ARTICLE IN PRESS

Tetrahedron Letters xxx (2015) xxx-xxx

Contents lists available at ScienceDirect



Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet



A convenient one-step reaction leading to a key discotic intermediate: mono-hydroxy-triphenylene at multi-gram scale

Weikang Xiao^a, Zhiqun He^{a,*}, Min Xu^a, Nan Wu^a, Xiangfei Kong^{a,†}, Xiping Jing^b

^a Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, PR China ^b College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

Article history: Received 24 September 2014 Revised 6 December 2014 Accepted 12 December 2014 Available online xxxx

Keywords: Mono-hydroxy-penta-alkoxytriphenylene Triphenylene Discotic liquid crystal Non-selective cleavage Ferric chloride

ABSTRACT

This work reveals a novel reaction route deviated from a Scholl coupling reaction with an interrogation into the mechanism. A catalytic function of FeCl₃ in the presence of protons plays a key role in the new reaction. It was discovered that by increasing the quantity of reagent FeCl₃ is able to shift the reaction product from a symmetrically hexa-substituted coupling one to a mono-hydrolysed coupling product. The discovery offers a chance to explore and understand the reaction mechanism further. The new reaction enables a convenient one-step synthesis of mono-hydroxy-penta-alkoxytriphenylene, a key discotic liquid crystal intermediate for organic electronic materials, from a simple 1,2-dialkoxybenzenes reactant at a yield up to 65%.

© 2014 Published by Elsevier Ltd.

Introduction

In 1910, Scholl and Mansfeld reported the formation of a C-C bond from two arenes which transformed into π -extended organics, such as quinine 1^1 and perylene 2 (from 1,1'-binaphthalene¹ or (1) naphthalene)² (Scheme 1) both by heating with an excess of neat anhydrous aluminium chloride. The reactions were named after the inventor and called the Scholl reaction. After one hundred year's elaboration, the Scholl reaction now represents a coupling reaction between two or more electron-rich aromatic substances promoted by Lewis acids (such as AlCl₃, FeCl₃ and MoCl₃) or protons (HCl,³ anhydrous HF,⁴ PhSO₃H⁵). The reagent AlCl₃ is a strong Lewis acid but non-oxidising, MoCl₃ is a weak Lewis acid, while FeCl₃ is a weak Lewis acid as well as an oxidant. Those with solvents are allowed to react at a relatively low temperature such as 25 °C. The mechanism for the coupling reactions mediated by non-oxidative AlCl₃ and oxidative FeCl₃ was believed to be different. It is suggested that the former goes through an arenium cation mechanism and the latter is a radical cation mechanism.⁶

The Scholl reaction has now become an important method utilised in the industrial synthesis of aromatic organics, such as 2,2',5,5'-tetra-alkoxybiphenyl **3** which can be prepared from 1,4-dialkoxybenzene with FeCl₃ in dichloromethane⁷ or AlCl₃ in

E-mail address: zhqhe@bjtu.edu.cn (Z. He).

http://dx.doi.org/10.1016/j.tetlet.2014.12.070 0040-4039/© 2014 Published by Elsevier Ltd.



Scheme 1. Aromatic organics synthesised by the Scholl reaction.

nitromethane⁸ as well as a polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) **4** using in situ polymerisation of 3,4-ethylenedioxythiophene with FeCl₃ in acetonitrile.⁹ The Scholl coupling reaction also led to the synthesis of a number of useful organics,¹⁰ especially discotic liquid crystal materials.^{6,10} For example, 2,3,6,7,10,11-hexa-alkoxytriphenylenes (**HAT**) **5** can be synthesised via a mix coupling between 2,3,4,5-tetra-alkoxybiphenyl and dialkoxybenzene^{7,11} or multiple coupling of 1,2-dialkoxybenzene

^{*} Corresponding author. Tel.: +86 10 51688675.

[†] Present address: College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, PR China.

