



An in depth study of the formation of new tetrathiafulvalene derivatives from 1,8-diketones

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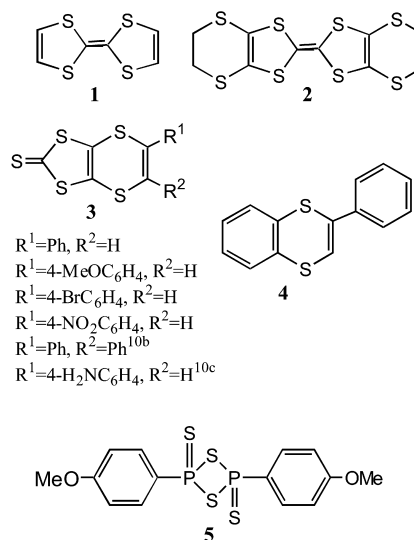
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Abstract—A detailed study of the reactions of phosphorus pentasulfide and Lawesson's reagent with a series of 4,5-bis(RCOCH₂S)-1,3-dithiole-2-thiones (R=Ph, 4-MeOC₆H₄, 4-Br C₆H₄, Me) has been carried out. These reactions lead to fusion of either an unsaturated 1,4-dithiin ring or a thiophene to the dithiole; the former in higher yield, while the latter is a significant product in the reactions with Lawesson's reagent; as well as small amounts of minor products. A mechanistic rationalization of these products is discussed in some detail. The new fused dithioles have been converted to novel series of fused TTF derivatives.

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1. Introduction

There has been continued interest in the synthesis of derivatives of tetrathiafulvalene, TTF **1**. This is due to the metallic behaviour of its radical cation salts with mono anions and charge transfer complexes with electron acceptors such as TCNQ, which exhibit semi-conducting, conducting and superconducting properties. It has been established that the physical properties of the radical cation salts depend on the electronic and structural features of TTF derivatives.¹ The most widely studied derivative, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) **2**, has yielded some salts which show superconducting properties, including κ -(BEDT-TTF)Cu[N(CN)₂Br] which has the highest critical temperature, $T_c=12.8$ K, for an organic superconductor.² In recent years, the electron-donating property of TTF has led to the synthesis of various analogues with different potential applications such as chromophores for dyes, nonlinear optics, synthetic light-harvesting systems, liquid crystals,³ dendrimers,^{4–6} phthalocyanines,^{4,5} polymers,⁷ and supramolecular switches.⁸ Obviously, such a wide range of application possibilities requires the synthesis of TTF derivatives bearing versatile functional groups.



To improve the conducting properties, efforts have been aimed at (i) extension of the conjugation of the molecule to delocalize the charges formed in the charge transfer salts and (ii) introduction of hydrogen bonding groups to produce specific attractive interactions with the anions in the derived radical cation salts.^{1b} So far, extension of conjugation has been achieved in the centre of the molecule,^{1b} but, there are just a few examples of the introduction of conjugation at the peripheral ethylene bridges,⁹ and they are achieved with conventional methods which have limited applications.

Keywords: 1,8-diketone ring formation; 1,4-dithiin; thiophene; BEDT-TTF; TTF.

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