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DIELS-ALDER CYCLOADDITION OF TETRACHLOROTHIOPHENE-S,S-DIOXIDE TO AZULENE

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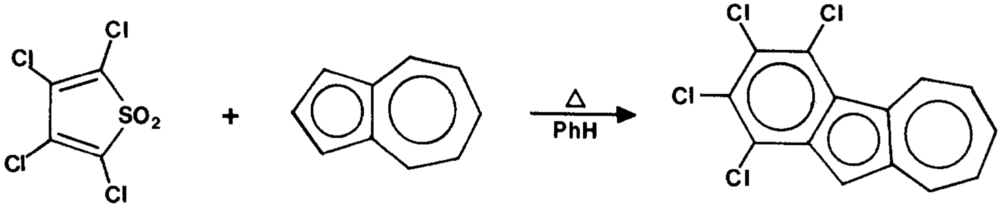
Summary: The cycloaddition of tetrachlorothiophene-S,S-dioxide to azulene occurs across the 1- and 2-positions to give 1,2,3,4-tetrachlorobenz[a]azulene.

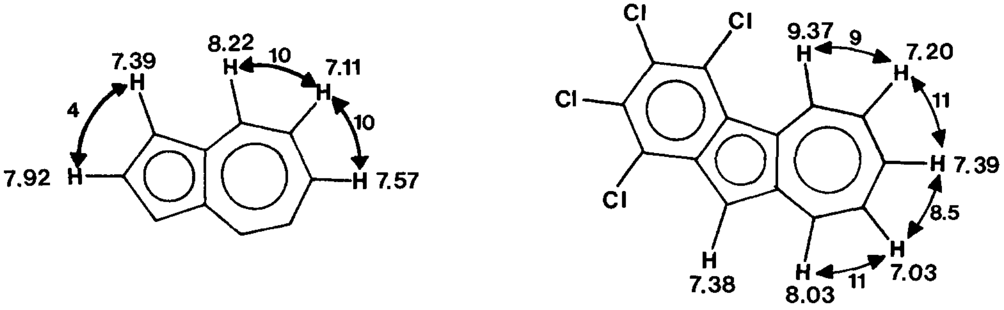
Tetrachlorothiophene-S,S-dioxide is a reactive Diels-Alder diene "with inverse electron-demand".[1] Cycloadditions of this diene are followed by loss of SO_2, and a large variety of olefinic compounds have been found to undergo cycloadditions to form 1,2,3,4-tetrachloro-1,3-cyclohexadiene derivatives. We have investigated the reaction of this diene with azulene, in order to determine whether azulene might function as a nucleophilic 6π addend as has been observed for the reactions of 6-dialkylaminofulvenes with thiophene dioxides.[2]

When azulene is refluxed in benzene with 1.5 equivalents of tetrachlorothiophene-S,S-dioxide for four hours under N_2, the azulene is completely consumed. After evaporation of solvent and chromatography, sharp green crystals, mp. 151-152°C, of the tetrachlorobenz[a]azulene are obtained in 30% yield.[3] The product must arise by a Diels-Alder cycloaddition across the 1,2-position of azulene, triggered by the nucleophilicity of the 1-position of azulene. Loss of SO_2 and subsequent aromatization, presumably by air oxidation, give the benzazulene.

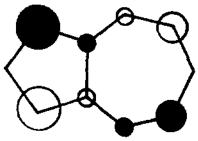


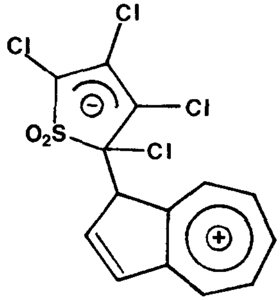
The structure of the aromatized cycloadduct was determined by 300 MHz NMR spectroscopy. The chemical shifts and coupling constants for the benzazulene are compared to those of azulene on the next page.

NMR data for azulene and tetrachlorobenz[a]azulene.



Why is the [4+2] adduct favored over the [6+4]? The HOMO of azulene is shown below. The addition across atoms 1 and 2 rather than atoms 1 and 8 of azulene is in accord with the opposite signs of the coefficients at 1 and 8, which is the wrong nodal pattern for simultaneous interaction with the termini of a diene LUMO. There is a node through C-1, so that the reaction is most likely stepwise involving a zwitteronic intermediate, 1, or is highly asynchronous, if concerted.





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Although this is a new compound, a variety of methods have been reported is available in the literature for the preparation of the parent 1,2-benz[a]azulene.[5]

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References and Notes

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