W. Xiao et al./Tetrahedron Letters xxx (2015) xxx-xxx

with FeCl₃ (3.2 equiv) and H₂SO₄ (70%).^{12a} Hexa-alkoxy-hexa-benzocoronene **6** was prepared from 1,3,5-tris-(dialkoxybiphenyl)benzene with FeCl₃ in a mixture of dichloromethane and nitromethane solvents.¹³

The Scholl coupling reaction has now been widely used in the preparation of symmetrically hexa-substituted HAT via direct trimerisation of 1,2-dialkoxybenzenes using FeCl₃^{12,14} or MoCl₅¹⁵ as oxidants. This method has been evolved over half a centenary since 1965 when the synthesis of 2,3,6,7,10,11-hexa-methoxytriphenylene was first reported.^{12b} A triphenylene derivative was prepared at a yield of 73% by the oxidative cyclisation of 1,2-dimethoxybenzene (veratrole) with chloranil in 70% aqueous sulfuric acid. Bengs synthesised hexa-hexyloxytriphenylene (HAT6) via the oxidative trimerisation of 1,2-dihexyloxy-benzene using FeCl₃ in 70% H₂SO₄ at 80 °C and reported a 20% yield of **HAT6**.¹⁶ A catalytic amount (0.3%) of sulfuric acid with FeCl₃ in dichloromethane was developed by Boden as a more suitable route for triphenylene. which has long alkoxy side groups, at a much shortened reaction time with an impressive yield of HAT (86%).¹⁴ In solvent-free conditions, Bai synthesised HATs using FeCl₃ in oxidative trimerisation of dialkoxybenzenes with a very high yield in the range of 80-95%.¹⁷

The structure of triphenylene (**TP**) is chemically stable and one of the simplest cores of discotic liquid crystals (**DLC**s) consisting of a flat and conjugated fused ring with six peripheral substituents.¹⁸ It has a strong tendency to form columnar phases, super in onedimensional charge transporting.¹⁹ Many synthetic methods^{18,20,21} with numerous derivatives have been developed, such as dimer,^{21,22} triad^{22b,23} and polymer.^{21,24} These progresses have made this class of discotic materials more accessible in optoelec-tronic applications.²⁵ In novel derivative preparations, mono- or multi-functionalised species have to be used. Among these, mono-hydroxy-penta-alkoxytriphenylene (**MHT**) is a most convenient intermediate for a wide range of structural designs. The active hydroxyl group can be a useful linking point to prepare **TP** derivatives. It is therefore considered as an important intermediate.

This work reports a newly discovered reaction, a one-step cyclisation reaction of 1,2-dialkoxybenzenes but in a condition only slightly different to the Scholl coupling described above. The reaction led to a completely different product—**MHT**—at a good yield up to 65% (rather than hexa-substituted **HAT** previously reported in the Scholl reaction). It is also the highest yield of **MHT** via a simple one-step reaction ever reported. This is an interesting finding, but it lead to an interrogation into our common knowledge about FeCl₃-mediated one-step Scholl coupling reaction, which seemed to be a popular method for the synthesis of symmetrically hexasubstituted **HAT**. The mechanism of the reaction was therefore explored.

Results and discussion

In our experimental exploration, a coupling reaction was carried out using 1,2-dialkoxybenzenes (**DAB**) as a starting material with a relatively large molar amount of reagent FeCl₃ in dichloromethane. It was surprisingly discovered that the coupling reaction ended in **MHT** (a mono-hydrolysed product) as shown in the reaction scheme in Table 1, rather than expected **HAT** (a hexa-alkoxysubstituted product). However, simple one-step reaction at a high yield of **MHT** has never been reported before.

The reaction shown in Table 1 is very similar to those reported in the literature,¹⁴ except that the molar ratio $r = n_{FeCl_3}/n_{DAB}$ (n_{FeCl_3} is the molar fraction of FeCl₃ and n_{DAB} is the molar fraction of **DAB**) and the product of the reaction were considerably different. In order to understand this reaction, a series of experimental

Table 1

Conditions of the one-step synthesis of MHT6



Entry	$r (= n_{\mathrm{FeCl}_3} / n_{\mathrm{DHB}})$	Temperature (°C)	Time (h)	Yield ^b (%)
1	3:1	0–3	11	12
2	11:3	0-3	9.5	18
3	13:3	0-3	9.5 ^a	58
4	5:1	0-3	6.0 ^a	63
5	20:3	0–3	4.5 ^a	62
6	25:3	0–3	3.5ª	63
7	10:1	0–3	2.5 ^a	65
8	40:3	0–3	2.5 ^a	64
9	20:1	0-3	2.5 ^a	65
10	10:1	40	0.75 ^a	55
11	10:1	20	1.0 ^a	59
12	10:1	-10	6.5 ^a	62
13	10:1	-20	48	47

^a The time required to maximise **MHT6** product and keep **HAT6** or multihydrolysed products at their minimum.

