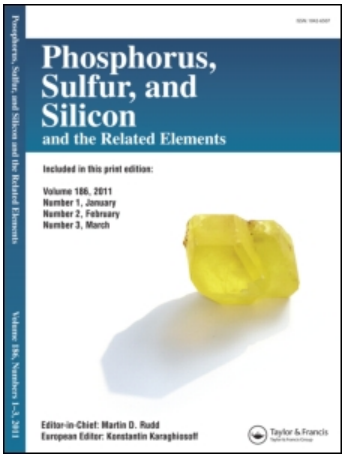

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Aitken, R. Alan , Hill, Lawrence and Massil, Tracy(1996) 'Construction of Extended and Polymeric 1,3-Dithiolane and Tetrathiafulvalene Derivatives using Cycloaddition of $Bu^n_3P.CS_2$', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 593 — 596
To link to this Article: DOI: 10.1080/10426509608545223
URL: http://dx.doi.org/10.1080/10426509608545223

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 593–596
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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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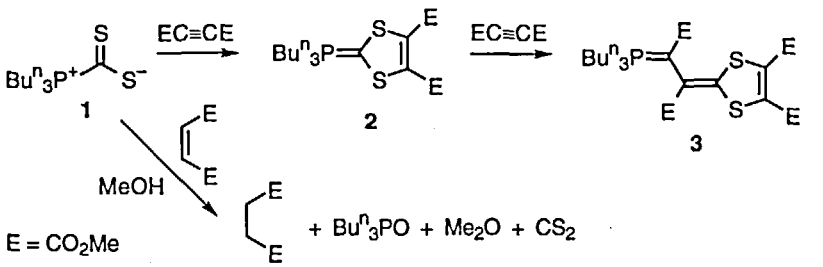
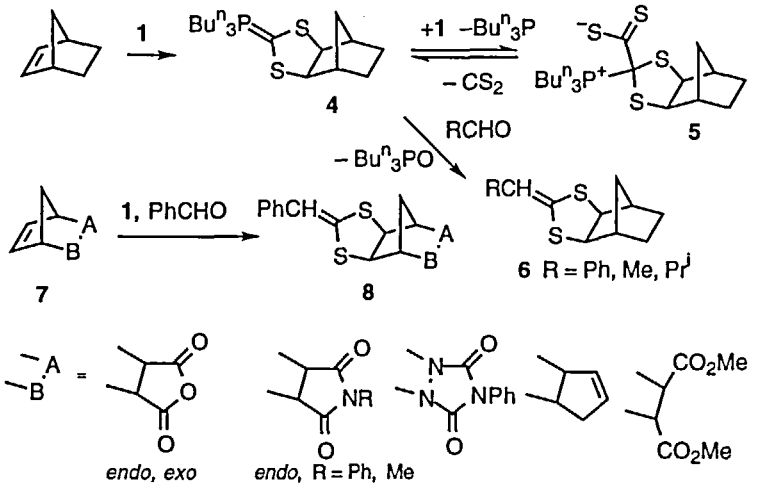
Abstract Cycloaddition of the adduct between Bu^n_3P and CS_2 to strained double bonds such as in norbornene gives novel zwitterionic products such as **5**. This dissociates to the ylide **4** so that carrying out the reaction in the presence of an aldehyde leads to a Wittig reaction to give 2-alkylidene-1,3-dithiolanes. The compound **5** reacts with acetylenic dipolarophiles by cycloaddition accompanied by loss of Bu^n_3P to give dihydro-TTF derivatives. Both these reaction types also occur for norbornadiene and by using this together with dialdehydes or diacetylenes a range of new sulfur-rich extended and polymeric structures have been obtained.

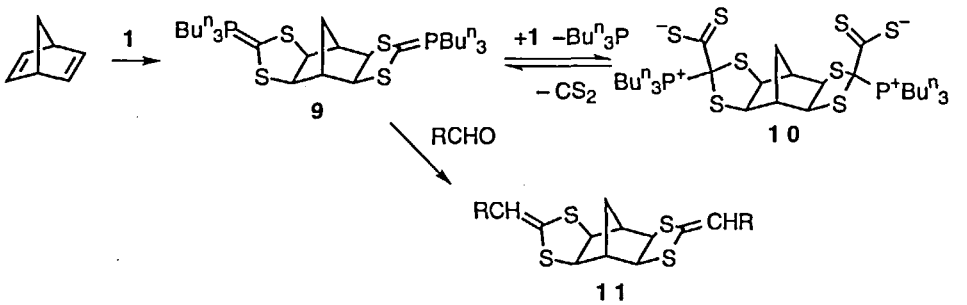
The red crystalline adduct **1** between Bu^n_3P and CS_2 was prepared at an early stage,[1] but it is only recently that its cycloaddition chemistry has been examined. With activated alkynes it adds through the two sulfur atoms to give the ylides **2** but in the absence of any trap these react further 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



