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FORMATION, STRUCTURE, and CONFORMATION OF A NEW RING SYSTEM: 8,10-DITHIABICYCLO[5.3.1]UNDECA-2,5-DIENE

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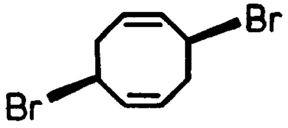
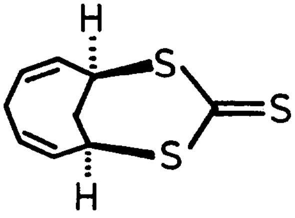
We have recently described[1-3] reactions of syn-3,7-dibromo-cis,cis-cycloocta-1,5-diene (I) with a number of ambident nucleophiles which resulted in the direct introduction of a one-atom bridge to give either the carbocyclic bicyclo[3.3.1]nona-2,6-diene ring system or a 9-hetero analogue. The success of these reactions prompted us to explore the possible formation of a three-atom bridge across the cyclooctadiene ring.

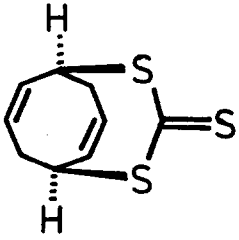
Reaction of dibromide (I) with sodium trithiocarbonate (Na_2CS_3) in aqueous acetonitrile at room temperature for 1.5 hr gave, in 33% yield, bright yellow plates, m.p. 132-134° (from CS_2) of a compound $C_9H_{10}S_3$ giving satisfactory microanalysis and osmometric m.wt. and m/e 214 (M^+). The ^1H n.m.r. (in CS_2) reveals the presence of 4 olefinic protons (τ 4.1-4.4, complex), 2 methine protons (τ 5.68), and 4 non-equivalent methylene protons (multiplets at τ 6.54, 6.78, 7.30, and 7.32). From this, and decoupling experiments one can assign to the product the bicyclo[5.3.1]structure (II) rather than the bicyclo[3.3.3]structure (III), the isochronous nature of the bridgehead methine protons (checked at different field strengths in several solvents) implying cis-bridging as shown.



(I)

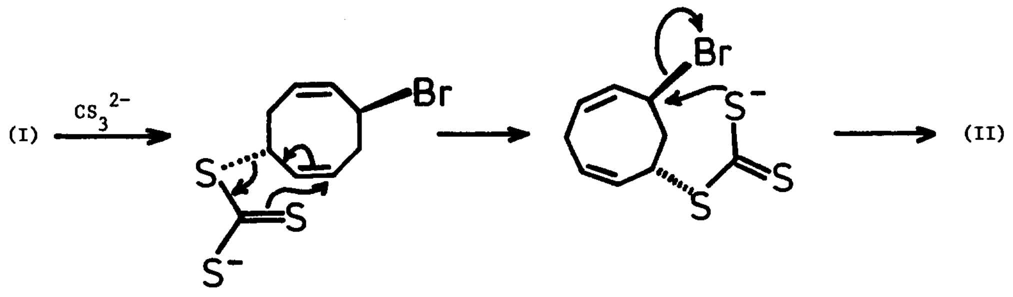


(II)



(III)

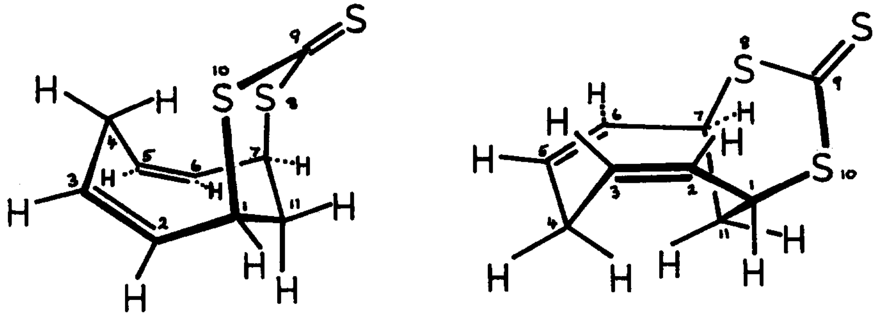
A plausible mechanism for the formation of (II) is given in the Scheme, the initial S_N2 attack on (I) to give the anion (IV) being followed by a [3,3] sigmatropic rearrangement[4] to



SCHEME (IV) (V)

(V) which can then cyclise to the relatively strain-free (II).

Compound (II) is of interest with respect to a comparison of its conformational properties in solution and in the solid state.[5] The two major conformational possibilities are shown in Figure 1, in the form labelled (BC) the carbocyclic cycloocta-1,4-diene ring[6] possesses a rigid boat-chair conformation,[7] and in form (TB), which has an enantiomeric form (TB'), the cyclooctadiene ring is a twist-boat.