^b Yield of **MHT6** calculated from the isolated product after column chromatography purification.

investigations were carried out. Taking **HAT6** as an example, the reaction was proceeded with 1,2-dihexyloxybenzene (**DHB**) as the reactant and manipulated by varying a number of conditions, such as the molar ratio of the reagent FeCl₃ to the reactant **DHB**, $r = n_{\text{FeCl}_3}/n_{\text{DHB}}$ (n_{DHB} is the molar fraction of **DHB**), the temperatures of the reactions and the optimised reaction times. If we monitor 2-mono-hydroxy-3,6,7,10,11-penta-hexyloxytriphenylene (**MHT6**) as the reaction product, yields of the reactions can be summarised in Table 1.

Careful experiments revealed that the reaction may potentially produce a number of products, including a symmetrically hexa-substituted product (**HAT6**), a mono-hydrolysed product (**MHT6**) and multiple hydrolysed products as shown in Scheme 2.

Our investigation discovered that upon varying molar ratios ($r = n_{FeCl_3}/n_{DHB}$) from 3:1 to 20:1 when fixing reaction temperatures at around 0–3 °C, it is possible to tune the reaction products from hexa-alkoxy-substituted **HAT6** to mono-hydrolysed **MHT6** gradually.

At a relatively low ratio \mathbf{r} , such as around 3/1, the reaction followed a Scholl coupling route and resulted in a high yield of symmetrically hexa-substituted **HAT6** product. This is very similar to that reported in the literature 14. In this condition, mono-hydrolysed product **MHT6** was only a side product with a yield generally less than 20%, while there were almost no further hydrolysed products. As the ratio \mathbf{r} increased, for example to 13:3 or more,





however, the reaction deviated from the typical Scholl coupling route. The mono-hydrolysed **MHT6** became the dominant product of the reaction, while the **HAT6** and multi-hydrolysed species were only side products. When the ratio r is over 5:1, it is noticeable from Table 1 that a further increase in ratio r will not improve the yield of **MHT6** product. Further increasing the molar ratio $r = n_{FeCl_3}/n_{DHB}$ was able to increase the yield of **MHT6** slightly, but it potentially enhanced the chance of further hydrolysed products as well, in which the latter is undesirable. To maximise the yield of **MHT6**, the ratios should be finely tuned to keep the side products (**HAT6** and multiple hydrolysed products) minimised.

Although a number of possible products may be produced with the reaction shown in Scheme 2, our investigation indicates that it is possible to control the reaction direction and finely tune the products dominated with either **MHT6** or **HAT6** in a quantitative way. **MHT6** can be produced with a consistently good yield of over 60% if **r** reaches 5:1 or higher. In the current work, we have achieved the best yield of **MHT6** at 65% using a ratio **r** of 10:1. This optimised ratio **r** is much higher than that required if the reaction were to go through a Scholl coupling route (**r** = 3:1).¹⁴

From Table 1, it can be seen that an increase in molar ratio r could speed up the reaction as well. Although the yields of **MHT6** could not be improved further if the molar ratio r reached 5:1 or over, the times required to synthesise **MHT6** via this reaction can be considerably reduced. Overall, a molar ratio r = 10:1 at 0-3 °C appears to be an optimised condition for **MHT6** to be synthesised in only 2.5 h. The reduction of reaction times is important as it greatly reduces the energy consumption and the cost involved in scaled-up production.

The temperatures of the reactions were also manipulated as they affect the rate of the reactions and hence the products. If the ratio **r** was fixed to 10:1, the reaction was then carried out in a temperature range from -20 °C to 40 °C (see Table 1). It can be seen that the reactions were slowed down in general as the temperatures were lowered. However, the hydrolysis reaction appeared to be more sensitive to the change in temperatures than the coupling reactions. If the reactions were carried out at -10 °C and -20 °C, the reactions became so slow that the further hydrolvsis reactions were significantly suppressed. At -20 °C, the reaction can be finished at the mono-hydrolysis (MHT6) stage without multiple hydrolysed products. If the reactions were conducted at 20 °C and 40 °C or above, MHT6 and the multiple hydrolysed products would occur at an early stage of the reactions, which may cause complications in the purification of the final products. Reaction around 0 °C appears to be a suitable temperature with ease of control where multiple hydrolysed products were sufficiently suppressed. The reactions are able to finish at the mono-hydrolysis dominated stage.

