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Synthesis of Symmetrical and Unsymmetrical Triphenylene Discotic Liquid Crystals Using Antimony(V)Chloride Under Scholl Oxidation

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Abstract

Triphenylene-based discotic liquid crystals, useful in studying the energy and charge migration in self-organized systems, are the most widely synthesized and studied discotic liquid crystals. In this paper, we report an efficient synthetic procedure for the preparation of symmetrical and unsymmetrical triphenylene discotic liquid crystals using antimony pentachloride as a novel reagent. Scholl oxidative trimarization of 1,2-dialkoxybenzenes with $SbCl_5$ yields hexaalkoxytriphenylenes in good yield, while the oxidative coupling of a 3,3',4,4'-tetraalkoxybiphenyl with a 1,2,3-trialkoxybenzene affords an unsymmetrically substituted heptaalkoxy-triphenylene derivative. The potential of this new reagent was compared with the other known reagents for the synthesis of alkoxytriphenylenes.

Keywords: Triphenylene; Discotic liquid crystal; Scholl reaction; Antimony pentachloride

Introduction

Despite its complicated nature, the Scholl reaction has been extensively used in organic synthesis [1-11]. In Scholl oxidation, a new C-C bond between two aryl moieties is generated under the influence of Friedel-Crafts catalyst. A Lewis acid and an oxidant is required to accomplish this reaction. Transition metal halides, such as, $FeCl_3$, $MoCl_5$, etc., which act both as Lewis acid and oxidant are often applied to achieve this condensation. Though this reaction was discovered more than a century ago [12], its mechanism is still under debate. Two possible reaction mechanisms, arenium cation mechanism [9] and radical cation mechanism [4], have been discussed in literature. Recently, the Scholl coupling has been well exploited in the synthesis of discotic liquid crystals (DLCs). DLCs are formed due to self-organization of disc-like molecules [13]. Depending upon the strength of molecular interactions, disc-like molecules can form nematic or columnar phases. The columnar phases formed by these molecules have been extensively studied for one-dimensional conducting properties and their applications in devices like, phovoltaic solar cells, light emitting diodes, sensors, thin film transistors, etc., have been sought. The chemistry and physics of DLCs have recently been reviewed in several research articles [14-31].

Since the discovery of DLCs, triphenylene-based DLCs remained the focal point of research in this field [32-37]. This is mainly because these materials are chemically and thermally stable, their chemistry is relatively easy and they show many different mesophases. Moreover, their one-dimensional conducting properties offer many potential applications. Accordingly, a large number of triphenylene (TP) discotics have so far been prepared to investigate their mesomorphic properties [15]. Hexaalkoxy-TPs are the most widely synthesised and studied discotic mesogens and a number of methods have been developed for their synthesis [34]. The synthesis of hexaalkoxy-TPs involves oxidative trimarization of 1,2-dialkoxybenzene which is one of the unusual cases of Scholl reaction where more than one aryl-aryl bonds are formed. 1,2-dimethoxybenzene (veratrole) was oxidatively trimerized using chloranil or $FeCl_3$ in concentrated H_2SO_4 at room temperature to obtain hexamethoxy-TP [38]. Initially TP discotics were prepared using this sluggish low yielding methodology but later the Leeds group developed an efficient methodology to prepare triphenylene hexaethers via oxidative trimerization of 1,2-dialkoxybenzene using $FeCl_3$ using only a catalytic amount of H_2SO_4 (0.3%) in dichloromethane followed by a reductive work-up using methanol [39]. Previously we have reported two other reagents, molybdenum pentachloride [40] and vanadium oxytrichloride [41], to be highly efficient for the preparation of triphenylene hexaethers. Here we discovered yet another reagent, antimony pentachloride ($SbCl_5$), which can be efficiently used to prepare hexaalkoxy-TP in good yield. Antimony pentachloride is a strong Lewis acid and its application in Friedel-Crafts reaction is well documented [42]. However, its application as Scholl oxidant for the synthesis of triphenylene discotics has so far not been reported. Here we report the synthesis of symmetrical and unsymmetrical triphenylene discotics using this new reagent.

