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Synthesis of Bridged Oligophenylenes from Fluorene. Part 2.[1] Quinquiphenyls to Deciphenyls

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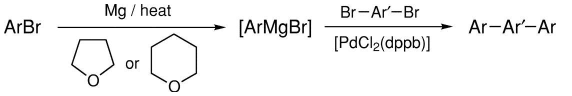
Organometallic derivatives of aryl bromides **2a**–**10a** have been coupled with aryl dihalides **11**–**16** in the presence of $PdCl_2$(dppb) catalyst to produce symmetrical bridged oligophenylenes **17**–**31** and **33** that contain five to ten conjugated benzene rings with one to four dialkylmethylene bridges; these products show useful solubility, high quantum efficiency of fluorescence and good photochemical stability.

We have recently reported the preparation of derivatives of *p*-oligophenylenes **1** ($n = 3$, 4), in which one or two dialkylmethylene bridges have been introduced between adjacent benzene rings.[1] These bridged oligophenylenes showed substantially greater solubility in common organic solvents than their unbridged counterparts **1**. Earlier studies of higher oligophenylenes **1** ($n > 4$) reported the wavelengths of absorption and fluorescence of quinqui-, sexi- and octiphenyls solubilized by multi-alkyl substitutions.[3,4] It was noted that alkyl substitution on internal rings or in *ortho*-positions on terminal rings shifted the absorption and fluorescence maxima to shorter-than-expected wavelengths by preventing coplanarity of adjacent benzene rings.[3,5] Higher oligophenylenes **1** ($n = 7$, 9, 10 and 15) recently synthesized by Suzuki coupling required the solubilizing effects of pairs of long-chain alkyl substituents on internal rings for their synthesis.[6] We have previously reported that bridged oligophenylenes (fluorenes) that contain 5–10 conjugated benzene rings show both enhanced solubility and increased wavelengths of absorption and fluorescence with high quantum efficiencies.[13] Herein we report the syntheses of these highly stable fluorene derivatives, which exhibit major fluorescence bands in the visible (395–430 nm).[13]

Our synthetic strategy for the preparation of bridged oligophenylenes involved the conversion of bromobenzenes **2a**–**6a** or bromofluorenes **7a**–**10a** into their corresponding arylmagnesium bromide derivatives or through their organolithium derivatives into organozinc halides. The bisfuran **32** was regiospecifically metallated[11] by Bu^{t}Li and converted into its organozinc derivative with $ZnCl_2$. Excess Grignard reagents or the organozinc halides in cyclic ether solvents were then coupled[1,12] (at 25–90 °C) with the aryl dihalides **11**–**16** in the presence of 0.25–1.0 mol% of the air-stable 1,4-(diphenylphosphino)butane/Pd^{II} complex, $PdCl_2$(dppb), as shown in eqn. (1). Some of the less-reactive bromoarenes formed Grignard reagents faster in tetrahydropyran (THP). The only significant co-products were the result of homocoupling reactions occurring during Grignard formation.



(1)

Standard work-ups[1] gave the bridged oligophenylene products **17**–**31** and **33**, which were purified in an Ace–Kauffman extractor[1] and then were recrystallised. Structures were confirmed by elemental assays and, for most compounds, by ^1H NMR spectra (300 MHz), the chemical shifts of aromatic H atoms were identified from COSY spectra. The absorption and fluorescence data reported earlier for **17**–**19**, **21a**, **22**–**31** and **33** confirmed[13] the all-*para* regiochemistry of the bridged oligophenylenes (*see* Scheme 1 opposite).

Techniques used: ^1H NMR and elemental analysis

References: 19

Table 1: Chemical shifts and coupling constants for **22**, **26**, **28**, **29** and **31**