(BC) (TB)

Figure 1

A detailed analysis of the proton spectrum (which will be described in full elsewhere) indicates the predominance of twist-boat forms in solution (TB) being in rapid equilibrium with its enantiomer (TB'); for example, in agreement with this, a coupling of only ca. 4 Hz is found between the bridgehead methines and vicinally-related olefinic protons, whereas the near eclipsing of these hydrogens in the (BC) form would imply a relatively large vicinal coupling constant.[8] Attempts to observe individual twist-boat forms with non-averaged couplings were

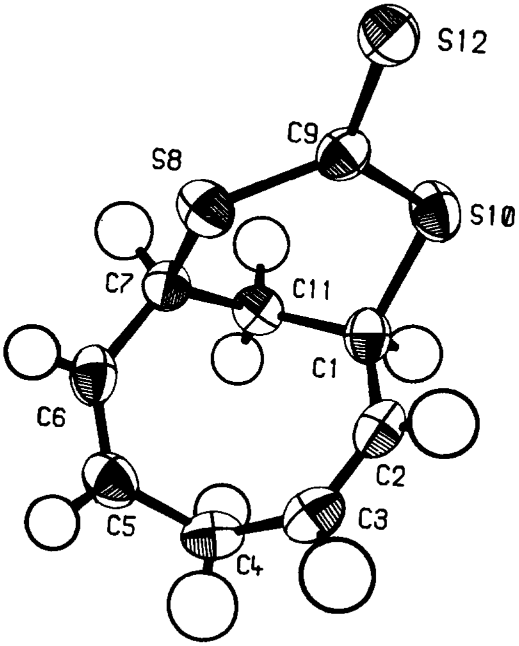


Figure 2

General view of the conformation of 9-thiono-8,10- dithia-bicyclo [5.3.1] undeca-2,5-diene in the crystal (monoclinic form)

made, however no changes attributable to kinetic effects were observed on measuring the ^1H n.m.r. spectrum of (II) at temperatures from ambient down to $-50^\circ C$ in CD_2Cl_2.

Two crystalline modifications of (II) have been obtained, an orthorhombic form, space groups Pbca, and a monoclinic form. The monoclinic form was chosen for detailed study, and has $\underline{a}$ = 13.004 (2), $\underline{b}$ = 5.967 (1), $\underline{c}$ = 12.680 (1), β = 101.75 (1)°, and space group $P2_1/\underline{n}$, $\underline{Z}$ = 4, $\underline{D}_c$ = 1.48. The structure was solved by direct methods employing 1449 significant X-ray intensities measured with a Hilger and Watts automatic diffractometer, and was refined to a final R factor 0.066. During the course of the analysis all the hydrogen atoms were located employing a difference Fourier map. Figure 2 shows a general view of the molecule in the monoclinic crystal, the carbocyclic ring possessing a twist-boat conformation: the molecule has all atoms in general positions, and both enantiomeric forms are present in the crystal. A close transannular approach of hydrogen atoms on C(4) and C(11), 2.16 (7) Å is noteworthy and the separation of C(4) and C(11) atoms themselves is 3.06 (1) Å.

It is interesting to note that, as in the case[5] of dibromide (I), the predominant molecular conformation found in solution, is the same form found to be present in the solid state.

Acknowledgement:

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References

1. E. Cuthbertson and D.D. MacNicol, J.C.S. Perkin I, 1974, 1893.
2. E. Cuthbertson and D.D. MacNicol, J.C.S. Chem. Comm., 1974, 498.
3. E. Cuthbertson and D.D. MacNicol, Tetrahedron Letters, 1974, 2367. (A double bridging process.)
4. For recent examples of similar facile rearrangements see, R.T. Arnold and C. Hoffmann, Synthetic Comm., 1972, 2, 27; R.E. Ireland and R.H. Mueller, J. Amer. Chem. Soc., 1972, 94, 5897; T. Hayashi, Tetrahedron Letters, 1974, 339.
5. For a detailed parallel study of (I) see: R.K. Mackenzie, D.D. MacNicol, H.H. Mills, R.A. Raphael, F.B. Wilson, and J.A. Zabkiewicz, J.C.S. Perkin II, 1972, 1632.
6. Unlike the cycloocta-1,5-diene ring system, the cycloocta-1,4-diene ring has been relatively neglected with respect to conformational investigation; see however: F.R. Ahmed, Acta Cryst., 1975, B31, 26. (Studies on dibenz[c,f]azocines.)
7. J.D. Dunitz and J. Waser, J. Amer. Chem. Soc., 1972, 94, 5645.
8. A value of J_{vic} of 8.5 Hz was observed in a model compound, see N.S. Bhacca, L.J. Luskus, and K.N. Houk, Chem. Comm., 1971, 109.