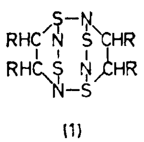
Cycloadditions with Tetrasulphur Tetranitride. Structure of the *trans*-Cyclo-octene Bis-adduct

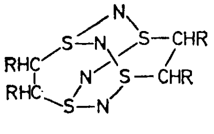
By William L. Mock* and Indu Mehrotra

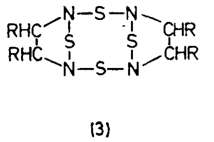
(*Department of Chemistry, University of Illinois at Chicago Circle, Box* 4348, *Chicago, Illinois* 60680)

Summary Degradative and spectroscopic (n.m.r.) structural evidence indicates an S(1),S(3) formulation for (*trans*-$C_8H_{14})_2S_4N_4$ (**4**), which is thought to form by a concerted mechanism.

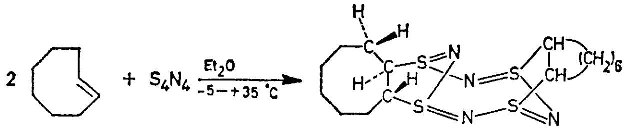
Tetrasulphur tetranitride (S_4N_4) reversibly forms bis-adducts with strained olefins (*e.g.*, norbornene). Various structures have been proposed: (**1**) (by analogy with Diels-Alder cycloaddition),[1] (**2**) (on the basis of MO calculations and orbital symmetry considerations),[2] and (**3**) (on the basis of n.m.r. and other spectral comparisons with model compounds).[3] Additionally, an S(1),S(3) bridged structure (**4**) and a N(1),N(5) bridged analogue of (**2**), as well as other S(1),N(2) and S(1),N(4) bridged adducts should be considered.


(1)

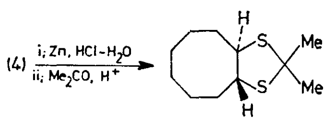

(2)


(3)

We now report an exceptionally ready cycloaddition between S_4N_4 and *trans*-cyclo-octene (97% yield, 1 h reflux, Et_2O), and a simple chemical and spectroscopic proof of the structure of the product, (**4**).[4] Reduction of (**4**) (m.p. *ca.* 143 °C, decomp.) with zinc and aqueous hydrochloric acid (15 h, 70 °C) followed by thioketalization (Me_2CO, H^+) yielded (**5**).† Degradation of (**4**) to an intermediate vicinal dithiol excludes all tentative bis-adduct structures having C–N bonds [(**1**), (**3**), etc.]. A choice between an S(1),S(3)



(4)

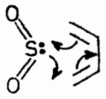


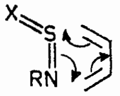
(5)

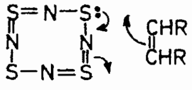
---

† Satisfactory elemental analyses were obtained for (**4**) and (**5**). The n.m.r. spectrum (270 MHz) of (**5**) exhibited a single methyl resonance, consistent with a *trans*-dithiol structure (equivalent acetonide methyl groups).

bis-adduct (**4**), and an S(1),S(5) bis-adduct (**2**) may be made on the basis of n.m.r. spectroscopy. The methine hydrogens (>CHS⩽) are chemically shifted from one another in (**4**) [$\delta(CDCl_3)$ 3·3, 4·7].‡ Inspection of models reveals that the symmetrically bridged structure (**2**) should have these protons in identical environments.§ Hence, (**4**) and its possible diastereomers are left as the only acceptable formulae. At present we suspect that our material is an inseparable mixture of *meso*- and *racemic-anti* adducts, since we can see no reason why a single diastereomer should be exclusively formed and since the m.p. range of the product varies slightly with the temperature at which the addition reaction is conducted.


(6)


(7, X = O, NR)


(8)

Besides providing novel organic–inorganic heterocycles, this cycloaddition extends the multiplicity with which higher-valent sulphur compounds undergo pericyclic reactions. As well as 1,1-(cheletropic)-addition (**6**)[5] and 1,2-addition (**7**)[6] with dienes, a sulphur bis-imine is now shown to undergo 1,3-addition with alkenes (**8**).[7] It is perhaps noteworthy that carbon–sulphur bond formation with S_4N_4 was correctly anticipated theoretically, although initial 1,5-addition was specified.[2] Considering potential stereorandomizing strain relief within a dipolar or diradical intermediate[6] from *trans*-cyclo-octene, a nonconcerted mechanism may provisionally be excluded for this stereospecific reaction.¶ Orbital symmetry constraints are readily satisfied for a synchronous process (**8**).

We thank the Rotary Foundation for Fellowship support (to I.M.).

(*Received*, 17*th November* 1975; *Com.* 1281.)

‡ All resonances are multiplets. Additionally, there is an eleven proton envelope centred at δ 1·8, with one further proton resolved at *ca.* δ 2·5. This latter resonance is possibly attributable to the *endo*-proton of an α-methylene ring residue, which is proximal to the bridging nitrogen in (**4**).

§ A possible alternative explanation, that these resonances correspond to the same protons in *meso*- and *racemic*-forms of (**2**), is unlikely since models reveal insignificant differences in such structures. However, considering ref. 7, a total of four diastereomers is possible for (**4**); that depicted is an *anti*-adduct, which may exist in *meso*- and *racemic*-forms, from (*RS,SR*) and (*RR,SS*) cyclo-octenes, respectively. It is favoured over a corresponding pair of *syn*-adducts (ref. 3) on the basis of steric considerations and by the crystal structure of the norbornadiene adduct (ref. 4).

¶ The cycloaddition is apparently reversible; *trans*-cyclo-octene may be displaced from the bis-adduct with an excess of norbornadiene (ref. 3).

[1] M. Becke-Goehring and D. Schläfer, *Z. Anorg. Chem.*, 1968, **356**, 234.

[2] R. Gleiter, *J. Chem. Soc.* (*A*), 1970, 3174.

[3] M. R. Brinkman and C. W. Allen, *J. Amer. Chem. Soc.*, 1972, **94**, 1550.

[4] While this work was in progress an *X*-ray crystallographic structure determination of the bis-norbornadiene adduct of S_4N_4 was reported: A. M. Griffin and G. M. Sheldrick, *Acta Cryst.*, 1975, **B31**, 895. Bonding to sulphur was demonstrated in concurrence with our conclusion.

[5] S. D. Turk and R. L. Cobb in '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 13; W. L. Mock, *J. Amer. Chem. Soc.*, 1975, **97**, 3666, 3673.

[6] G. Kresze in '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 453; W. L. Mock and R. M. Nugent, *J. Amer. Chem. Soc.*, 1975, **97**, 6521, 6526.

[7] The details of S-N bonding in these heterocycles is a matter of continued interest. Alternate double bonding such as we depict in (4) may represent a single Kekule mesomer as with S_4N_4 [represented in (8)], or may in fact be a potential tautomer as in $S_4N_4F_4$ or $S_4N_4[ONMe_2]_4$; G. A. Wiegers and A. Vos, *Acta Cryst.*, 1961, **14**, 562; 1963, **16**, 152; R. A. Forder and G. M. Sheldrick, *J. Fluorine Chem.*, 1971, **1**, 23. Crystallographic evidence favours the former (ref. 4).