

Short Note

3,5-Bis(4-dodecylthiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one

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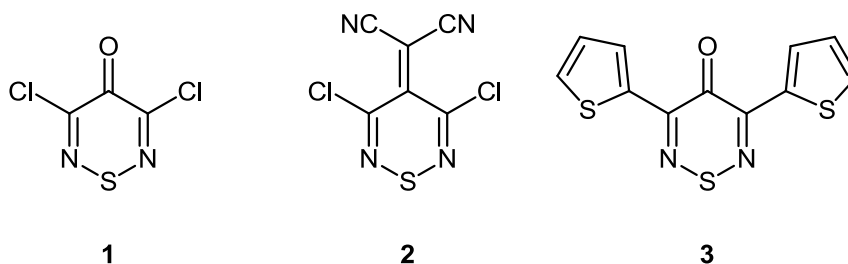
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Abstract: 3,5-Dichloro-4*H*-1,2,6-thiadiazin-4-one **1** reacts with (4-dodecylthiophen-2-yl)trimethylstannane **4** (2.2 equiv.) and Pd(Ph₃P)₂Cl₂ (5 mol%) in acetonitrile at *ca.* 82 °C to give 3,5-bis(4-dodecylthiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one **5** in 93% yield.

Keywords: 1,2,6-thiadiazines; thiophenes; heterocycles; oligomers

Surprisingly little has appeared in the literature on nonoxidized 4*H*-1,2,6-thiadiazines. Monocyclic 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one **1** [1] and its 4-dicyanomethylene analogue 2-(3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)malononitrile **2** [2,3] have been prepared (Scheme 1), the former in two steps starting from dichloromalononitrile and the latter in one step from tetracyanoethylene (TCNE). Both are useful precursors to several polycyclic 1,2,6-thiadiazine systems [4,5]. For several years now we have been developing the chemistry of both these heterocyclic scaffolds [2–10].

Scheme 1. Structures of 4*H*-1,2,6-thiadiazines **1–3**.

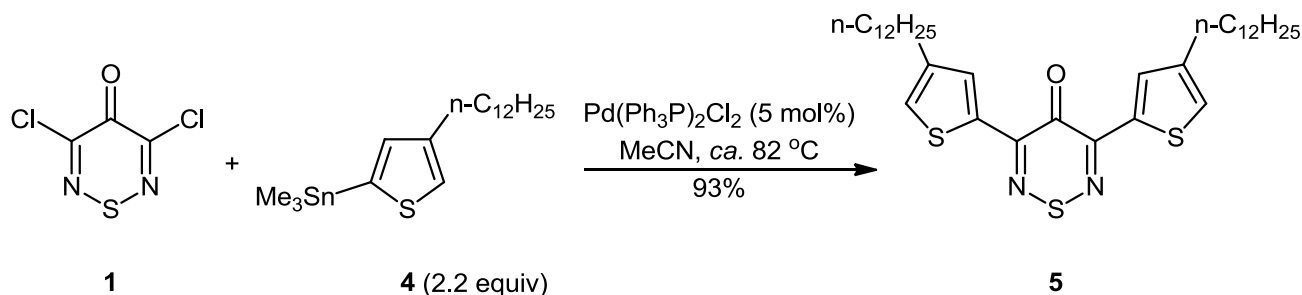


Recently, we described the palladium catalysed Suzuki and Stille coupling reactions of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one **1** which enabled the preparation of symmetrical biaryl and biheteroarylthiadiazinones such as 3,5-di(thiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one **3** [7] (Scheme 1). Based on this structural unit we postulated the construction of conjugated polymers such as the

thiophene/thiadiazinone polymers. To achieve this we required access to thiophene substituted thiadiazinone with solubilizing alkyl chains, as such; the synthesis of 3,5-bis(4-dodecylthiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one **5** was targeted.

The reaction of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one **1** with (4-dodecylthiophen-2-yl)trimethylstannane **4** (2.2 equiv.) in the presence of Pd(Ph₃P)₂Cl₂ (5 mol%) proceeded smoothly in acetonitrile at ca. 82 °C to give 3,5-bis(4-dodecylthiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one **5** in 93% yield (Scheme 2).

Scheme 2. Synthesis of 3,5-bis(4-dodecylthiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one **5**.



Experimental

Acetonitrile was distilled from CaH₂ and stored over 4 Å molecular sieves. The reaction mixture and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F₂₅₄). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used using Merck Silica Gel 60 (less than 0.063 mm). Melting points were determined using a PolyTherm-A, Wagner & Munz, Kofler-Hotstage Microscope apparatus. IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with Pike Miracle Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w respectively. ¹H-NMR spectra were recorded on a BrukerAvance 500 machine at 500 MHz, while ¹³C-NMR spectra were recorded at 125 MHz. Deuterated chloroform was used for homonuclear lock and the signals are referenced to the deuterated solvent peak. Low resolution (EI) mass spectrum was recorded on a Shimadzu Q2010 GCMS with direct inlet probe. Microanalysis was performed at London Metropolitan University on a Perkin Elmer 2400 Series II CHN Analyzer.

3,5-Bis(4-dodecylthiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one (5). To a solution of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one **1** (50 mg, 0.273 mmol) in MeCN (2 mL) at ca. 20 °C, were added (4-dodecylthiophen-2-yl)trimethylstannane **4** (249 mg, 0.60 mmol) and Pd(Ph₃P)₂Cl₂ (9.6 mg, 0.014 mmol) and the reaction was heated at reflux until no starting material remained (TLC). The reaction mixture was then left to cool to ca. 20 °C, diluted (DCM) and adsorbed onto silica. Chromatography (hexane/DCM, 7:3) gave the *title compound* **5** (156 mg, 93%) as yellow needles, m.p. 65.5–67 °C (from *n*-pentane); *R*_f 0.70 (hexane/DCM, 7:3); (found: C, 68.4; H, 8.8; N, 4.5. C₃₅H₅₄N₂OS₃ requires C, 68.4; H, 8.9; N, 4.6%); λ_{max}(DCM)/nm 229 (log ε 3.40), 265 (3.59), 356 inf (3.36), 382 (3.65), 399 inf (3.75), 415 (3.82), 439 (3.81); ν_{max}/cm⁻¹ 2955w, 2918s, 2851m, 1616m, 1464m, 1412m, 1393w, 1341w, 1250w, 1236w, 1225w, 1200w, 1188w, 1103w, 953w, 876w, 864m, 816w, 791w, 764w; δ_H (500 MHz; CDCl₃) 8.11 (1H, s, thienyl *H*), 7.24 (1H, s, thienyl *H*), 2.67–2.62 (2H, m), 1.26 (20H, br s), 0.88 (3H, t, *J* 11.0,

CH_3); δ_{C} (125 MHz; CDCl_3) one carbon (t) resonance missing 161.5 (s), 153.9 (s), 144.2 (s), 136.3 (s), 133.3 (d), 128.6 (d), 31.91 (t), 30.5 (t), 30.4 (t), 29.7 (t), 29.65 (t), 29.6 (t), 29.4 (t), 29.35 (t), 29.3 (t), 22.7 (t), 14.1 (q, CH_3); m/z (EI) 615 ($\text{M}^+ + 1$, 41%), 614 (M^+ , 100), 460 (24), 306 (10), 276 (7), 168 (5), 155 (10), 149 (13), 137 (10), 125 (11), 122 (43), 111 (16), 109 (14), 97 (29), 95 (19), 83 (22), 71 (28), 57 (49).

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