheral chains can make excellent discotic liquid crystals showing great promise in electronic devices. Vanadium oxytrichloride was found to be a novel reagent for the preparation of various triphenylene derivatives. Symmetrically substituted hexaalkoxytriphenylenes were obtained from *o*-dialkoxybenzenes by oxidative trimerization with VOCl_3 in high yields. Oxidative coupling of a 3,3',4,4'-tetraalkoxybiphenyl with 1,2-dialkoxybenzenes yielded unsymmetrically substituted derivatives of triphenylene; a direct coupling of a 3,3',4,4'-tetraalkoxybiphenyl with alkoxyphenol produced monofunctionalized triphenylenes.

Liquid crystal phases formed by disk-shaped molecules, now commonly known as discotic liquid crystals [1], have attracted a great deal of attention in recent years in view of their promising applications in opto-electronic devices [2]. Triphenylene derivatives occupy a prominent position in the family of discotic liquid crystals. Various hexaalkoxytriphenylene discotic liquid crystals have been studied extensively for their one-dimensional conducting [2], photoconducting [2, 3], luminescence [4] and one-dimensional energy transfer [5] properties. Because of these interesting properties, several research groups are currently working on the synthesis of symmetrical, unsymmetrical and functionalized triphenylene discotic liquid crystals [6]. We have recently reported the synthesis of various symmetrical, unsymmetrical and mono-functionalized triphenylene derivatives using a novel reagent MoCl_5 [7]. Our continued search has now resulted in the discovery of yet another reagent, vanadium oxytrichloride, for the synthesis of a variety of triphenylene derivatives.

Hitherto, only three oxidizing agents; chloranil, iron(III) chloride and molybdenum pentachloride have been known for the oxidative trimerization of 1,2-dialkoxybenzene to hexaalkoxytriphenylene. The trimerization involves three consecutive Scholl reactions [8], but surprisingly under normal Scholl conditions using aluminium chloride and nitrobenzene this does not work well [8]. The synthesis of hexamethoxytriphenylene has been achieved by

oxidative trimerization of 1,2-dimethoxybenzene (veratrol) in H_2SO_4 using chloranil or iron(III) chloride as oxidant [8]. To prepare various triphenylene discotic liquid crystals requiring long alkyl chains, the methyl groups of hexamethoxytriphenylene are dealkylated and the resultant hexaphenol is realkylated with the appropriate alkyl halide to give different hexaalkoxytriphenylene discotics. The trimerization using chloranil is limited to the preparation of hexamethoxytriphenylene; with higher homologues such as 1,2-dihexyloxybenzene it gives only a poor yield of hexahexyloxytriphenylene with many side products.

The use of FeCl_3 as oxidant was further explored by Ringsdorf and co-workers, who reported the synthesis of hexahexyloxytriphenylene by the trimerization of 1,2-dihexyloxybenzene in 70% H_2SO_4 at 80°C using iron(III) chloride in 20% yield [9]. A further modification in this process has been made by Boden and co-workers who used only a catalytic amount of H_2SO_4 (0.3%) in dichloromethane [10].

The well-defined synthesis of unsymmetrical and low degree substituted triphenylenes by the use of organometallic chemistry and FeCl_3 has been reported recently [11, 12]. These sophisticated methods are useful for the preparation of low degree substituted triphenylenes but difficult to apply to large scale production. Electrochemical trimerization of dialkoxybenzenes is also applicable on the small scale for the preparation of hexaalkoxytriphenylenes [13].

