# Palladium-catalysed Coupling of Trialkylstannyltetrathiafulvalenes with Aryl Halides

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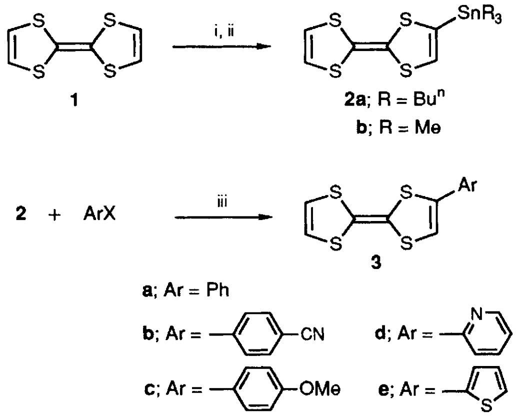
Trialkylstannyltetrathiafulvalenes undergo palladium-catalysed cross- and homo-coupling reactions to give aryl-substituted tetrathiafulvalenes and bitetrathiafulvalene; the methodology has been applied to the synthesis of *p*-phenylenebistetrathiafulvalene and 2,5-thiophenediylbistetrathiafulvalene.

Although tetrathiafulvalene (TTF) **1** is of great importance as a π-electron donor in organic conductors, the methodology for preparing monofunctionalized TTF derivatives is still very limited. We now describe a novel method for the preparation of aryl-substituted tetrathiafulvalenes consisting of the synthesis of trialkylstannyl-TTF **2** followed by the palladium-catalysed coupling of **2** with aryl halides.

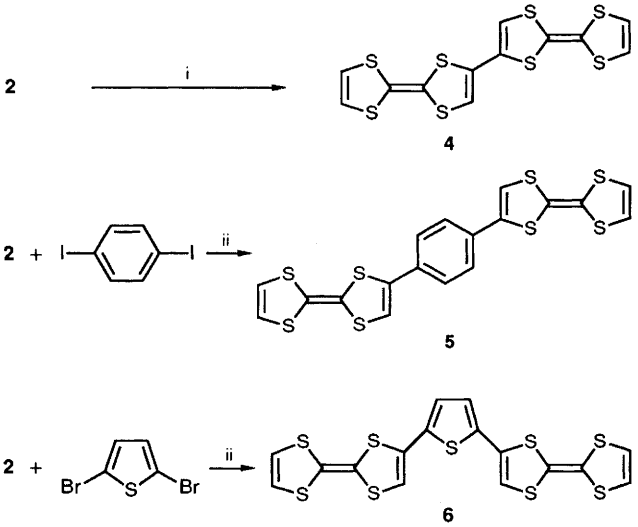
The TTF monoanion, which can be easily prepared from TTF with butyllithium or lithium diisopropylamide, is known to disproportionate even at low temperature.[1] Therefore, monometalated TTF derivatives are usually difficult to employ directly for cross-coupling reactions with organic halides. However, monotrialkyltin-substituted derivatives of TTF can be prepared and employed for palladium-catalysed coupling reactions.

Trialkylstannyltetrathiafulvalenes **2** can be prepared from monolithiated TTF with trialkyltin chloride. Thus, reaction of TTF with 1 equiv. of buthyllithium, followed by treatment with tributyl- or trimethyl-tin chlorides gave **2a** and **2b** in 75 and 85% yields, respectively. Tributylstannyl-TTF **2a** can be isolated by column chromatography on deactivated alumina (activity: V). However, trimethylstannyl-TTF **2b** was obtained as a mixture containing a small amount of TTF, after column chromatography on deactivated alumina. Therefore, a mixture containing over 90% of **2b** was used for further reactions.

A typical procedure for the palladium-catalysed cross-coupling reaction[2] involves reaction of aryl halide (1 equiv.) with trialkylstannyl-TTF **2** (1 equiv.) in the presence of $Pd(PPh_3)_4$ (0.1 equiv.) in refluxing toluene. The product **3** are



**Scheme 1** *Reagents and conditions*: i, butyllithium, THF, −78 °C; ii, $R_3SnCl$ then −78 °C, room temperature, 3 h; iii, $Pd(PPh_3)_4$, toluene, reflux



**Scheme 2** *Reagents and conditions*: i, $PdCl_2(CH_3CN)_2$, HMPA, room temperature; ii, $Pd(PPh_3)_4$, toluene, reflux