Experimental Section

In a typical reaction (Scheme 1), $SbCl_5$ (4.48 g, 0.015 mol) was added to a solution of 1,2-dibutoxybenzene (1.5 g, 0.0067 mol) in 15 ml of dry CH_2Cl_2. The reaction mixture was stirred at room temperature for 30 min under anhydrous conditions. It was then poured over cold MeOH (50 ml), diluted with water (50 ml) and extracted with hexane (4×30 ml). The combined extracts were washed with water and brine, dried over anhydrous sodium sulphate, the solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel, yielding 1.15 g (78%) of hexabutoxytriphenylene. All the symmetrical hexaalkoxy-triphenylenes were prepared in the same manner and their yield is reported in table 1. They were fully characterized from their spectral and elemental analysis. All the hexaalkoxy-TP exhibit similar ^1H NMR differing only in the aliphatic protons.

Typical ^1H NMR data for the compound **2a:** $\delta_H(CDCl_3)$ 7.83 (s, 6H),

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4.23 (m, 12H), 1.94 (m, 12H), 1.6-1.3 (m, 12H), 0.9 (t, 18H). Elemental anal.: **2a**: calculated for $C_{42}H_{60}O_6$, C 76.33, H 9.15; found, C 76.45, H 8.94%; **2b**: calculated for $C_{48}H_{72}O_6$, C 77.38, H 9.74; found, C 77.62, H 9.44%; **2c**: calculated for $C_{54}H_{84}O_6$, C 78.21, H 10.21; found, C 78.4, H 10.44%. Thermal behaviour: **2a**: Cr 89.9 Col$_p$ 145.6 I; **2b**: Cr 71.4 Col$_h$ 121.5 I; **2c**: Cr 67.4 Col$_h$ 100.0 I.

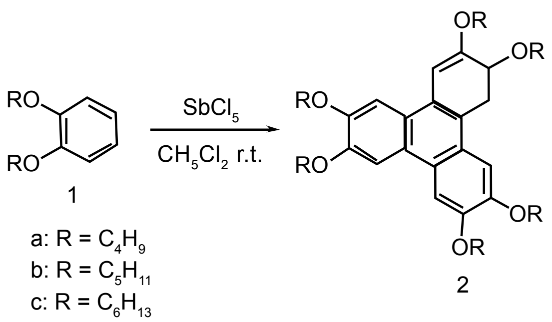
To prepare an unsymmetrical heptaalkoxy-TP derivative **5** (Scheme 2), SbCl$_5$ was added to a solution of 3,3',4,4'-tetrabutyloxybiphenyl **3**, and 1,2,3-tributyloxybenzene **4** in dichloromethane. Typical work-up give 1,2,3,6,7,10,11-heptabutyloxy-TP **5** in about 25% yield (Table 1, entry 7). ^{1}H NMR: δ_H(CDCl$_3$) 9.2 (s, 1 H), 7.8 (s, 2 H), 7.8 (s, 1 H), 7.7 (s, 1 H), 4.2 (m, 12 H), 4.0 (t, *J* 7.1, 2 H), 1.9 (m, 14 H), 1.6 (m, 14 H) and 1.0 (m, 21 H). Elemental anal.: **5**: calculated for $C_{46}H_{68}O_7$, C 75.37, H 9.35; found, C 75.0, H 9.44%. Thermal behaviour: Cr 65.5 Col 70.1 I.

