

Synthesis of Tetrathiafulvalene (TTF) Derivatives bearing Long Alkyl Chains

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The preparation of tetrathiafulvalene derivatives [(**3**), (**7a**), and (**7b**)] substituted with hydrophobic alkyl chains is described.

Many modifications to the tetrathiafulvalene (TTF) ring skeleton (**1**) have been reported over the last decade, motivated by the study of organic metals.^{1,2} For example, derivatives of current interest contain sulphur or selenium heterocycles fused to the TTF system,³ or extended conjugation between the 1,3-dithiole rings.⁴ Recently, a new class of TTF derivatives (**2**) bearing four alkylthio or alkylseleno chains of various lengths attached through sulphur or selenium has been prepared.^{5,6} We now report that, using completely different methodology, we have prepared the first TTF derivatives (**3**), (**7a**), and (**7b**) bearing two or four long alkyl chains attached through carbon.[†] These hydrophobic compounds could be important as precursors to electroactive Langmuir-Blodgett films and conducting salts, where ordered stacking is facilitated by intermolecular side-chain interactions.⁸

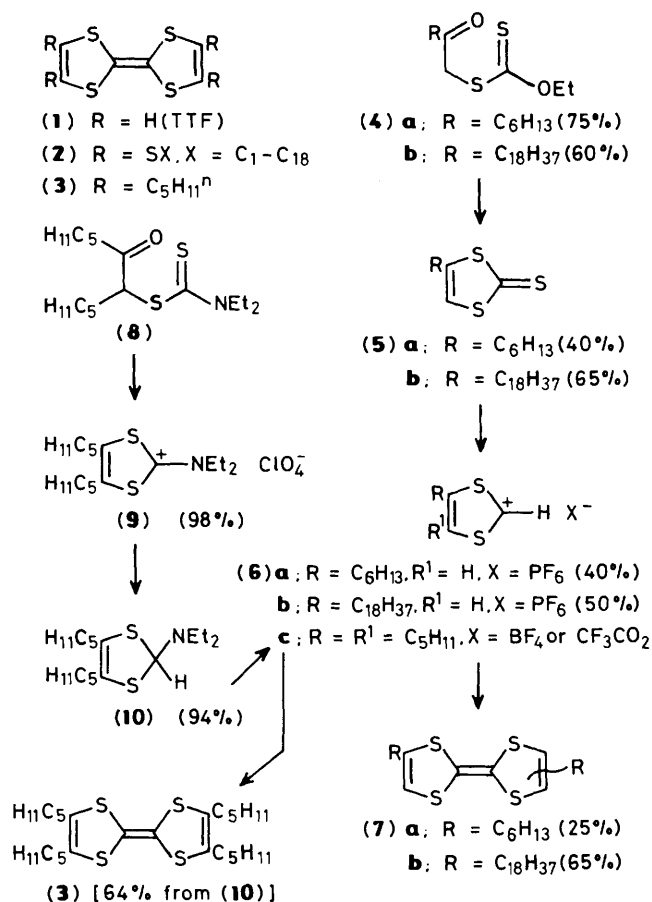
Our synthetic route to the TTF derivatives (**3**), (**7a**), and (**7b**) is shown in Scheme 1. Reaction of 1-bromo-octan-2-one and 1-bromoeicosan-2-one (prepared from oct-1-ene and

eicos-1-ene, respectively) with potassium *O*-ethyl xanthate gave *S*- β -oxoalkyl *O*-alkyl dithiocarbonate derivatives (**4**). Cyclisation of (**4**) occurred on treatment with phosphorus pentasulphide in toluene to yield 4-alkyl-1,3-dithiole-2-thione derivatives (**5**). The crystalline 4-hexyl- and 4-octadecyl-1,3-dithiolium salts (**6**) were readily obtained by oxidation of (**5**) with *meta*-chloroperbenzoic acid. Treatment of the salts (**6**) with triethylamine yielded the disubstituted tetrathiafulvalene derivatives (**7**), each assumed to be a mixture of the two possible geometrical isomers.[‡] Compound (**7a**) (25% yield), a viscous oil, was purified by column chromatography on silica gel [eluant hexane-ether (3:1 v/v)]; compound (**7b**) (65% yield) is a solid (m.p. 33°C).

A modification of this route has yielded tetrapentyltetrathiafulvalene (**3**). The dithiocarbamate derivative (**8**) was cyclised with perchloric acid to yield 2-diethylamino-4,5-dipentyl-1,3-dithiolium perchlorate (**9**). Reduction of the salt (**9**) with sodium borohydride gave compound (**10**), which was

[†] Diphenyl-TTF bearing C₄ and C₁₀ chains attached to the phenyl rings has reported.⁷

[‡] Mueller-Westerhoff *et al.*⁷ believe that only the *trans*-isomer is formed when 4-phenyl-1,3-dithiole-2-ones are coupled, but this was not proven.



Scheme 1

converted into the target molecule (3) as follows. Treatment of (10) with tetrafluoroboric acid or trifluoroacetic acid yielded the cation salt (6c) as a red oil which was not purified [δ_{H} (CDCl₃) 11.33 (s)]. Reaction of the salt (6c) with triethylamine followed by column chromatography on silica gel (eluent hexane) afforded the TTF derivative (3) as red crystals [64%, m.p. 48–49 °C (from pentane)]. Alternatively, the salt (6c) could be treated with trimethylsilyl trifluoromethanesulphonate followed by trimethylamine, in a one-pot procedure, to yield (3) in 62% yield.

In conclusion, we have established methodology that is suitable for the preparation of TTF derivatives substituted with two or four hydrophobic alkyl chains of various lengths.

We thank S.E.R.C. for funding this work, and K.K. thanks the British Council for financial support to visit Durham University.

Received, 3rd May 1988; Com. 8/01746H

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