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ADDITIONAL EVIDENCE FOR THE EXISTENCE OF A BENZOTHIIRENE

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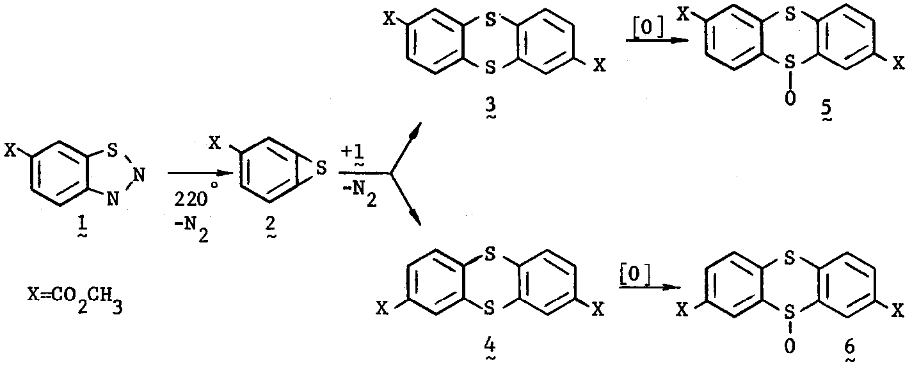
Evidence is reported herein that heating 6-carbomethoxy-1,2,3-benzothiadiazole, 1, yields nitrogen and 3-carbomethoxybenzothiirene, 2, which subsequently forms 2,7- and 2,8-dicarbomethoxythianthrene, 3 and 4, respectively (Equation 1).

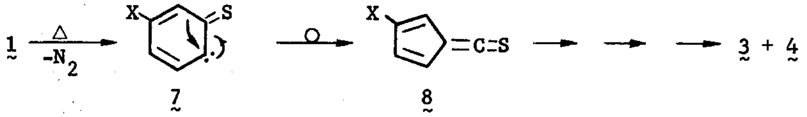


(1)

Previously 3-methylbenzothiirene was suggested as an intermediate in conversion of sodium 2-bromo-4-methylbenzenethiolate to 2,7- and 2,8-dimethylthianthrenes.[1] Conversion of 1,2,3-benzothiadiazoles by thermolysis or photolysis to thianthrenes is well known.[2] However, proof that benzothiirenes are intermediates in these latter reactions has not appeared. (It is not clear from the work reported in this paper as to whether benzothiirene exists as a transition state or in the ground state.)