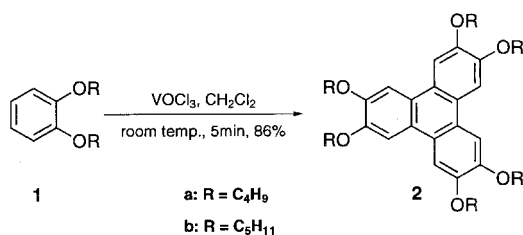
All the reagents so far reported for the preparation of triphenylene derivatives are solids, insoluble in organic

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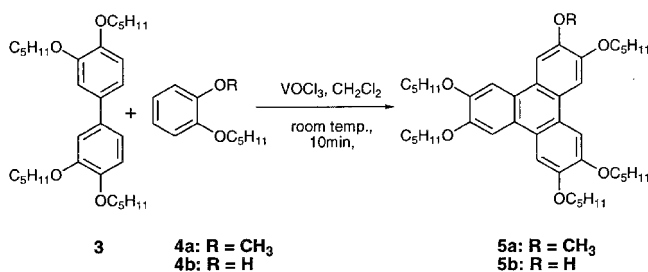
solvents, and the handling of these moisture sensitive reagents is inconvenient. To overcome these problems, we focused attention on a liquid oxidizing agent, vanadium oxytrichloride, that can be readily handled using standard syringe techniques or by using an addition funnel. The use of VOCl_3 in oxidative phenolic couplings is well documented [14].

We have discovered that vanadium oxytrichloride may be used as a novel reagent for the oxidative trimerization of 1,2-dialkoxybenzenes to hexaalkoxytriphenylenes in high yields. 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, commercially available (Aldrich #20,089-1) VOCl_3 (1.1 ml, 0.0115 mol) was added drop-wise to a solution of 1,2-dibutyloxybenzene (1.1 g, 0.005 mol) in 10 ml of dry dichloromethane, with or without conc. H_2SO_4 (0.2–0.4%). The reaction mixture was stirred at room temperature for 5–10 min under N_2 atmosphere. Methanol (5 ml) was then added, then water (20 ml) and the mixture was extracted with CH_2Cl_2 (4 × 20 ml). The crude product was purified by column chromatography over silica gel yielding 0.935 g (86%) of hexabutyloxytriphenylene. The product was characterized by its spectral data, phase behaviour and by direct comparison with an authentic sample.

The synthesis of unsymmetrical 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'-tetrapentyloxybiphenyl **3**, prepared by classical Ullman coupling of dipentyloxy mono iodobenzene, was coupled with 2-pentyl-oxyanisole **4a**, 2-methoxy-3,6,7,10,11-pentapentyloxytriphenylene **5a** was formed in 71% yield.



Scheme 1.



Scheme 2.

Table. Preparation of triphenylene derivatives using VOCl_3 in CH_2Cl_2 solution.

Starting materials	% of H_2SO_4	Product	Yield/%
1a	0.0	2a	86
1a	0.2–0.4	2a	79
1b	0.0	2b	85
1b	0.2–0.4	2b	83
3 + 4a	0.0	5a	68
3 + 4a	0.2–0.4	5a	71
3 + 4b	0.0	5b	30
3 + 4b	0.2–0.4	5b	35

Monofunctionalized triphenylene can be prepared by direct coupling of a 3,3',4,4'-tetraalkoxybiphenyl and monoalkoxyphenol. Thus, oxidative coupling of 3,3',4,4'-tetrapentyloxybiphenyl **3** and 2-pentyloxyphenol **4b**, using VOCl_3 under similar reaction conditions, yielded 2-hydroxy-3-methoxy-6,7,10,11-tetrapentyloxytriphenylene **5b** in about 35% yield (scheme 2). However, this reaction was sluggish and the isolation of the product difficult. Yields from various reactions are given in the table.

VOCl_3 has a high solubility in various organic solvents, which could be a reason for the almost spontaneous trimerization of dialkoxy benzenes into hexaalkoxytriphenylenes. The handling of the reagent and work-up of the reaction are very easy; there is no need to use concentrated sulphuric acid, which is an obvious advantage, and the product yields are high. The potential of this new reagent is currently under investigation for the synthesis of various symmetrical, unsymmetrical and functionalized triphenylenes in different solvents.

