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## Phosphorus, Sulfur, and Silicon and the Related Elements

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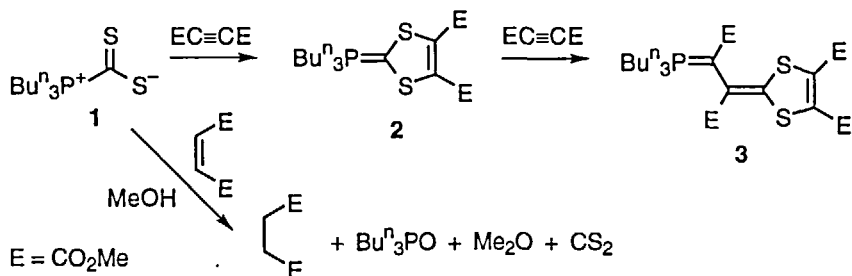
## CONSTRUCTION OF EXTENDED AND POLYMERIC 1,3-DITHIOLANE AND TETRATHIAFULVALENE DERIVATIVES USING CYCLOADDITION OF $\text{Bu}^n\text{P}\cdot\text{CS}_2$

R. ALAN AITKEN\* and LAWRENCE HILL

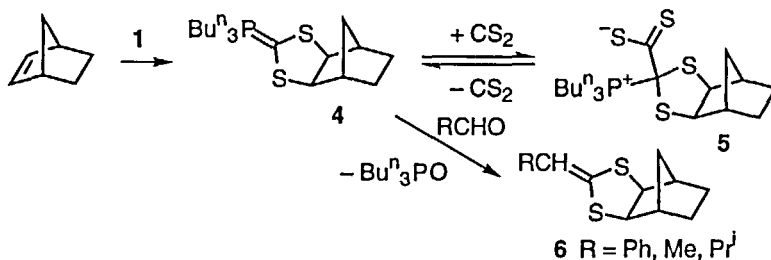
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**Abstract** Cycloaddition of the adduct between  $\text{Bu}^n\text{P}$  and  $\text{CS}_2$  to strained double bonds such as in norbornene gives novel zwitterionic products such as **5**. The compound **5** reacts with acetylenic dipolarophiles by cycloaddition accompanied by loss of  $\text{Bu}^n\text{P}$  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.

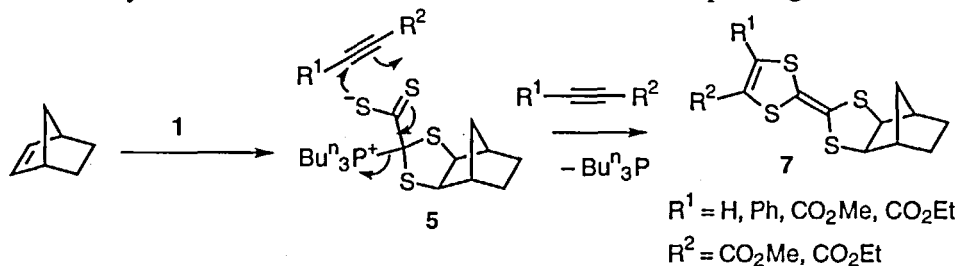
The red crystalline adduct **1** between  $\text{Bu}^n\text{P}$  and  $\text{CS}_2$  was prepared at an early stage,<sup>1</sup> but it is only recently that its cycloaddition chemistry has been examined. With activated alkynes it adds through the two sulfur atoms to give the ylides **2** but in the absence of any trap these react further to give the 1 : 2 adducts **3**.<sup>2</sup> 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.<sup>3</sup> Recently we described the reaction of **1** with norbornene to give the stable zwitterionic structure **5** as a



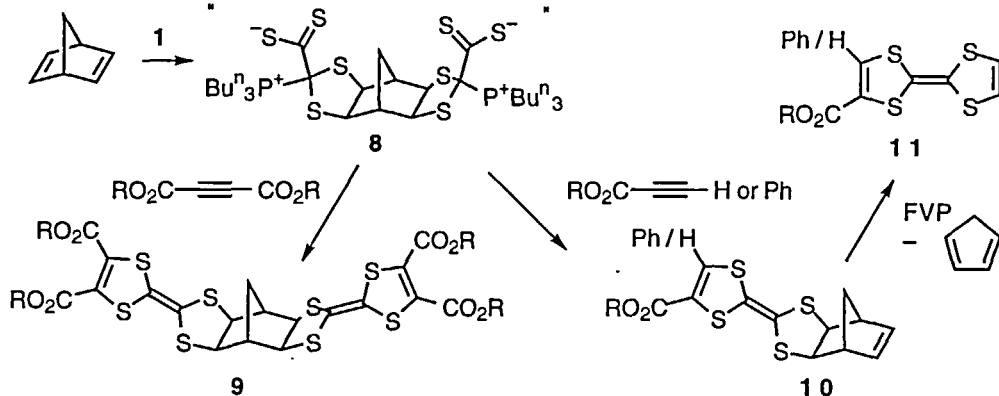
pink solid.<sup>4</sup> In  $\text{CH}_2\text{Cl}_2$  this dissociates significantly to the ylide **4** which can be trapped by a Wittig reaction with added aldehydes to give the tricyclic alkylidenedithiolanes **6**.<sup>4</sup>



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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