This article was downloaded by: [Purdue University] On: 21 January 2015, At: 13:14 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Synthesis of Monoand Bifunctionalised Tetrathiafulvalene Derivatives using Tetrathiafulvalenyllithiums and the Appropriate p-Toluenesulfonyl Reagent

Graeme Cooke^a

^a School of Chemical Sciences, University of East Anglia, Norwich, Norfolk, NR4 7TJ Published online: 21 Aug 2006.

To cite this article: Graeme Cooke (1996) Synthesis of Mono-and Bifunctionalised Tetrathiafulvalene Derivatives using Tetrathiafulvalenyllithiums and the Appropriate p-Toluenesulfonyl Reagent, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:15, 2917-2923, DOI: <u>10.1080/00397919608005228</u>

To link to this article: <u>http://dx.doi.org/10.1080/00397919608005228</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no

representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

SYNTHESIS OF MONO- AND BIFUNCTIONALISED TETRATHIAFULVALENE DERIVATIVES USING TETRATHIAFULVALENYLLITHIUMS AND THE APPROPRIATE *p*-TOLUENESULFONYL REAGENT.

Graeme Cooke

School of Chemical Sciences, University of East Anglia, Norwich, Norfolk, NR4 7TJ.

Abstract: Tetrathiafulvalenyllithium has been used to synthesise monofunctionalised TTF derivatives using the appropriate p-toluenesulfonyl- reagent. An improved route for forming 4,5-bifunctionalised derivatives is also reported.

At the forefront of recent attention regarding new molecular conductors, has been the synthesis of functionalised tetrathiafulvalene (TTF, 1) derivatives.¹ Interest has recently been diverted from the traditional investigations of the novel conducting and solid-state properties of TTF complexes and salts, to the implementation of the TTF unit into supramolecular and macromolecular systems.² Monofunctionalised and 4,5-bifunctionalised TTF derivatives can provide materials with novel solid-state structures,³ and building-blocks for the synthesis of supramolecular systems.⁴ We now report convenient

procedures for the synthesis of mono- and bifunctionalised TTF derivatives using tetrathiafulvalenyllithiums and the appropriate *p*-toluesulfonyl-reagent.

The azido group is a particularly attractive starting group in organic synthesis,⁵ hence a TTF derivative bearing this functional group would highly desirable building block. The reaction of а be tetrathiafulvalenyllithium⁶ with Ts-N=N=N⁷ (Scheme 1) affords the triazene derivative 3 as a red precipitate. The subsequent reaction of 3 pvrophosphate⁸ tetrasodium vields with aqueous 4azidotetrathiafulvalene which was trapped without further purification with DMAD to give 6 in good yield (65%). In endeavours to synthesise the isocyanate derivative, 2 was reacted with one equivalent of Ts-N=C=O, which gave the desired 4-isocyanato-TTF 4 (20%) together with dervative 5, presumably by a competing reaction of 2 with electrophilic carbon of the isocyanate functionality, which are consistent with previously published data.⁹ The modest yield of 4 is offset by the convenience of this one-pot procedure and has obvious advantages over the previously reported multi-step synthesis.¹⁰

The synthesis of 4,5-bifunctionalised TTF derivatives are usually achieved using phosphite mediated cross-coupling reactions of vinylene trithiocarbonate and the appropriate 1,3-dithiole-2 thione.¹¹ However, the multi-step synthesis often culminates in a cross-coupling reaction, which can providing the functionalities withstand the reaction conditions, give at best statistical yields of the desired unsymmetrical derivative. Recently the synthesis of 4,5-bifunctionalised TTF derivatives have been achieved





in one-pot procedures relying upon a disproportionation of 2. 12,13However, this route has proven to be capricious, particularly in scale-up reactions. We now report an improved method of producing these derivatives using ortho-lithiation of the corresponding monofunctionalised derivative, 14,15 followed by trapping the resulting anion with the appropriate *p*-toluenesulfonyl reagent to give **10-12** in reliably good yield (Scheme 2).





EXPERIMENTAL.

Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 IR spectrophotometer. ¹H NMR spectra were measured at 90 MHz using a JEOL FX 90 Q spectrometer. Mass spectra were obtained on a MS 25 spectrometer, operating at 70eV. Compounds **7-9** were prepared according to the previously reported methods.^{12,13} Satisfactory analytical data were obtained for derivatives **4,10 - 12**.