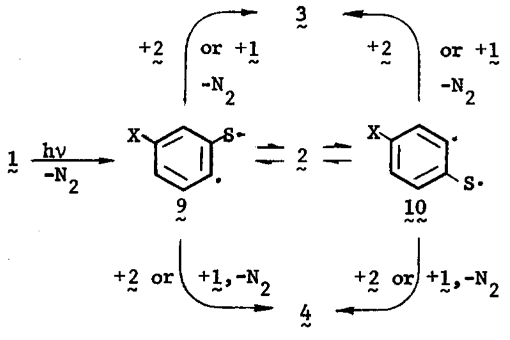
Heating a 2g sample of benzothiadiazole 1 to 220° for 5 hr in an evacuated sealed tube gave a black, amorphous reaction product. (Caution: a thick-walled tube is required due to pressure buildup.) Careful column chromatography (silica gel:benzene) of this product gave a white solid: (25%) infrared, nuclear magnetic resonance, and mass spectra were virtually indistinguishable from authentic 2,7-dicarbomethoxythianthrene, 3.[3] (R_f and blue fluorescence in U.V. light on TLC plates further confirmed the identity of this material as dicarbomethoxythianthrene(s).) At this point this sample is necessarily either pure 2,7-thianthrene 3 or a mixture of 2,7-thianthrene 3 and an isomeric disubstituted thianthrene. In order to learn which of these two possibilities was correct, a minor part[6] of this solid was mixed with almost 1 molar equivalent of iodobenzene dichloride in aqueous pyridine.[7] Chromatography of the product of this reaction (silica gel:benzene-20% $CHCl_3$,$CHCl_3$) produced a white solid: infrared, nuclear magnetic resonance, and mass spectra were highly similar to authentic 2,7-dicarbomethoxythianthrene-5-oxide, 5.[3] (R_f on TLC plates was identical.) These spectral properties show that this sample must be either pure sulfoxide 5 or a mixture of this sulfoxide and one or more isomeric sulfoxides. To determine the composition of this solid 90 MHz pulsed fourier transform pmr spectra of a solution of this solid in $CDCl_3$ containing successively larger amounts of $Eu(fod)_3$[8] were obtained. The last of these, Spectrum I, contains all of the peaks of sulfoxide 5, (See Spectrum II for the actual spectrum of authentic sulfoxide 5 under these conditions) *and more*. When the peaks of sulfoxide 5 are subtracted by computer processing from Spectrum I, there results Spectrum III, exactly that expected of 2,8-dicarbomethoxythianthrene-10-oxide, 6.[9] The only logical explanation of this data is that heating benzothiadiazole 1 yields a mixture of both 2,7- and 2,8-dicarbomethoxythianthrene, 3 and 4 respectively, which can be subsequently oxidized to a mixture of 2,7-dicarbomethoxythianthrene-5-oxide, 5, and 2,8-dicarbomethoxythianthrene-10-oxide, 6, (Equation 1).

Logical explanations as to why *two* isomeric thianthrenes form rather than the expected single isomer are four-fold: (1) Benzothiadiazole 1 may isomerize to the 5-substituted isomer prior to loss of nitrogen. Then either isomer should provide a 2,7-disubstituted thianthrene when reacting with some partner of the same stereochemistry. However, reaction of one isomer with a partner of the other stereochemistry would provide a 2,8-disubstituted thianthrene. This explanation was rejected because it is unprecedented in the literature for this or similar compounds. Further, loss of nitrogen should occur much faster than rearrangement. (2) Heating benzothiadiazole 1 may yield only 2,7-thianthrene 3 which isomerizes to 2,8-thianthrene 4 due to the high temperature of the experiment. This explanation was discounted by the results of heating 2,7-thianthrene 3 under the identical conditions of the experiment. Neither isomerization or decomposition occurred. (3) Loss of nitrogen from benzothiadiazole 1 may yield an α-thioxocarbene, 7, which undergoes Wolf-type rearrangement[10] to give 3-carbomethoxy-6-fulventhione, 8.



(2)

Further rearrangements of fulvene 8 could conceivably produce both 2,7-thianthrene 3 and 2,8-thianthrene 4 (Equation 2). A fruitless attempt to trap fulventhiones during decomposition of benzothiadiazole in high boiling alcohols has been reported.[11] Since thioesters should have formed if fulventhione was present, this explanation was discarded. (4) Loss of nitrogen from benzothiadiazole 1 may produce a *m*-substituted diradical[12], 9, which ring closes to 3-carbomethoxybenzothiirene, 2. Subsequent ring opening of benzothiirene 2 should produce both *m*- and p-substituted diradicals, 9 and 10, respectively. Reaction of either diradical with benzothiirene 2 or benzothiadiazole 1 could yield either disubstituted thianthrene (Scheme I).



