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LETTERS

Thieno[3,4-*c*]thiophenes: novel synthesis of 1,3-dicarbomethoxy-4,6-dicyanothieno[3,4-*c*]thiophene

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Abstract

The first thieno[3,4-*c*]thiophene bearing all EWGs has been synthesized and found to be very stable.
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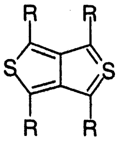
Keywords: Pummerer-cyanation; in situ Pummerer reaction; thieno[3,4-*c*]thiophene; S-transfer reaction.

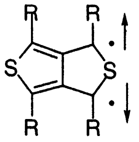
The annelation of two thiophene rings gives rise to four isomeric thienothiophenes, of which thieno[3,4-*c*]thiophene (**1**) is unknown in its basic form. Calculations have predicted it to be of high energy precluding isolation.[1] However, the first tetrasubstituted derivative (**2**) was made in 1969 and proved to be quite stable in the solid state.[2] The stability was attributed to the buttressing effect of the four bulky phenyl groups. Photoelectron spectroscopic studies on **2** by two different groups of investigators and calculations in the 1970s indicated that **1** was best represented as a singlet 1,3-biradical.[3,4]

Other tetrasubstituted derivatives (**3**–**7**) have been reported.[5–7] The tetra S-alkyl-substituted derivatives **4**–**7** were made by a remarkable dimerization of the corresponding S-alkyl-substituted cyclopropenethiones, the mechanism of which has only been recently elucidated.[8] All of these derivatives have bulky substituents and it was believed that steric bulk was a necessary attribute for stability.

However, some years ago the synthesis of an electronically stabilized thieno[3,4-*c*]thiophene (**8**) was reported from our laboratory.[9]



1 R =H
2 R =Ph
3 R =2-Thienyl
4 R =SEt
5 R =SPr
6 R =SisoPr
7 R =StBu



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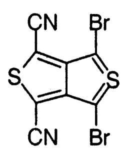

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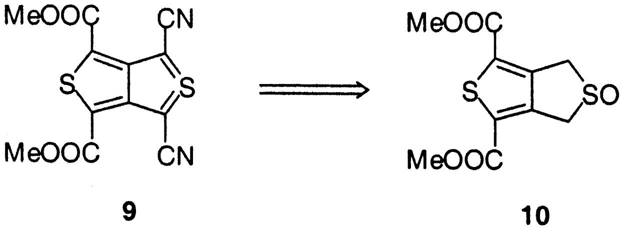
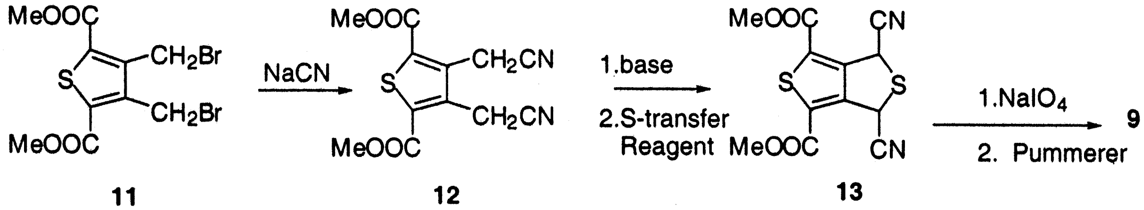
The objective of the present study was the synthesis of a thieno[3,4-*c*]thiophene bearing only electron-withdrawing groups (EWGs). A specific target was the synthesis of the title compound **9** from the well-known precursor **10**, via an unusual tandem Pummerer–cyanation route (Scheme 1).



Scheme 1.

This was indeed achieved, albeit in miniscular yield, in a one-pot reaction of sulfoxide **10**[10] with lithium hexamethyldisilazide to effect a base-catalyzed Pummerer reaction, followed by dilithiation and treatment with the CN^+ transfer reagent viz. *N*-cyano-1,2,3-benzotriazole.[11] An X-ray crystallographic analysis confirmed the structure. In view of the extremely poor yield encountered in this route, an alternate approach was sought. This envisioned the introduction of the nitrile functionality prior to the insertion of sulfur via a sulfur-transfer reagent in the presence of base (Scheme 2).



Scheme 2.

The known dibromide **11**[12] was converted into the dinitrile **12**. Reaction of **12** with phthalimido-disulfide as the sulfur-transfer reagent in the presence of triethyl amine (TEA) failed, but the use of sulfur monochloride in the presence of TEA led to the product **9** directly in 25% yield and not to the sulfide **13**.

However, the use of thionyl chloride in the presence of TEA gave a 70% yield of product **9**. Dicarbomethoxy-dicyano derivative **9** is very stable in the solid state as well as in solution, as evidenced by no change in the UV–vis spectrum for several weeks. Compounds **2**–**8** are violet in the solid state and their solutions ($\lambda_{max} \sim 530$ nm) are red to violet with a reddish fluorescence. In contrast, **9** is red in the solid state and yellowish to orange in solution (λ_{max} 476 nm), and exhibits greenish fluorescence. It undergoes reversible electrochemical reduction to the radical anion at −0.40 V and to the dianion at −1.10 V.[13]

In conclusion, a nonclassical thieno[3,4-*c*]thiophene bearing all EWGs has been synthesized using several novel routes and shown to be very stable in the solid state as well as in solution. The presence of large buttressing groups is not necessary to confer stability to this system. Efforts are under way in our laboratory to synthesize analogous derivatives as potential new electron-acceptors.

Acknowledgements

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