4,5-Dimethoxycarbonyl-1-(4-tetrathiafulvalenyl)-1,2,3-triazole (6):

To a stirring solution of TTF 1 (0.25 g, 1.23 mmol) in dry Et₂O (50 mL) at -78 °C under dry nitrogen, is added freshly-prepared LDA (1.1 equiv.) [from diisopropylamine (0.2 mL, 1.35 mmol) and nBuLi (1.6M, 0.9 mL)] in dry Et₂O (10 mL) dropwise over 15 min, after which time a thick yellow precipitate had formed. After 4 h at -78°C TsN3 (0.26 g, 1.35 mmol) was added and the mixture was maintained at -78°C for a further 5 h. A solution of Na4PO7.10H₂O (2 g, 4.48 mmol) in distilled H₂O (100 ml) was then added and the subsequent mixture was allowed to warm to 20°C over 12h. The crude mixture was then poured onto water (100 mL), the

TETRATHIAFULVALENYLLITHIUMS

aqueous layer was separated and further extracted with CH₂Cl₂ (3 x 100 mL). The combined organic extracts were dried (MgSO4), filtered and evaporated *in vacuo*, to afford the crude product which was purified by column chromatography (silica), eluted with toluene to give **6** as a red solid; yield: 0.31 g (65%); mp 148 -149 $^{\circ}$ C.

C12H9N3O4S4 calc. C 37.21 H 2.33 N 10.85 found 37.16 2.45 10.62 ¹H NMR (CDCl3/ TMS): δ = 7. 25 (1 H, s), 6.33 (2 H, s), 3.98 (6H, s). MS (EI): m/z = 384 (M⁺).

4-Isocyanatotetrathiafulvalene (4).

Compounds (4) and (5) were prepared anologously to (6) using TsNCO (0.26g, 1.35 mmol). There are obtained:

4-Isocyanatotetrathiafulvalene (4): as a purple solid; yield: 0.062 mg (20%); mp 74-77 $^{\circ}$ C (lit.¹⁰ 75-78 $^{\circ}$ C).

4-Toluenesulfonamidotetrathiafulvalene (5): as a red solid; yield: 0.24 g (48%); mp > $210 \, {}^{\circ}$ C.

C14H11NO3S5 calc. C 41.90 H 2.74 N 3.49 found 42.16 2.85 3.58 ¹H NMR (CD3COCD3/ TMS): δ= 7.90 (2H, d, Ar), 7. 40 (1 H, s), 7.23 (2H, d, Ar), 6.40 (2 H, s), 3.40 (1H, s, NH), 2.40 (3H, s). MS (DCI): m/z = 401 (M⁺). υ max (cm⁻¹): 3275, 1680, 1150.

4,5-Dichlorotetrathiafulvalene (10); A General Method:

To a stirring solution of 7^{12} (0.29 g, 1.23 mmol) and TMEDA (0.20 mL, 1.35 mmol) in dry Et₂O (50 mL) at -78 °C under dry nitrogen , LDA (1.1 equiv.) [from diisopropylamine (0.2 mL, 1.35 mmol) and nBuLi (1.6M, 0.9 mL)] was added. After 3 h TsCl (0.26 g, 1.35 mmol) was added in one portion and the mixture was maintained at -78°C for 5 h and then allowed to warm to 20°C overnight. The crude mixture was then poured onto water (100 mL), the aqueous layer was separated and further extracted with CH₂Cl₂ (3 x 200 mL). The combined organic extracts were dried (MgSO₄), filtered and evaporated *in vacuo*, to afford the crude product which was purified by column chromatography (silica), eluted with petroleum ether (40/60) to give **10** as a red solid; yield: 0.23 g (69 %); mp 103-106 °C (lit.¹⁴ 103-106 °C).

REFERENCES.

- (1) Bryce, M. R. Chem. Soc. Rev., **1991**, 20, 355.
- Jorgensen, T.; Hansen, T. K.; Becher, J. Chem. Soc. Rev., 1994, 23, 41.
- Batsanov, A. S.; Bryce, M. R.; Cooke, G.; Heaton, J. N.; Howard,
 J. A. K. J. Chem. Soc. Chem. Commun., 1993, 1701.
- (4) Garin, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.;
 Wegener, S.; Yufit, D. S.; Howard, J. A. K. Synthesis, 1994, 489.

TETRATHIAFULVALENYLLITHIUMS

- Patai, S,; Ed., "The Chemistry of the Azido Group", Interscience, New York, N. Y. 1971.
- (6) Green, D. C. J. Org. Chem., 1979, 44, 1476.
- (7) Doering, W. V. E.; De Puy, C. H. J. Am. Chem. Soc., 1953, 75, 5955.
- Smith, P. A. S.; Rowe, C. D.; Bruner, L. B. *J. Org. Chem.*, **1969**, *34*, 3430.
- Batsanov, A. S.; Bryce, M. R.; Cooke, G. Dhindsa, A.S.; Heaton, J. N.; Howard, J. A. K.; Moore, A. J.; Petty, M. C. *Chem. Mater.*, **1994**, *6*, 1419.
- Panetta, C. A.; Baghdadchi, J.; Metzger, R. M. Mol. Cryst. Liq.
 Cryst., 1984, 107, 103.
- (11) Svenstrup, N.; Becher, J. Synthesis, 1995, 215.
- (12) Bryce, M. R.; Cooke, G. Synthesis, 1991, 4, 263.
- (13) Cooke, G.; Heath, S. L.; Powell, A. K. Synthesis, 1995, 1411.

(Received in the Netherlands 09 February 1996)