Scheme I

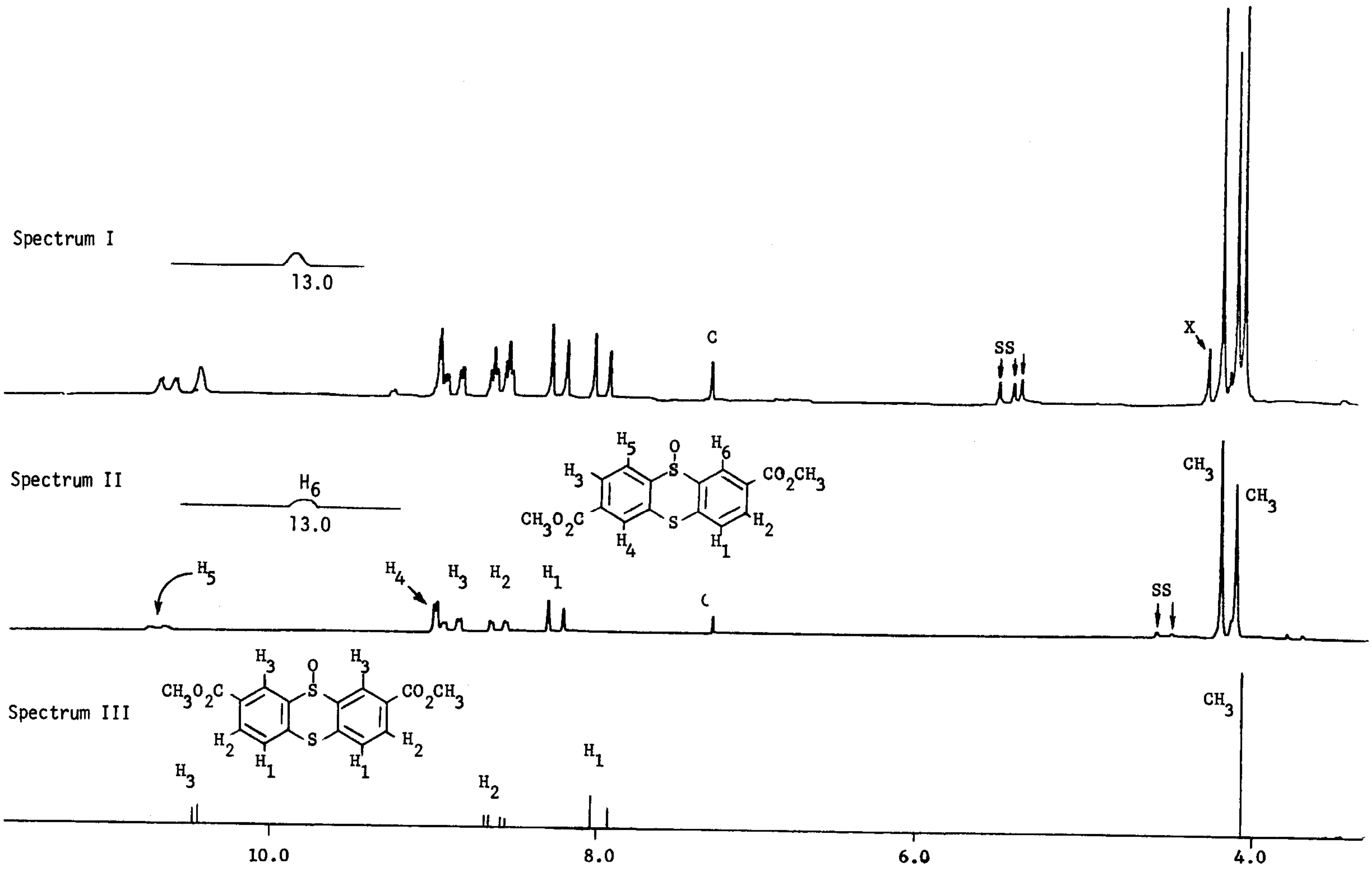


Figure 1

Spectrum I: Eu(fod)3 shifted 90 MHz. pmr spectrum of the mixture of sulfoxides resulting from iodobenzene dichloride oxidation of the thianthrenes from heating 6-carbomethoxy-1,2,3-benzothiadiazole, 1. All chemical shifts are in ppm (δ) from internal TMS. Spectrum II: Authentic 2,7-dicarbomethoxythianthrene-5-oxide under the same conditions as Spectrum I. Spectrum III: Drawing of signals obtained by subtracting Spectrum II from Spectrum I. (These peaks are assigned to 2,8-dicarbomethoxythianthrene-10-oxide.) C=$CHCl_3$; SS=spinning side bands; X=unknown compound, perhaps 2,8-dicarbomethoxythianthrene-5-oxide.