Results and Discussion

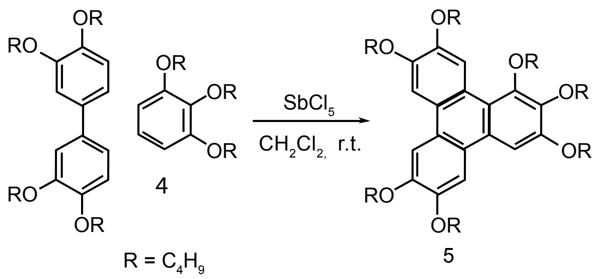
The trimerization of 1,2-dialkoxybenzene to hexaalkoxy-TP is presented in Scheme 1. Addition of antimony pentachloride (2.5 equivalent) to a solution of 1,2-dialkoxybenzene in dichloromethane yields 2,3,6,7,10,11-hexaalkoxy-TPs in 30 min (Table 1). It has been reported that the addition of a catalytic amount of mineral acid improves yields in some cases [15,16]. However it is also known that Lewis acids can complex with mineral acids [4], reducing the effective amount of the oxidant and thus yield of the final product. Therefore, reactions were carried out under both conditions and results are collected in table 1. As can be seen from table 1, entry 2, addition of acid decreases the yield, indicating complex formation between the Lewis acid and mineral acid. Further, increasing the amount of SbCl$_5$ from 2.5 eq to 3.2 eq (Table 1, entry 4) does not increase the yield of final pure product probably due to the formation of other side products at the expense of hexaalkoxy-TP. All the products were characterized from their spectral data, phase behaviour and a direct comparison with an authentic sample and found to be in full agreement with literature data [15].

Entry	Substrate	Oxidant (equivalent)	H$_2$SO$_4$ (%)	Time (min)	Product	Yield
1	**1a**	SbCl$_5$ (2.5)	0.0	30	**2a**	78
2	**1a**	SbCl$_5$ (2.5)	0.3	30	**2a**	70
3	**1a**	SbCl$_5$ (2.5)	0.0	180	**2a**	70
4	**1a**	SbCl$_5$ (3.2)	0.0	30	**2a**	50
5	**1b**	SbCl$_5$ (2.5)	0.0	30	**2b**	55
6	**1c**	SbCl$_5$ (2.5)	0.0	30	**2c**	59
7	**3 + 4**	SbCl$_5$ (2.5)	0.0	30	**5**	25
8	**1a**	FeCl$_3$ (2.5)	0.3	30	**2a**	65
9	**1a**	MoCl$_5$ (2.5)	0.3	30	**2a**	74
10	**1a**	VOCl$_3$ (2.5)	0.3	30	**2a**	81

Table 1: Preparation of hexaalkoxy-TPs using SbCl$_5$ in CH$_2$Cl$_2$ solution.



Scheme 1: Synthesis of symmetrical hexaalkoxy-TPs via oxidative trimerization of 1,2-dialkoxybenzene using antimony pentachloride.



Scheme 2: Synthesis of unsymmetrical heptaalkoxy-TPs via oxidative coupling of a 1,2,3-trialkoxybenzene with a tetraalkoxybiphenyl.

To compare the potential of SbCl$_5$ with respect to other three Lewis acids viz, FeCl$_3$, MoCl$_5$ and VOCl$_3$, known for the synthesis of hexaalkoxy-TPs, reactions were carried out under identical conditions using 1,2-dibutyloxybenzene as substrate (Table 1, entries 8-10). It may be noted that the optimised reaction conditions for different reagents could be different. Therefore, the best yield for various reagents could be different under optimised conditions. From the data, it is clear that under the one set of identical reaction conditions, SbCl$_5$ is slightly better than FeCl$_3$ but not the best reagent known in literature for this trimerization.

As reported for other reagents viz, FeCl$_3$, MoCl$_5$ and VOCl$_3$, this reagent can also be used for the synthesis of unsymmetrical TPs, albeit in poor yield, under similar reaction conditions (Scheme 2). Thus, when 3,3',4,4'-tetrapentyloxybiphenyl **3**, was coupled with a 1,2,3-trialkoxybenzene **4**, 1,2,3,6,7,10,11-heptabutyloxy-TP **5** is formed in about 25% yield (Table 1, entry 7).

Conclusion

In conclusion, Antimony(V) chloride, a new reagent, was found to be useful in the synthesis of symmetrical and unsymmetrical alkoxy-triphenylene DLCs. The reagent may be explored for the synthesis of various other discotic liquid crystals involving iner- or intramolecular Scholl oxidation.

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