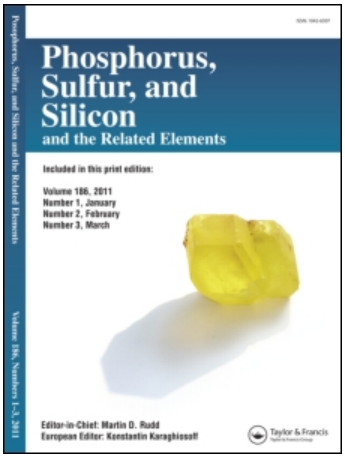

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIONS OF THIOPHENES AND ACETYLENES IN POLAR AND APOLAR SOLVENTS

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To cite this Article Reinhoudt, D. N. , Trompenaars, W. P. and Geevers, J.(1979) 'REACTIONS OF THIOPHENES AND ACETYLENES IN POLAR AND APOLAR SOLVENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 253 — 254
To link to this Article: DOI: 10.1080/03086647908080400
URL: http://dx.doi.org/10.1080/03086647908080400

Phosphorus and Sulfur
1979, Vol. 6, pp. 253–254

REACTIONS OF THIOPHENES AND ACETYLENES IN POLAR AND APOLAR SOLVENTS

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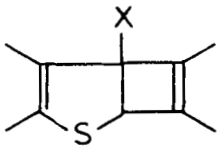
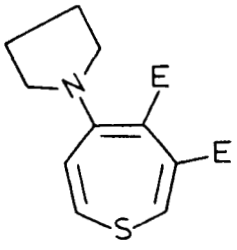
Although the aromatic 6π-electron system of thiophenes is rather unreactive in cycloaddition reactions we have found that several thiophene derivatives react with acetylenes. Alkylthiophenes undergo (2+2)-cycloaddition reactions with electron-deficient acetylenes in apolar solvents in the presence of Lewis acids to give 2-thia-bicyclo[3.2.0]hept-3,6-dienes (1). These compounds show isomerization via an a,a-Cope rearrangement at temperatures of 100 to 150°C.

3-(Pyrrolidin-1-yl)thiophenes react with dimethyl acetylenedicarboxylate (DMAD) in apolar solvents via a (2+2)-cycloaddition to give 1. The temperature required for this conversion increases strongly when electron-withdrawing substituents (C_6H_5, $COOCH_3$) are present at the 4-(and 5-) positions of the thiophene ring. The 5-(pyrrolidin-1-yl)-2-thiabicyclo[3.2.0]hept-3,6-dienes obtained undergo a rapid isomerisation at the reaction temperature ($\lesssim$ -30°C) to yield antiaromatic thiepines (2). These compounds are thermally unstable and eliminate sulphur even at -30°C



1.



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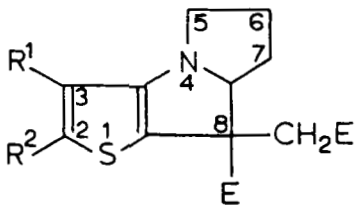

3.

In polar solvents like methanol, acetonitrile or nitromethane these 3-(pyrrolidin-1-yl)thiophenes react with DMAD in a completely different manner and 6,7,7a,8-tetrahydro-5H-thieno[3,2-b] pyrrolizines(3) are obtained in yields of 45 - 65%. The formation of these products in polar solvents is explained in terms of an addition of the electron-rich thiophene to the electron-deficient acetylene triple bond followed by intramolecular proton abstraction and 1,5-dipolar cyclisation.
The mechanism and scope of this novel type of reaction together with possible applications for the synthesis of natural products will be discussed.