

Palladium-catalysed Coupling of Trialkylstannyltetrathiafulvalenes with Aryl Halides

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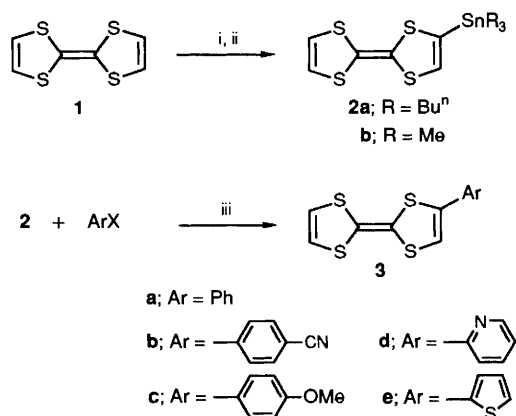
Trialkylstannyltetrathiafulvalenes undergo palladium-catalysed cross- and homo-coupling reactions to give aryl-substituted tetrathiafulvalenes and bitetrathiafulvalene; the methodology has been applied to the synthesis of *p*-phenylenebistetrathiafulvalene and 2,5-thiophenediylbistetrathiafulvalene.

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.

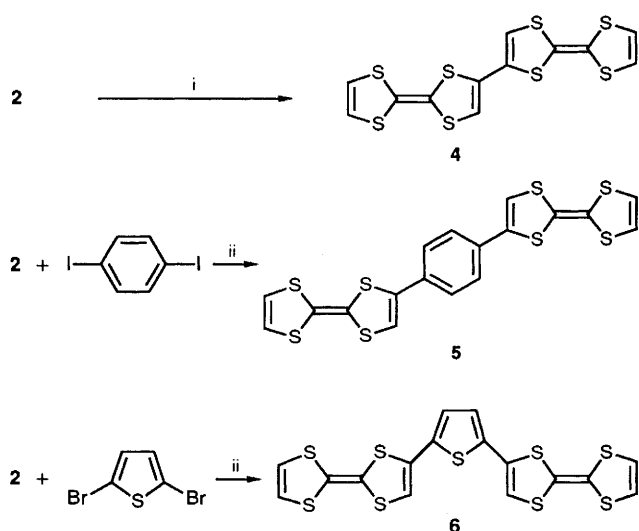
The TTF monoanion, which can be easily prepared from TTF with butyllithium or lithium diisopropylamide, is known to disproportionate even at low temperature.¹ Therefore, monometalated TTF derivatives are usually difficult to employ directly for cross-coupling reactions with organic halides. However, 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 butyllithium, 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 reaction² involves reaction of aryl halide (1 equiv.) with trialkylstannyl-TTF **2** (1 equiv.) in the presence of Pd(PPh₃)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, $\text{Pd}(\text{PPh}_3)_4$, toluene, reflux



Scheme 2 Reagents and conditions: i, $\text{PdCl}_2(\text{CH}_3\text{CN})_2$, HMPA, room temperature; ii, $\text{Pd}(\text{PPh}_3)_4$, toluene, reflux

Table 1 Reaction of trialkylstannyl-TTF derivatives **2** with the aryl halides in the presence of $\text{Pd}(\text{PPh}_3)_4$

| Reagent | Aryl halide | Time/h | Yield ^a (%) | Product |
|-----------|-----------------------------|--------|------------------------|-----------|
| 2b | Iodobenzene | 3 | 67 | 3a |
| 2b | Bromobenzene | 5 | 59 | 3a |
| 2a | Iodobenzene | 5 | 53 | 3a |
| 2b | <i>p</i> -Bromobenzonitrile | 3 | 98 | 3b |
| 2a | <i>p</i> -Bromobenzonitrile | 5 | 95 | 3b |
| 2b | <i>p</i> -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

Table 2 Cyclic voltammetric^a and melting-point data data for TTF derivatives

| Compound | $E_1^{1/2}/\text{V}$ | $E_2^{1/2}/\text{V}$ | M.p./ $^{\circ}\text{C}$ |
|-----------|----------------------|----------------------|---|
| 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: $\text{NBu}_4^+ \text{ClO}_4^-$ (0.1 mol dm^{-3}) in dry benzonitrile under argon at 20°C , vs. Ag/AgCl, Pt electrode.

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.

Furthermore, the palladium-catalysed homo-coupling of **2** occurs using $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ in hexamethylphosphoric triamide (HMPA).⁴ Thus, the reactions of **2a** and **2b** in the presence of 0.5 equiv. of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ 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 $\text{Pd}(\text{PPh}_3)_4$ 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 $\text{Pd}(\text{PPh}_3)_4$ (0.2 equiv.) produces the corresponding coupling product **6** in 52% yield.

Upon electrochemical oxidation (cyclic voltammetry, Table 2), aryltetrathiafulvalenes **3** show similar $E_1^{1/2}$ -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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