Pergamon

Tetrahedron Letters 40 (1999) 8611–8613

TETRAHEDRON
LETTERS

Fluorocarbonyltetrathiafulvalene: an effective building block for the production of tetrathiafulvalene esters and amides

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Received 10 August 1999; accepted 22 September 1999

Abstract

4-Fluorocarbonyltetrathiafulvalene has been synthesised under mild conditions, and has been reacted with alcohols and amides to furnish esters and amides in near quantitative yield.

Keywords: tetrathiafulvalene; fluorocarbonyl; esters; amides.

The tetrathiafulvalene (TTF) moiety, by virtue of its ability to become readily oxidised to its radical cationic and dicationic states, has become an ubiquitous π-electron donor moiety for the development of conducting charge–transfer complexes.[1] More recently, attention has focused on utilising this multi-stage redox behaviour as a platform to develop novel sensors and devices.[2] A commonly used intermediate in the synthesis of these systems is 4-chlorocarbonyltetrathiafulvalene, which can upon reaction with alcohols and amines give rise to esters and amides, respectively.[3] The acid chloride has previously been prepared from 4-carboxytetrathiafulvalene **1** and oxalyl chloride in benzene. However, this route is capricious and often gives rise to low yields of the desired acid chloride which is difficult to obtain in an analytically pure form.[4] Furthermore, the yields of TTF esters and amides from this reagent are moderate. Recently, TTF esters have also been prepared in moderate yield from **1** using DCC/DMAP catalysed esterification procedures.[5] TTF amides have also been prepared from 4-lithio-TTF and an appropriate alkyl- and aryl-isocyanate.[6] However, this route is hampered by low yields of products and a limited choice of commercially available isocyanates. To circumvent these problems we have synthesised 4-fluorocarbonyltetrathiafulvalene **2**, which can be prepared in excellent yield and high purity from **1**. Furthermore, we have shown that **2** can react with a variety of alcohols and amines to furnish TTF esters and amides in near quantitative yields.

Reaction of **1** with cyanuric fluoride and pyridine in CH_2Cl_2 reproducibly provides the acid fluoride **2** as a deep red solid in 83% yield (Scheme 1).[7] In contrast to the TTF acid chloride, **2** is prepared

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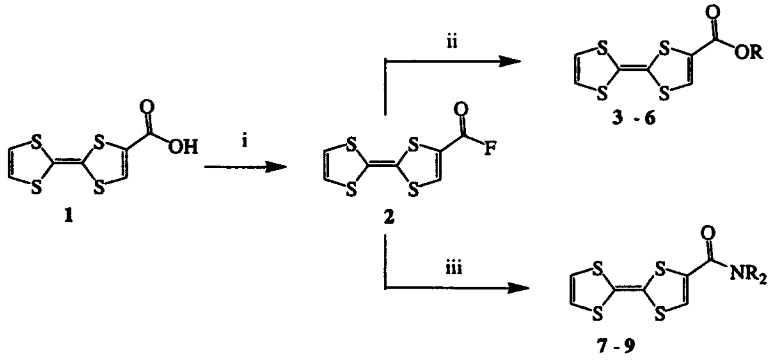
PII: S0040-4039(99)01804-3

under mild conditions and gives rise to material which can readily be purified by recrystallisation or column chromatography. Furthermore, we have established that **2** is shelf-stable, and can be stored at room temperature indefinitely without noticeable decomposition.



Scheme 1. (i) Cyanuric fluoride, pyridine, CH_2Cl_2; (ii) ROH, DMAP; (iii) R_1R_2NH

We have reacted **2** with a range of alcohols to give rise to the TTF esters **3–6**.[8] These reactions were sluggish, however, upon the addition of 4-(dimethylamino)-pyridine (DMAP) high yields of the corresponding esters were obtained (Table 1). The formation of TTF amides from **2** and a range of amines were much more efficient. The reactions were essentially complete within 15 min. Furthermore, the presence of a base was not required for the synthesis of derivatives **7–9**, which alleviates problems associated with base sensitive functionalities and removes the necessity for an aqueous work-up. Poorly nucleophilic aniline reacts sluggishly with **2**, however, the rate of formation of **9** is dramatically increased upon the addition of DMAP.

Table 1
Preparation of TTF esters **3–6** and amides **7–9** from **2**

Product	Alcohol/amine	Time	% Yield	mp /lit. mp (°C)
3	EtOH	12 h	99	79–81 / 79.5–80.5[9]
4	BuOH	12 h	97	72-73 / 72-73[10]
5	PhOH	12 h	95	133 /136
6	$CH_3(CH_2)_{15}OH$	12 h	93	71-72 / 71/72[6]
7	$CH_3(CH_2)_{17}NH_2$	15 min	99	96-99 / 96-99[6]
8	Me_2NH	15 min	98	169-171 / 169-170[10]
9	$PhNH_2$	12 h	97	148-151 / 147-150[6]

In summary, we have shown that **2** is a useful and versatile reagent for the preparation of TTF esters and amides, and provides a versatile building block in the arsenal of methods available to produce functionalised TTF derivatives in high yield. We are currently utilising compound **2** as a material to produce new TTF functionalised molecular and polymeric assemblies.

Acknowledgements

G.C. gratefully acknowledges financial support from the Royal Society of Chemistry and the EPSRC National Mass Spectrometry Service Centre, Swansea, for performing mass spectral analysis on compounds **2–9**.

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7. A suspension of compound **1** (see: Garin, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.; Wegner, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, 491) (1.0 g, 4 mmol) and pyridine (0.65 mL, 8 mmol) in dry CH_2Cl_2 (25 mL) was cooled to 0°C under a nitrogen atmosphere. To this was added cyanuric fluoride (1.44 mL, 8 mmol) and the contents were stirred at 25°C for 90 min, by which time a deep red solution had formed. Water (25 mL) was added, and the organic layer was separated, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was chromatographed (SiO_2, CH_2Cl_2) to afford **2** (0.83 g, 83%) as a deep red solid. Mp 146–148°C. ^1H NMR (270 MHz): 7.60 (s, 1H), 6.34 (s, 2H). MS (EI): 250. Anal. calcd for $C_7H_3FOS_4$: C, 33.60; H, 1.20. Found: C, 33.58; H, 1.25. IR (KBr): 1769 (C=O) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}=478 nm.
8. To a solution of **2** (0.2 mmol) in dry CH_2Cl_2 (5 mL) and DMAP (0.2 mmol) (for the synthesis of esters and **9**) were added the appropriate alcohol or amine (0.2 mmol). The reaction was stirred at room temperature until TLC indicated the reaction was complete (15 min–12 h). The resulting products were purified using flash chromatography.
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