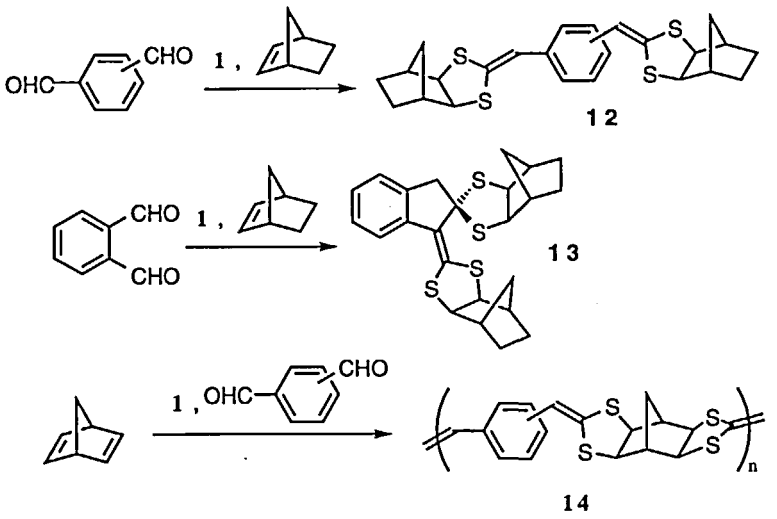
pink solid.[4] In CH_2Cl_2 this dissociates significantly to the ylide **4** which can be trapped by a Wittig reaction with added aldehydes to give the tricyclic alkylidenedithiolanes **6**. The same reaction can be applied to a range of strained double bond compounds **7** readily available from Diels-Alder reactions of cyclopentadiene to give the products **8**.[4]



The reaction of **1** with norbornadiene gives an insoluble pink adduct of uncertain structure but this behaves as though it were **10**. As for norbornene, performing the reaction in the presence of an aldehyde leads to trapping of the ylide form in a Wittig reaction to give a mixture of *E* and *Z* isomers of **11**.

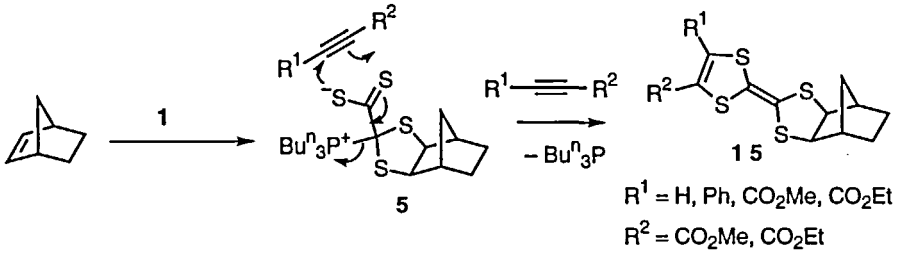


Reaction of the isomeric benzene dialdehydes with **1** and norbornene gives the expected bis-dithiolanes **12** for terephthalaldehyde and isophthalaldehyde but for phthalaldehyde the unexpected rearrangement product **13** is formed and its structure has been confirmed by X-ray methods.

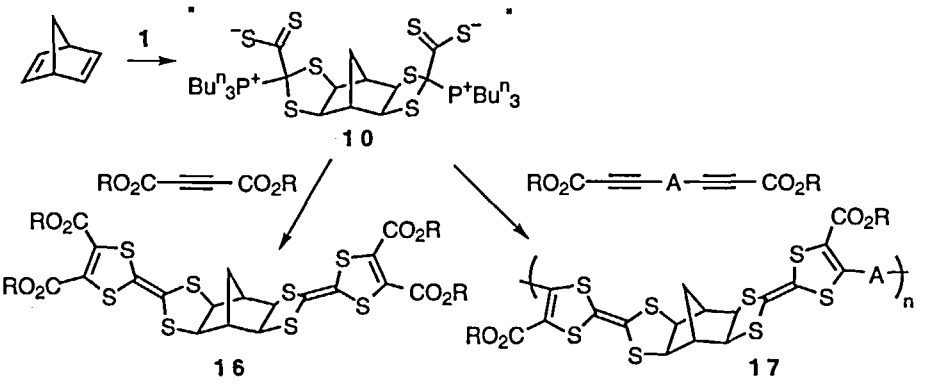


When the *m* and *p* dialdehydes are reacted with **1** and norbornadiene the novel sulfur-rich polymers **14** are produced although due to their insolubility the molecular weight of these could not be determined.

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 **15**.[5] These are readily obtained in pure form by chromatography, albeit only in moderate yield and this represents an exceptionally direct route to such compounds. The corresponding reaction of the



norbornadiene adduct **10** leads to the bridged bis-dihydro-TTF compounds **16**. The X-ray structure of the compound **16** (R = Me) has been obtained and shows that all the sulfurs lie essentially in a plane. The electrical properties of these molecules are currently under investigation and they are expected to be of considerable interest in this connection. Once again this process can be adapted to polymer formation and preliminary studies on reaction of **10** with diacetylenes suggest that the polymeric structures **17** should be accessible.



Acknowledgement We thank the Engineering and Physical Sciences Research Council for financial support of this work (GR/J 38895).

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