The reactions above were also evaluated for other reactants of different side chain length, such as $\mathbf{R} = \mathbf{C}_{5}\mathbf{H}_{11}$, with a ratio of ferric chloride/1,2-dipentyloxy-benzene = 10:1 at 0–3 °C. The reaction yielded 64% 2-mono-hydroxy-3,6,7,10,11-penta-pentyloxytriphenylene (**MHT5**) in 3 h. This is comparable to that of **MHT6** above. The result suggests that the reaction in Table 1 could be a universal methodology in the synthesis of **MHTs** with different side groups.

Hydrolysed products, such as monohydroxy-, or even multihydroxy-triphenylenes, have been reported as side products during the cyclic trimerisation of dialkoxybenzenes using FeCl₃.^{15,26,27} An investigation aiming to synthesise **MHT** was attempted by Kumar¹⁵ via coupling of dialkoxybenzene with MoCl₅ as the oxidative reagent. Only a butyl side group reactant produced a yield of 25% of mono-hydrolysed product, while as with other reactants yield of mono-hydrolysed product was low (<20%). In order to improve the yield of mono-hydrolysed product on a statistical account, Schulte²⁸ modified the reaction using a mixture of two starting materials, 1,2-dialkoxybenzenes and 2-methoxyphenol (Guaiacol) with a combination of FeCl₃ and H₂SO₄ reagents and a yield of 27% mono-hydrolysed product was obtained. If the reagent was replaced with FeCl₃ in nitromethane, the reaction time can be reduced but the yield of mono-hydrolysed product remained in the range of 15–20%.²⁶ Kong broke into a 35% yield of reaction with a mixed starting material (1,2-dialkoxybenzene and 1-hydroxy-2-alkoxybenzene) and FeCl₃ but in a mixed solvent of dichloromethane.²⁷ Such a high yield of **MHTs** up to 65% by a one-step reaction in current work is impressive.

It is not yet known, however, why an increase in the quantity of reagent FeCl₃ alone will cause the reaction to deviate from its original Scholl coupling to a hydrolysed product?

By carefully monitoring the product development during the course of the reactions using a thin layer chromatograph and spectra, we have discovered that the reaction products were continuously changed at different stages. At the initial stage, the coupling product of **HAT6** was developed first as a main product. As the reactions continued, the main product gradually turned to the mono-hydrolysed product of **MHT6**. Multi-hydrolysed products may have occurred if the reaction was prolonged. When monitoring **MHT6** development carefully, it was possible to find a suitable combination of reaction conditions (the ratio *r*, the temperature and the time) to control the reaction finishing at **MHT6** as a main product in good time where the multi-hydrolysed products were suppressed. This tells us that the hydrolysis was a follow-up reaction of Scholl coupling after the **TP** core was formed.

In order to prove this, an additional experiment was carried out using a similarly enhanced ratio \mathbf{r} to a cross-coupling reaction between two compounds—tetra-alkoxybiphenyl and dialkoxybenzene—that is, a molar ratio of FeCl₃/**DHB**/3,3',4,4'-tetra-hexyloxybiphenyl (**THBP**) was 30:2:1 at a temperature of ~0 °C (Scheme 3). One may expect that the products ended up with a much more complicated mixture than those gained from only one reactant if hydrolysis starts at the initial stage. Statistically, reactants may also have a chance to contribute to the hydrolysis in addition to the triphenylene ring. On the contrary, however, it was surprising to find that instead of complicated hydrolysed products, a high yield (82%) of mono-hydrolysed triphenylene **MHT6** was obtained in 3 h. The reactant appeared to prefer coupling rather than hydrolysis. The hydrolysis may have become easier as the conjugation of aromatic rings was becoming larger.