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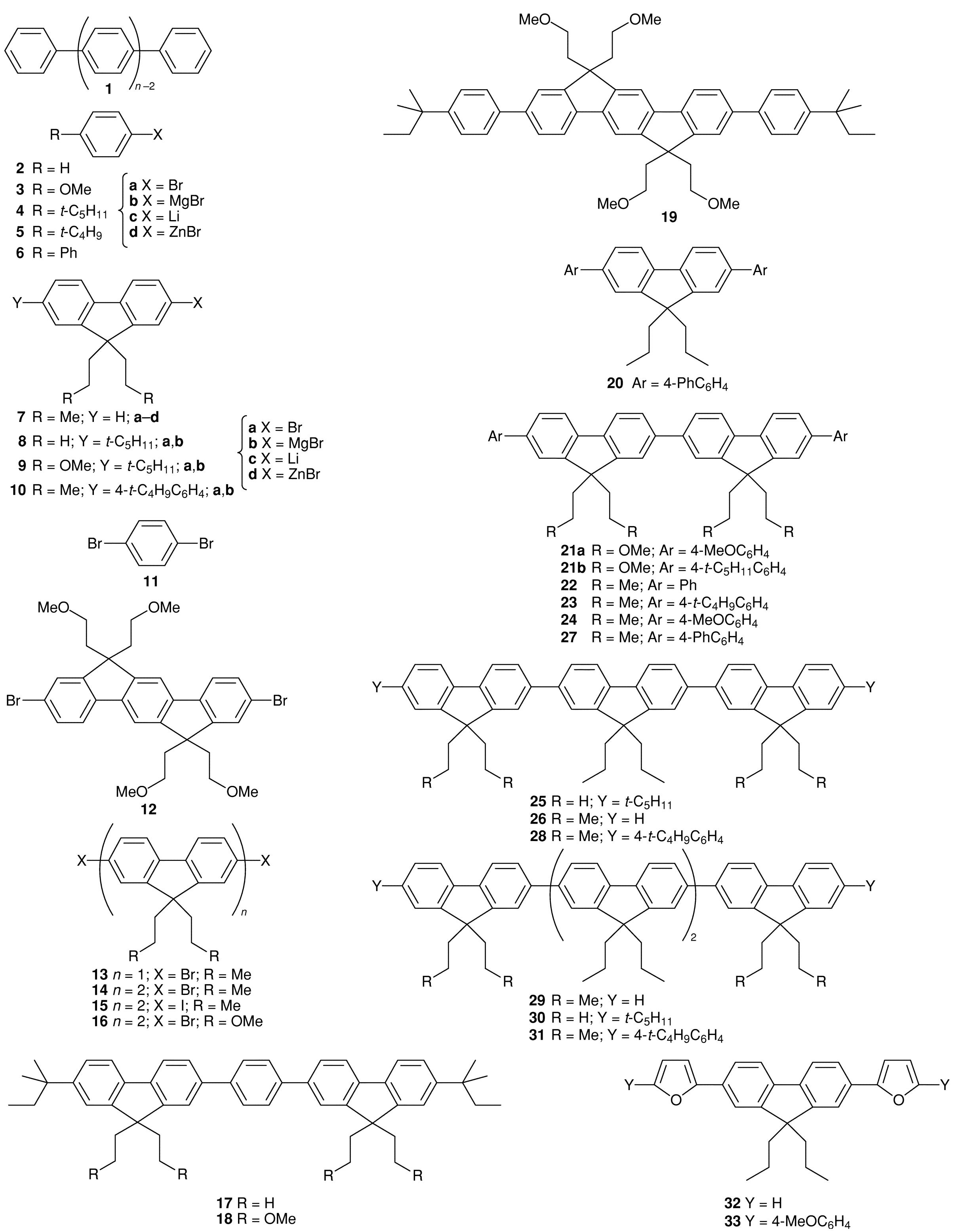

1

2 R = H
3 R = OMe
4 R = t-C_5H_{11}
5 R = t-C_4H_9
6 R = Ph
a X = Br
b X = MgBr
c X = Li
d X = ZnBr

7 R = Me; Y = H; **a**–**d**
8 R = H; Y = t-C_5H_{11}; **a**,**b**
9 R = OMe; Y = t-C_5H_{11}; **a**,**b**
10 R = Me; Y = 4-t-$C_4H_9C_6H_4$; **a**,**b**
a X = Br
b X = MgBr
c X = Li
d X = ZnBr

11

12

13 n = 1; X = Br; R = Me
14 n = 2; X = Br; R = Me
15 n = 2; X = I; R = Me
16 n = 2; X = Br; R = OMe

17 R = H
18 R = OMe

19

20 Ar = 4-PhC_6H_4

21a R = OMe; Ar = 4-$MeOC_6H_4$
21b R = OMe; Ar = 4-t-$C_5H_{11}C_6H_4$
22 R = Me; Ar = Ph
23 R = Me; Ar = 4-t-$C_4H_9C_6H_4$
24 R = Me; Ar = 4-$MeOC_6H_4$
27 R = Me; Ar = 4-PhC_6H_4

25 R = H; Y = t-C_5H_{11}
26 R = Me; Y = H
28 R = Me; Y = 4-t-$C_4H_9C_6H_4$

29 R = Me; Y = H
30 R = H; Y = t-C_5H_{11}
31 R = Me; Y = 4-t-$C_4H_9C_6H_4$

32 Y = H
33 Y = 4-$MeOC_6H_4$

Scheme 1

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