

Short Note

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

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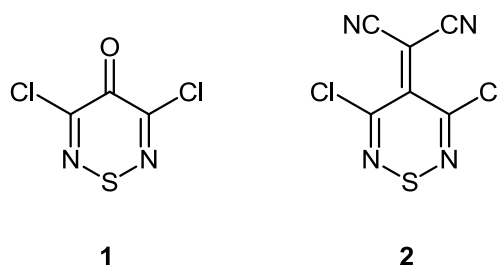
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Abstract: 3-Chloro-5-trifluoromethanesulfonate-4*H*-1,2,6-thiadiazin-4-one **3** reacts with (4-dodecylthiophen-2-yl)trimethylstannane **5** (1 equiv.) in the presence of Pd(Ph₃P)₂Cl₂ (5 mol%) in benzene at *ca.* 20 °C for 5 h to give 3-chloro-5-(4-dodecylthien-2-yl)-1,2,6-thiadiazinone **6** in 87% 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].

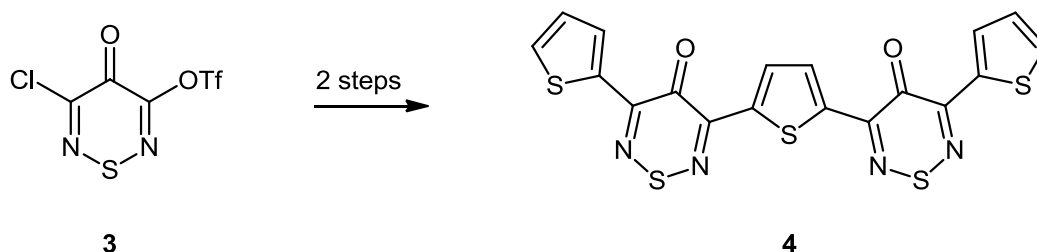
Scheme 1. Structures of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one **1** and 2-(3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)malononitrile **2**.



Recently, we described the chemoselective Stille reactions of 3-chloro-5-trifluoromethanesulfonate-4*H*-1,2,6-thiadiazin-4-one **3** which enabled the preparation of unsymmetrical biheteroaryl

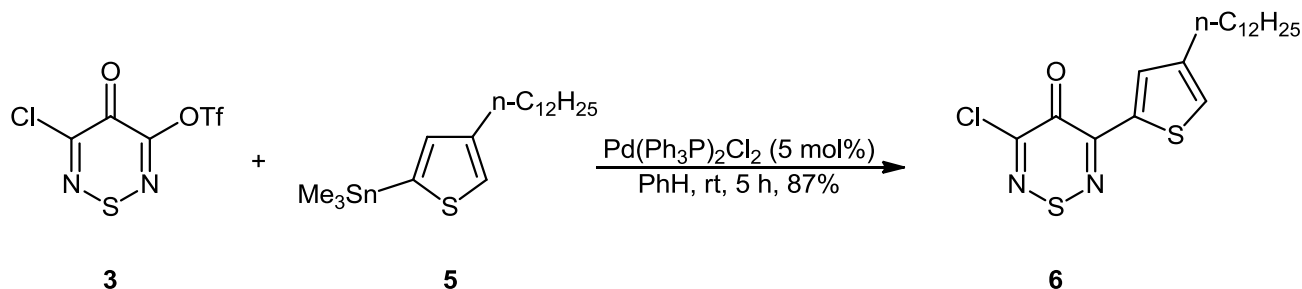
thiadiazinones and oligomers such as 5,5'-(thiophene-2,5-diyl)bis[3-(thiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one] **4** (Scheme 2) [8]. This potentially useful pentamer for optoelectronic materials was unfortunately poorly soluble, as such; the synthesis of an analogue bearing alkyl chains was targeted. To achieve this we required a high yielding synthesis of a alkylthiophene substituted 3-chloro-1,2,6-thiadiazin-4-one.

Scheme 2. Preparation of 5,5'-(thiophene-2,5-diyl)bis[3-(thiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one] **4** from 3-chloro-5-trifluoromethanesulfonate-4*H*-1,2,6-thiadiazin-4-one **3**.



The reaction of 3-chloro-5-trifluoromethanesulfonate-4*H*-1,2,6-thiadiazin-4-one **3** with (4-dodecylthiophen-2-yl)trimethylstannane **5** (1 equiv.) in the presence of $\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2$ (5 mol%) proceeded smoothly in benzene (PhH) at *ca.* 20 °C for 5 h and the desired product 3-chloro-5-(4-dodecylthiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one **6** was isolated in 87% yield (Scheme 3).

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



Experimental

Benzene and acetonitrile was distilled from CaH_2 , respectively 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 ^{13}C -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-Chloro-5-trifluoromethanesulfonate-4*H*-1,2,6-thiadiazin-4-one **3** [8] and 2-trimethylstannyl-4-dodecylthiophene **5** were prepared according to literature procedures [11].

3-Chloro-5-(4-dodecylthiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one (6). To a stirred solution of 3-chloro-5-trifluoromethanesulfonate-4*H*-1,2,6-thiadiazin-4-one **3** (150 mg, 0.506 mmol) in PhH (4 mL) at *ca.* 20 °C, was added 2-trimethylstannyl-4-dodecylthiophene **5** (210 mg, 0.506 mmol) and Pd(Ph₃P)₂Cl₂ (17.6 mg, 0.025 mmol) and the mixture was stirred until no starting material remained (TLC). The reaction mixture was then adsorbed onto silica and chromatography (hexane/DCM, 7:3) gave the *title compound 6* (175.6 mg, 87%) as yellow needles, m.p. 74–76 °C (from pentane/DCM, 0 °C); *R_f* 0.54 (hexane/DCM, 7:3); (found: C, 57.28; H, 7.00; N, 6.94. C₁₉H₂₇ClN₂OS₂ requires C, 57.19; H, 6.82; N, 7.02%); λ_{max} (DCM)/nm 278 (log ϵ 3.60), 370 (3.99), 385 inf (3.91); ν_{max} /cm⁻¹ 2949w, 2914s, 2847m, 1645s, 1539w, 1464m, 1422m, 1379w, 1314m, 1285m, 1246w, 1196w, 1180m, 1138m, 1082w, 1020w, 986w, 947w, 872w, 860s, 703s; δ_{H} (500 MHz; CDCl₃) 8.11 (1H, d, *J* 1.0 Hz, thienyl *H*), 7.29 (1H, s, thienyl *H*), 2.64 (2H, t, *J* 7.8 Hz), 1.31–1.25 (19H, m), 0.88 (3H, t, *J* 7.0 Hz, CH₃); δ_{C} (125 MHz; CDCl₃) one carbon (t) resonance missing 159.4 (s), 152.9 (s), 150.9 (s), 144.7 (s), 135.6 (s), 134.6 (d), 129.8 (d), 31.9 (t), 30.4 (t), 30.3 (t), 29.7 (t), 29.6 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.2 (t), 22.7 (t), 14.1 (q, CH₃); *m/z* (EI) 400 (*M*⁺+1, 10%), 398 (*M*⁺-1, 24), 365 (4), 309 (3), 276 (3), 257 (5), 246 (42), 244 (100), 155 (6), 122 (30), 97 (12), 93 (10), 55 (10).

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