The only difference between the reactions in Table 1 and Scheme 3 was the number of the starting materials. The reaction in Table 1 is much simpler than those in Scheme 3 as only one simple starting material is required. It is also interesting to find that although the reaction condition in Scheme 3 is non-selective, the yield (of **MHT**) is much higher than a specifically designed selective reaction,²⁹ in which an isopropoxy group acted as a cleavage group and claimed a yield of 68–72% of 2-hydroxy-3-methoxy-tetra-alkyloxytriphenylenes.

Although the coupling reactions between two (or more) arenes with Lewis acids (such as AlCl₃ and FeCl₃) or protons were discovered over one hundred years ago, their mechanisms are still under



Scheme 3. Cross-coupling reaction to produce MHT6

Please cite this article in press as: Xiao, W.; et al. Tetrahedron Lett. (2015), http://dx.doi.org/10.1016/j.tetlet.2014.12.070

4

debate even to this day.¹⁰ Due to previously-reported hydrolysis during Scholl coupling only being a side reaction, its mechanism has rarely been discussed and is poorly understood. It therefore remains a mystery.

Cleavage ethers by acid have been known for a long time, but they often require refluxing at high temperatures.³⁰ The easy hydrolysis at a low temperature in the current work is a new finding. The quantitative relation of the hydrolysis reaction to the amount of FeCl₃ implied that FeCl₃ played a key role in the hydrolysis reaction. In order to determine if FeCl₃ promotes hydrolysis, a testing reaction was carried out by adding FeCl₃ to a reaction vessel at a ratio of 10:1 in two batches, that is, a portion of 3:1 and then 7:1. Initially only 3 portions $(n_{FeCl_3}/n_{DHB} = 3:1)$ of FeCl₃ was added. At the second stage, the remaining 7 portions $(n_{\text{FeCl}_3}/n_{\text{DHB}} = 7:1)$ of FeCl₃ were added. The reaction with the first 3:1 portion followed a Scholl coupling and formed **HAT6** as the main product as expected. The second 7:1 portion turned the reaction towards a predominantly hydrolysis product and yielded MHT6 to over 60%. This indicates that FeCl₃ is not only limited to an oxidant in C-C coupling, but also has a key function in promoting hydrolysis or removing the alkoxy group.

It has been suggested^{6.14} that the coupling reaction follows an arenium cation mechanism—proton (acid) is released during the Scholl coupling reaction. It is therefore important to investigate the role of acid in the hydrolysis reaction as well.

In order to verify what functionalities of the reagents are responsible for the hydrolysis in the reaction revealed in Table 1, purified **HAT6** was selected as a reactant and CH_2Cl_2 as a solvent. Three test experiments, with acid only (Test 1), with FeCl₃ only (Test 2) and with both FeCl₃ and acid (Test 3) were set out at room temperature (Table 2).

If purified **HAT6** was therefore taken as a starting material in the reaction with a molar ratio of $n_{FeCl_3}/n_{HAT} = 30 : 1$, it was found that the reaction failed to hydrolyse the **HAT6** (Table 2, Test 2). However, if concd sulfuric acid was added to the reaction mixture $(n_{FeCl_3}/n_{HAT}/n_{H_2SO_4} = 30 : 1 : 3)$, the hydrolysis started instantly (Test 3(a)). The reaction was able to finish with a relatively high yield of **MHT6** over 60%. In contrast, if only acids, either sulfuric acid (concd) or hydrochloric acid (concd) were used without FeCl₃, there was no hydrolysis in the sulfuric acid case and a trace of hydrolysis (~1%) in the hydrochloric acid case as seen in Test 1 in Table 2. It appears that both FeCl₃ and acid must co-exist as a prerequisite condition for hydrolysis to start. Neither FeCl₃ nor acid is effective at hydrolysing **HAT6** on its own.

The above experiment was also carried out with a combination of FeCl₃ and externally added concd hydrochloric acid ($n_{FeCl_3}/n_{HAT}/n_{HCl} = 30:1:6$) (Test 3(b)). There was hydrolysis, but only with a low yield (~10%) of **MHT6** formed. This is interesting, and understandable. In a Scholl coupling reaction, reactionreleased HCl is anhydrous. If the coupling reaction does follow an arenium cation mechanism and releases acid, such acid may be considered as a 'dry acid' compared with commercial concd hydrochloric acid, which is only about 37% containing a large amount of water. The above coupling reaction requires an anhydrous



Scheme 4. A schematic illustration of intermediate stages of the reaction.

condition. Water might react with and consume FeCl₃ to de-activate its catalytic function.

