4,9,12,15-Tetrathiatricyclo[5.3.3.3^{2,6}]hexadeca-1,6-diene

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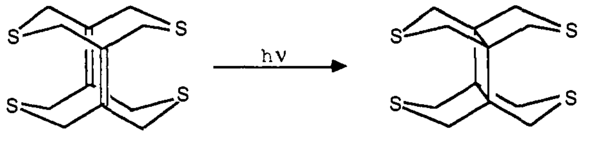
Molecules with carbon–carbon double bonds held near each other in space can display unusual reactivity and have been the subject of many recent studies.[1] We wish to report the synthesis of the tetrathiadiene **1** and its novel photoisomerization to **2**.



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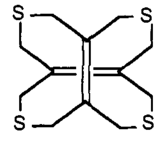

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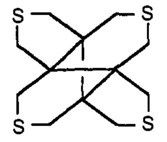

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Compound **1** is formed by the cesium–carbonate-promoted fourfold coupling of tetrakis(thiomethyl)ethene and tetrakis(bromomethyl)ethene.[2] Cesium salts have been touted as being particularly effective in promoting intramolecular reactions of this kind.[3] In the present case, with syringe–pump addition of reagents, yields of **1** greater than 30% can be obtained.[4] The remaining material is insoluble, presumably polymeric, organic material. Using other bases, such as barium carbonate, leads to lower yields and less clean products.

A priori, the cyclized product could be either **1** or **3**, its criss-crossed isomer. Each should have the same general spectroscopic features (a single AB pattern in the ^{1}H NMR spectrum and two signals in the ^{13}C NMR spectrum). The compound is crystalline, but numerous attempts failed to produce crystals appropriate for X-ray analysis.

In an effort to derivatize **1**, a sample of it was photolyzed in triethyl phosphite, the intent being to extrude sulfur from the molecule.[5] Instead, a single compound, isomeric with **1**, was formed. It also shows a single AB pattern in the ^{1}H NMR and two signals in the ^{13}C NMR, consistent with structure **2**. The isomeric cyclobutane, **4**, is not consistent with this data since it has two different sets of diastereotopic hydrogens and three different types of carbon. The structure of **2** was confirmed by Raney nickel[6] desulfurization to give octamethylcyclobutane, a known compound[7] which was identical by NMR, mass spectrometry, and gas chromatographic retention time with an independently prepared sample.

Molecular mechanics calculations using Allinger's MM2 force field[8] suggest that the cyclobutane product is less stable than the diene by about 35 kcal mol^{-1}. In diene **1** the double bonds lie almost directly on top of each other with a spacing of 2.76 Å. The cyclobutane product has nearly equal carbon–carbon bond lengths, 1.56 and 1.57 Å.

The photocyclization of **1** is not limited to triethyl phosphite as a solvent. It occurs readily in THF, chloroform, and acetonitrile. Since compound **1** is only sparingly soluble in these solvents, and **2** is less so, these reactions are heterogeneous. In one experiment, aluminum foil was used to shield the lower portion of the photolysis vessel containing undissolved **1**, and conversion to products occurred at comparable rates, suggesting that the photochemical reaction occurs in solution rather than in the solid state. When identical samples were photolyzed to low conversion with various wavelengths of light, the reaction proceeded only with light in the 300–320-nm range. This result is consistent with the observation of efficient photolysis in Pyrex flasks with Rayonet 300-nm "sunlight" lamps.

While intramolecular 2 + 2 cycloadditions of nonconjugated olefins can be facile with far UV light,[9] we know of no other examples which use near-visible wavelengths. This cycloaddition has been predicted to be particularly facile when the double bonds are separated by three atoms,[10] as in **1**. Compound **3** also has this same spacing, but the intramolecular reaction is likely to be much more difficult due to the lack of overlap of the two double bonds and the higher strain in **4**.

We are currently studying the photochemistry of **1** in more detail and attempting to prepare the isomeric diene **3** by a directed route.

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[4] In a representative preparation, a Sage model 355 dual-syringe pump was used to add solutions of 0.665 g (3.13 mmol) of tetrakis(thiomethyl)ethene and 1.250 g (3.13 mmol) of tetrakis(bromomethyl)ethene, each dissolved in 20 mL of anhydrous DMF, to a stirred suspension of 2.21 g (6.78 mmol) of cesium carbonate in 200 mL of anhydrous DMF under a nitrogen atmosphere over a 3-day period. The solids were washed with water and Soxhlet-extracted with chloroform to give 0.240 g (33%) of **1**: ^{1}H NMR δ 4.74 (d, J = 13.5 Hz, 1 H), 3.23 (d, J = 13.5 Hz, 1H); ^{13}C NMR (multiplicities from INEPT) δ 33.7 (t), 125.9 (s); mass spectrum, *m/e* (relative intensity) 77 (23), 97 (54), 111 (100), 112 (28), 188 (53). Anal. ($C_{12}H_{16}S_4$) C, H, S.

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The Exoclathrate Al($C_7H_8NO_2$)$_3$·12H_2O. A Facial Geometry Imposed by Extensive Hydrogen Bonding with the Ice I Structure

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As part of a program to study the coordination chemistry of posttransition metals, we are examining the complexes formed by aluminum[1,2] and gallium[2] with selected bidentate monobasic ligands. The controversial role of Al in certain (often neurological) disease states[3] and the use of ^{67}Ga in tumor detection[4] are specific reasons for studying these two elements. Subsequent to our reports of the 3-hydroxy-4-pyrone complexes of these group 13 elements,[1,2] we have been studying their complexes with a variety of 3-hydroxy-4-pyridinones[5] (**1**). Our interest in the 3-hydroxy-4-

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