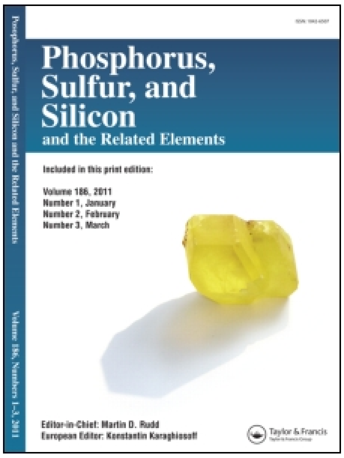

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CONSTRUCTION OF EXTENDED AND POLYMERIC 1,3-DITHIOLANE AND TETRATHIAFULVALENE DERIVATIVES USING CYCLOADDITION OF $Bu^n{}_3P{\bullet}CS_2$

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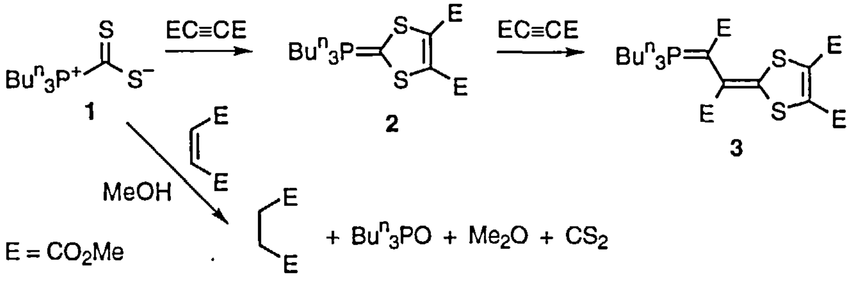
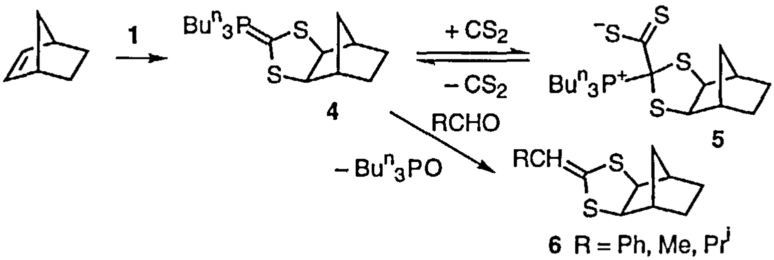
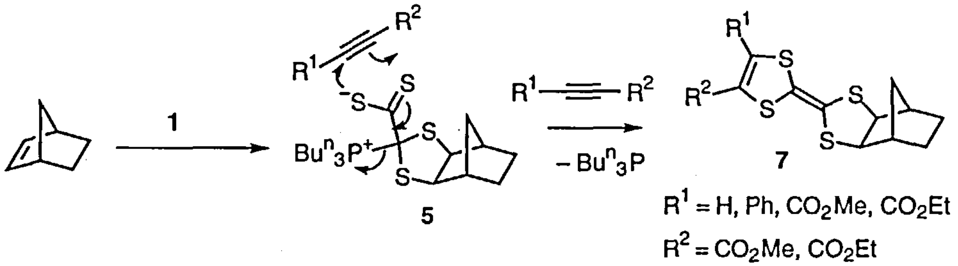
Abstract Cycloaddition of the adduct between $Bu^n{}_3P$ and CS_2 to strained double bonds such as in norbornene gives novel zwitterionic products such as **5**. The compound **5** reacts with acetylenic dipolarophiles by cycloaddition accompanied by loss of $Bu^n{}_3P$ to give dihydro-TTF derivatives. The corresponding reaction also occurs for norbornadiene and by using this a range of new extended sulfur-rich structures and substituted TTFs have been obtained.

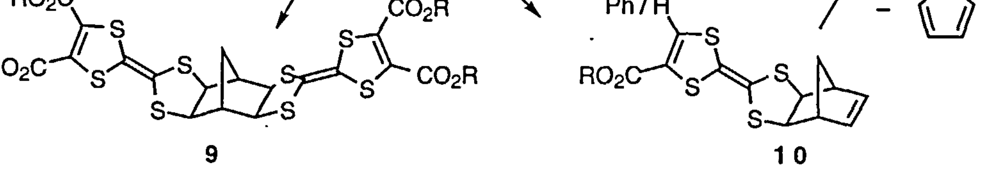
The red crystalline adduct **1** between $Bu^n{}_3P$ and CS_2 was prepared at an early stage,[1] but it is only recently that its cycloaddition chemistry has been examined. With activated alkynes it adds through the two sulfur atoms to give the ylides **2** but in the absence of any trap these react further to give the 1 : 2 adducts **3**.[2] The only previous report of reaction of **1** with a double bond was the reaction with dimethyl maleate to give dimethyl fumarate as shown but this is unlikely to involve a cycloaddition reaction.[3] Recently we described the reaction of **1** with norbornene to give the stable zwitterionic structure **5** as a pink solid.[4] In CH_2Cl_2 this dissociates significantly to the ylide **4** which can be trapped by a Wittig reaction with added aldehydes to give the tricyclic alkylidenedithiolanes **6**.[4]





An important recent discovery is that **5** reacts with acetylenic dipolarophiles in a completely different way as shown below, by cycloaddition and loss of the phosphine to form the dihydrotetrathiafulvalene derivatives **7**. The corresponding reaction of the norbornadiene adduct **8** leads to the bridged bis-dihydro-TTF compounds **9**. The X-ray structure of the compound **9** (R = Me) has been obtained and shows that all the sulfurs lie essentially in a plane. With less highly stabilised dipolarophiles such as propiolates and phenylpropiolates, the addition takes place only once and the adducts **10** undergo loss of cyclopentadiene upon FVP to provide a useful synthesis of substituted TTFs **11**.





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