Evidence from our current work suggests the possibility of an existing coupling reaction-released acid (such as HCl), which further supports arenium cation mechanism at the coupling stage.⁶ We believe that it is the 'dry' HCl which has triggered the hydrolysis. To further prove this, an experiment was also carried out at $\mathbf{r} = \mathbf{n}_{\text{FeCl}_2} / \mathbf{n}_{\text{DHB}} = 10:1$, but in presence of a base, NaHCO₃ (3 portions), to neutralise the reaction-released acid at room temperature. It was observed that the hydrolysis was considerably slowed down and the yield of MHT6 was substantially reduced (about 20% at the 5 h reaction time). These demonstrate that quenching the reaction-released H⁺ effectively reduced the hydrolysis reaction. Therefore, the reaction-released acid plays a key role in hydrolysis as well. It can be seen from the experiments that both FeCl₃ and H⁺ are required to hydrolyse **HAT** into **MHT**. This would suggest that both FeCl₃ and acid are responsible for the hydrolysis reaction in Table 1.

From the discussion above, we proposed that our current reaction as shown in Table 1 might go through two stages: (i) a Scholl coupling stage and (ii) a hydrolysis stage. The reaction in Table 1 may be expanded into Scheme 4.

Considering that our current reaction is involved in not only polar reagents but also strong acid, a radical intermediate mechanism is quite unlikely. The arenium cation mechanism may be also applicable and responsible to the release of the H^+ proton in the reaction. The proton may activate the Ar–OR on the TP core by the formation of a (Ar–OH–R)⁺ cation as an intermediate while the extra Cl⁻ attacks the –R to form a substitute RCl, leaving Ar–OH behind. As the conjugation in the **TP** core becomes larger, the intermediate cation can be more stabilised, but more substituted groups drop off to form **TP**–OH during the hydrolysis process. The cleavage of the ether group may be illustrated as shown in Scheme 5.

Triphenylene is a popular discotic liquid crystalline functional organic. To add functionality to the **TP** core, unsymmetrically substituted structures are unavoidable. Mono-hydroxy-penta-alk-oxytriphenylene (**MHT**) is a key intermediate with a functional hydroxyl linking group, which is particular useful in asymmetric synthesis and novel organic electronic material development. However, for a long time the synthesis of **MHT** has proven either complicated, involving multiple steps of synthesis, or with a very low yield via a one-step reaction. This has considerably limited its applications and therefore has become the focus of many investigations.^{26,27,31}

Table	2
-------	---

Exploring the functionalities of FeCl₃ and acid

Test	Reactions	Observation
1	(a) 1 equiv HAT6 with 3 equiv concd H_2SO_4 only	No hydrolysis observed
	(b) 1 equiv HAT6 with 6 equiv concd HCl only	Trace ($\sim 1\%$) hydrolysis observed
2	1 equiv HAT6 with 30 equiv $FeCl_3$ only	No hydrolysis observed. A small portion will turn to more complicated mixtures when prolonging the reaction
3	(a) 1 equiv HAT6 with 30 equiv FeCl ₃ plus 3 equiv concd H ₂ SO ₄ (b) 1 equiv HAT6 with 30 equiv FeCl ₃ plus 6 equiv concd HCl	Hydrolysis occurred which can be controlled to produce a relatively high yield of MHTG (\sim 60%) Low yield \sim 10% hydrolysis observed

W. Xiao et al./Tetrahedron Letters xxx (2015) xxx-xxx



Scheme 5. A schematic mechanism on the formation of MHT.