**Table 1** Reaction of trialkylstannyl-TTF derivatives **2** with the aryl halides in the presence of $Pd(PPh_3)_4$

| Reagent | Aryl halide | Time/h | Yield[a] (%) | Product |
|---|---|---|---|---|
| **2b** | Iodobenzene | 3 | 67 | **3a** |
| **2b** | Bromobenzene | 5 | 59 | **3a** |
| **2a** | Iodobenzene | 5 | 53 | **3a** |
| **2b** | *p*-Bromobenzonitrile | 3 | 98 | **3b** |
| **2a** | *p*-Bromobenzonitrile | 5 | 95 | **3b** |
| **2b** | *p*-Iodoanisole | 5 | 33 | **3c** |
| **2b** | 2-Bromopyridine | 4 | 82 | **3d** |
| **2a** | 2-Bromopyridine | 6 | 57 | **3d** |
| **2b** | 2-Bromothiophene | 3 | 62 | **3e** |

[a] Isolated yield.

purified by column chromatography on alumina (activity: III). As shown in Table 1, the reaction of iodobenzene (1 equiv.) with trimethylstannyl-TTF **2b** (1 equiv.) in refluxing toluene produces **3a**[3] in 67% yield, whereas the palladium-catalysed reaction of both bromobenzene with **2b** and iodobenzene with **2a** gave **3a** in somewhat lower yields. The presence of electron-withdrawing groups on the aryl halide raises the yield of cross-coupling reactions. Thus, the palladium-catalysed reaction of *p*-bromobenzonitrile with **2a** and **2b** produces **3b** in 98 and 95% yields, respectively. However, the similar cross-coupling of *p*-iodoanisole with **2b** affords **3c** only in 33% yield. Interestingly, the palladium-catalysed coupling of 2-bromopyridine with **2b** produces **3d** in 82% yield, whereas the similar reaction with **2a** gives **3d** in only 57% yield. The coupling reaction of 2-bromothiophene with **2b** under the same conditions also gives the coupling product **3e** in 62% yield.

**Table 2** Cyclic voltammetric[a] and melting-point data data for TTF derivatives

| Compound | $E_1^{\frac{1}{2}}$/V | $E_2^{\frac{1}{2}}$/V | M.p./°C |
|---|---|---|---|
| TTF | 0.36 | 0.74 | |
| **3a** | 0.38 | 0.80 | 79.5–81 (lit.[3]; 78–81) |
| **3b** | 0.47 | 0.87 | 210.5–213 (decomp.) |
| **3c** | 0.38 | 0.80 | 160–162 (decomp.) |
| **3d** | 0.39 | 0.85 | 173–175 |
| **3e** | 0.41 | 0.80 | 79–80 |
| **4** | 0.43 | 0.84 | 225–226 (decomp.) |
| **5** | 0.35 | 0.82 | 237–239 (decomp.) (lit.[5]; 241.9–242.4) |
| **6** | 0.38 | 0.81 | 212–214 (decomp.) |

[a] *Experimental conditions*: $NBu_4^+$ $ClO_4^-$ (0.1 mol dm$^{-3}$) in dry benzonitrile under argon at 20 °C, *vs.* Ag/Ag Cl, Pt electrode.

Furthermore, the palladium-catalysed homo-coupling of **2** occurs using $PdCl_2(CH_3CN)_2$ in hexamethylphosphoric triamide (HMPA).[4] Thus, the reactions of **2a** and **2b** in the presence of 0.5 equiv. of $PdCl_2(CH_3CN)_2$ in HMPA at room temperature produces bitetrathiafulvalene **4** in 25 and 62% yields, respectively. As to the palladium-catalysed couplings, trimethylstannyl derivative always gives better results than the tributylstannyl derivatives.

The palladium-catalysed coupling described in this paper can be employed for the synthesis of useful TTF derivatives. Thus, the reaction of *p*-diiodobenzene with 2 equiv. of **2b** in the presence of 0.2 equiv. of $Pd(PPh_3)_4$ in refluxing toluene resulted in the formation of *p*-phenylenebistetrathiafulvalene **5**[5] in 61% yield. In a similar manner, the cross-coupling of 2,5-dibromothiophene with 2 equiv. of **2b** in the presence of $Pd(PPh_3)_4$ (0.2 equiv.) produces the corresponding coupling product **6** in 52% yield.

Upon electrochemical oxidation (cyclic voltammetry, Table 2), aryltetrathiafulvalenes **3** show similar $E_1^{\frac{1}{2}}$-values except for **3b**, in which the presence of an electron-withdrawing cyano group increases the ionization potential. As has been reported previously, tetramethylthiobitetrathiafulvalene shows three redox waves.[6] However, **4** exhibits two redox waves corresponding to two two-electron transfers. Interestingly, **5** and **6** also show only two oxidation waves. Therefore, the compounds **4**–**6** are oxidized by two two-electron steps.

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