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References

- [1] CHANDRASEKHAR, S., 1993, *Liq. Cryst.*, **14**, 3; CHANDRASEKHAR, S., and KUMAR, S., 1997, *Science Spectra*, **8**, 66.
- [2] CHANDRASEKHAR, S., 1998, in *Hand Book of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Wiley-VCH), Chap. VIII; BODEN, N., and MOVAGHAR, B., 1998, *ibid*, Chap. IX.
- [3] ADAM, D., CLOSS, F., FREY, T., FUNHOFF, D., HAARER, D., RINGSDORF, H., SCHUHMACHER, P., and SIEMENSMEYER, K., 1993, *Phys. Rev. Lett.*, **70**, 457; ADAM, D., SCHUHMACHER, P., SIMMERER, J., HÄUSSLING, L., SIEMENSMEYER, K., ETZBACH, K. H., RINGSDORF, H., and HAARER, D., 1994, *Nature*, **371**, 141.
- [4] STAPPE, I. H., STUMPFLEN, V., WENDORFF, J. H., SPOHN, D. B., and MOBIUS, D., 1997, *Liq. Cryst.*, **23**, 613.
- [5] MARKOVITSI, D., GERMAIN, A., MILLIE, P., LECUYER, P., GALLOS, L. K., ARGYRAKIS, P., BENGS, H., and RINGSDORF, H., 1995, *J. phys. Chem.*, **99**, 1005;

- MARGUET, S., MARKOVITSI, D., MILLIE, P., SIGAL, H., and KUMAR, S., 1998, *J. phys. Chem. B*, **102**, 4697 and references therein.
- [6] KUMAR, S., and MANICKAM, M., 1998, *Synthesis*, 1119 and references therein.
- [7] KUMAR, S., and MANICKAM, M., 1997, *J. chem. Soc., chem. Commun.*, 1615.
- [8] MATHESON, I. M., MUSGRAVE, O. C., and WEBSTER, C. J., 1965, *J. chem. Soc., chem. Commun.*, 278; MUSGRAVE, O. C., and WEBSTER, C. J., 1971, *J. chem. Soc.*, 139; PIATELLI, M., FATTORUSSO, E., NICOLAUS, R. A., and MAGNO, S., 1965, *Tetrahedron*, **21**, 3229; DESTRASDE, C., MONDON, M. C., and MALTHÊTE, J., 1979, *J. de Phys. Colloq.*, **40**, C3-17; MUSGRAVE, O. C., 1969, *Chem. Rev.*, **69**, 499.
- [9] BENGIS, H., KARTHAUS, O., RINGSDORF, H., BAEHR, C., EBERT, M., and WENDORFF, J. H., 1991, *Liq. Cryst.*, **10**, 161.
- [10] BODEN, N., BORNER, R. C., BUSHBY, R. J., CAMMIDGE, A. N., and JESUDASON, M. V., 1993, *Liq. Cryst.*, **15**, 851; BODEN, N., BORNER, R. C., BUSHBY, R. J., and CAMMIDGE, A. N., 1994, *J. chem. Soc., chem. Commun.*, 465.
- [11] BORNER, R. C., and JACKSON, R. F. W., 1994, *J. chem. Soc., chem. Commun.*, 845.
- [12] GOODBY, J. W., HIRD, M., TOYNE, K. J., and WATSON, T., 1994, *J. chem. Soc., chem. Commun.*, 1701.
- [13] BECHGAARD, K., and PARKER, V. D., 1972, *J. Am. chem. Soc.*, **94**, 4749; LE BERRE, V., ANGELY, L., SIMONET-GUEGUEN, N., and SIMONET, J., 1987, *J. chem. Soc., chem. Commun.*, 984; LE BERRE, V., SIMONET, J., and BATAIL, P., 1984, *J. electroanal. Chem.*, **169**, 325; CHAPUZET, J., and SIMONET, J., 1991, *Tetrahedron*, **47**, 791.
- [14] CARRICK, W. L., KARAPINKA, G. L., and KWIATKOWSKI, G. T., 1969, *J. org. Chem.*, **34**, 2388; SCHWARTZ, M. A., ROSE, B. F., HOLTON, R. A., SCOTT, S. W., and VISHNUVAJALA, B., 1977, *J. Am. chem. Soc.*, **99**, 2571.