A number of methods have been developed to synthesise **MHTs** and can be summarised in Scheme 6: **Ia** non-selective^{31,32} or **Ib** selective³³ cleavage of alkoxytriphenylene; **II** cross-coupling between a 3,3',4,4'-tetra-alkoxybiphenyl and a 1,2-disubstituted benzene;^{15,29} **III** cross-coupling of a mixture of 1,2-dialkoxybenzene and 2-alkoxyphenol;^{27,28} **IV** one-step trimerisation of dialkoxybenzene.^{15,26}

Among these methods, routes Ia, Ib and II can be high-yield reactions, but they are less advantageous due to the reactions involving multisteps to synthesise the starting materials. This made the synthetic procedures laborious and time-consuming. Although route **IV** appears to be a simple and straightforward reaction, it has suffered from a very low reaction yield in the past. The only example that broke the 20% limit was reported by Kumar using a butyl-substituted reactant and achieved 25% MHT product mediated by MoCl₅.¹⁵ Due to the low yield of the reaction, route **IV** is practically not feasible as a synthetic method in the past. Route III is in fact a modified approach to route IV aiming to improve the yield of MHT on a statistical account. It did enhance the yield, but not significantly. In the literature, the best yield of MHT via route III was 35% by that time.²⁷ Our Current work achieved a significant breakthrough into a new record by route IV. The impressively high vield of reaction (>60%) in synthesis of MHT by only one-step is by far the highest ever reported to date.

A simple reaction route with a high enough yield of the reaction is an important issue to scale up synthetic quantity in supporting novel material developments. Current result is very exciting as it allows synthesis of this important intermediate at a multi-gram scale, which is one-step forwards to a large scale production. The breakthrough in **MHT** synthesis may push forwards in novel organic electronic material developments and their further applications in optoelectronic devices.



Conclusions

In summary, a novel and simple one-step reaction has been discovered. The new reaction is able to synthesise mono-hydrolysed triphenylene (**MHT**) simply from 1,2-dialkoxybenzene at a good yield up to 65%. The new reaction goes through two stages: the coupling stage where hexa-alkoxy substituted triphenylene (**HAT**) was evolved and the second stage in which the hydrolysed **MHT** product was formed. Our work reveals that FeCl₃ plays dual functions: an oxidative reagent in the coupling stage and a catalyst in the hydrolysis stage. The ratio of FeCl₃ to the starting materials is the key in control of the reaction product. Both FeCl₃ and the coupling-released acid are responsible for the hydrolysis reaction. An arenium cation is proposed as the intermediate.

Current work challenged our common knowledge of the Scholl coupling reaction. It offers us a chance to understand this reaction further. At the same time, the reaction reported here offers a novel route to synthesise mono-hydrolysed triphenylenes and maybe other arenes in a convenient way at multigram scale.

Acknowledgments

Authors would like to express their thanks to the support from the Chemical Analysis Centre at the Peking University. This work was funded by NNSF China (21174016, 11474017), RFDP (20120009110031).

Supplementary data

Supplementary data (synthetic procedures of compounds described in this work and the characterisations) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.12.070.

References and notes

- 1. Scholl, R.; Mansfeld, J. Ber. Dtsch. Chem. Ges. 1910, 43, 1734–1746.
- Scholl, R.; Seer, C.; Weitzenbök, R. *Ber. Dtsch. Chem. Ges.* 1910, *43*, 2202–2209.
 (a) Baddeley, G.; Kenner, J. *J. Chem. Soc.* 1935, 303–309; (b) Baddeley, G. *J. Chem.*
- Soc. 1950, 994–997.
 (a) Simons, J. H.; McArthur, R. E. *J. Ind. Eng. Chem.* 1947, *39*, 364–367; (b) Tinker, J. M.; Weinmar, V. M.; Linch, A. L. U.S. Patent 2,258,394, 1941.
- M., Weinnar, V. M., Ench, A. E. O.S. Patent 2,238,334, 1341.
 Nenitzescu, C. D.; Balaban, A. T. Chem. Ber. 1958, 91, 2109–2116.
- Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. Angew. Chem., Int. Ed. 2013, 52, 9900–9930.
- Boden, N.; Bushby, R. J.; Lu, Z.; Headdock, G. Tetrahedron Lett. 2000, 41, 10117– 10120
- Nishinaga, A.; Hayashi, H.; Matsuura, T. Bull. Chem. Soc. Jpn. 1974, 47, 1813– 1814.
- Hohnholz, D.; MacDiarmid, A. G.; Sarno, D. M.; Jones, W. E., Jr. Chem. Commun. 2001, 2444–2445.
- 10. Sarhanw, A. A. O.; Bolm, C. Chem. Soc. Rev. 2009, 38, 2730–2744.
- (a) Boden, N.; Bushby, R. J.; Cammidge, A. N. J. Chem. Soc., Chem. Commun. 1994, 465–466; (b) Boden, N.; Bushby, R. J.; Cammidge, A. N.; Headdock, G. Synthesis 1995, 31–32.
- (a) Naarmann, H.; Hanack, M.; Mattmer, R. Synthesis 1994, 477–478; (b) Matheson, I. M.; Musgrave, O. C.; Webster, C. J. Chem. Commun. (London) 1965, 278–279; (c) Musgrave, O. C. Chem. Rev. 1969, 69, 499–531.
- 13. Wadumethrige, S. H.; Rathore, R. Org. Lett. 2008, 10, 5139–5142.