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References

1. J. I. G. Cadogan, J. T. Sharp, and M. J. Trattles, Chem. Comm., 900 (1974).

2. K. P. Zeller, H. Meier, and E. Muller, Tetrahedron Lett., 537 (1971); P. Jacobson and H. Jassen Ann. Chem., 277, 218 (1893).

3. Authentic 2,7-dicarbomethoxythianthrene was prepared by esterification of the corresponding diacid. The diacid was synthesized by adding a mixture of butyl lithium and 2,7-dibromothianthrene to Dry Ice at -78°. (Ref. 4). Authentic 2,7-dicarbomethoxythianthrene-5-oxide, 5, was prepared in the usual way by use of iodobenzene dichloride.

4. 2,7-Dibromothianthrene, mp 204-5°, was obtained from a mixture of p-bromothiophenol and fuming sulfuric acid (Ref. 5).

5. H. J. Shine, C. F. Dais, and R. J. Small, J. Org. Chem., 29, 21 (1964).

6. The remainder of the sample was recrystallized to yield pure 2,7-dicarbomethoxythianthrene. The filtrate provided a semi-solid sample which was oxidized (iodobenzene dichloride) and analyzed at 90 MHz with a shift reagent (exactly as described in this paper for the minor part of the sample). The resulting spectrum showed decreased intensity for each peak of sulfoxide 5 (See Spectrum II for peaks of authentic sulfoxide 5) and increased intensity for each peak assigned to sulfoxide 6 (Spectrum III). (Thus this sample consists of sulfoxide 5 and one other component, assigned as sulfoxide 6.) Extensive and repeated chromatography did not separate these components further.

7. A dilute solution of less than one equivalent of the dichloride effectively suppresses formation of sulfone, or disulfoxide.

8. Eu(fod)$_3$ is tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium III.

9. Since sulfoxide 6 has a plane of symmetry, only one peak due to the protons of two identical carbomethoxy groups should appear (See Spectrum III). Further, only three aryl hydrogen absorptions are expected, as is observed. The peak for H$_1$ should be furtherest upfield since it is not directly effected by the anisotropy of either a carbonyl or a sulfoxide group. It should also show ortho hydrogen splitting as observed. H$_2$, under the influence of an adjacent carbonyl group, should produce a peak downfield of H$_1$ and show both ortho and meta hydrogen splitting, as observed. The peak for H$_3$ should be far downfield due to the anisotropy effects of both a carbonyl and a sulfoxide group and show only meta proton coupling. (Splitting of this peak is gradually lost as it is shifted further and further downfield as the concentration of shift reagent is increased.)

   Sulfoxide 6 is the logical major product of oxidation of 2,8-thianthrene 4. The S$_5$ sulfur atom is para to both electron withdrawing groups and by resonance should be "electron poor" relative to S$_{10}$ which is meta to the electron withdrawing groups. (A small amount of 2,8-dicarbomethoxythianthrene-5-oxide may have been produced. See the notes on Spectrum III for peak "X".) Further, the expected chemical shifts of the protons in the pmr spectrum of 2,8-dicarbomethoxythianthrene-5-oxide would be very different from that expected of sulfoxide 6. For example, the peak of the aryl hydrogen which only shows ortho coupling should be shifted very far downfield due to the anisotropy of the sulfoxide group.

10. Such a rearrangement has been noted in photo-decomposition of thiadiazole: A. Krantz and J. Laureni, J. Amer. Chem. Soc., 96, 6768 (1974), and reference 11.

11. H. Meier and H. Buhl, J. Heterocycl. Chem., 12, 605 (1975).

12. Use of a diradical to depict the intermediate is arbitrary; α-thioxocarbenes would serve as well.