6

W. Xiao et al./Tetrahedron Letters xxx (2015) xxx-xxx

- Boden, N.; Borner, R. C.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. Liq. Cryst. 1993, 15, 851–858.
- 15. Kumar, S.; Manickam, M. Chem. Commun. 1997, 1615–1616.
- Bengs, H.; Karthaus, O.; Ringsdorf, H.; Baehr, C.; Ebert, M.; Wendorff, J. H. *Liq. Cryst.* **1991**, *10*, 161–168.
- 17. Bai, W.; Lin, J. Synth. Commun. 2011, 41, 903-906.
- (a) Cammidge, A. N.; Bushby, R. J. In Handbook of Liquid Crystals, Vol. 28: Synthesis and Structural Features; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 2011; pp 693–748; (b) Kumar, S. Liq. Cryst. 2004, 31, 1037–1059; (c) Kumar, S. Chemistry of Discotic Liquid Crystals: From Monomers to Polymers; CRC Press: Boca Raton, 2011.
- 19. Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* 1994, 371, 141–143.
- 20. Pérez, D.; Guitián, E. Chem. Soc. Rev. 2004, 33, 274–283.
- 21. Kumar, S. Liq. Cryst. 2005, 32, 1089–1113.
- 22. (a) Mao, H.; He, Z.; Wang, J.; Zhang, C.; Xie, P.; Zhang, R. J. Luminescence 2007, 122–123, 942–945; (b) Li, J.; He, Z.; Gopee, H.; Cammidge, A. N. Org. Lett. 2010, 12, 472–475; (c) Kaller, M.; Deck, C.; Meister, A.; Hause, G.; Baro, A.; Laschat, S. Chem. Eur. J. 2010, 16, 6326–6337.

- 23. Kong, X.; He, Z.; Zhang, Y.; Mu, L.; Liang, C.; Chen, B.; Jing, X.; Cammidge, A. N. Org. Lett. 2011, 13, 764–767.
- 24. Stewart, D.; McHattie, G. S.; Imrie, C. T. J. Mater. Chem. 1998, 8, 47-51.
- (a) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* 2007, 36, 1902–1929;
 (b) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* 2007, 46, 4832–4887.
- 26. Kumar, S.; Lakshmi, B. Tetrahedron Lett. 2005, 46, 2603–2605.
- 27. Kong, X.; He, Z.; Gopee, H.; Jing, X.; Cammidge, A. N. Tetrahedron Lett. 2011, 52, 77–79.
- Schulte, J. L.; Laschat, S.; Vill, V.; Nishikawa, E.; Finkelmann, H.; Nimtz, M. Eur. J. Org. Chem. 1998, 2499–2506.
- 29. Bushby, R. J.; Lu, Z. Synthesis 2001, 763–767.
- 30. Burwell, R. L. Chem. Rev. 1954, 54, 615–685.
- 31. Pal, S. K.; Bisoyi, H. K.; Kumar, S. Tetrahedron 2007, 63, 6874-6878.
- 32. Kumar, S.; Manickam, M. Synthesis 1998, 1119–1122.
- (a) Henderson, P.; Ringsdorf, H.; Schuhmacher, P. *Liq. Cryst.* 1995, *18*, 191–195;
 (b) Boden, N.; Bushby, R. J.; Cammidge, A. N.; El-Mansoury, A.; Martin, P. S.; Lu, Z. J. Mater. Chem. 1999, *9*, 1391–1402.