1,3,5,2,4-Trithiadiazepine

Janet L. Morris, Charles W. Rees, and David J. Rigg

Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

1,3$\lambda^4\delta^2$,5,2,4-Trithiadiazepine (**6**) and its benzo derivative (**4**) are stable crystalline compounds which are synthesised from bis(sulphenyl chlorides) and bis(trimethylsilyl)sulphurdiimide; spectroscopic and chemical properties show the heterocyclic ring to be a 10π aromatic system.

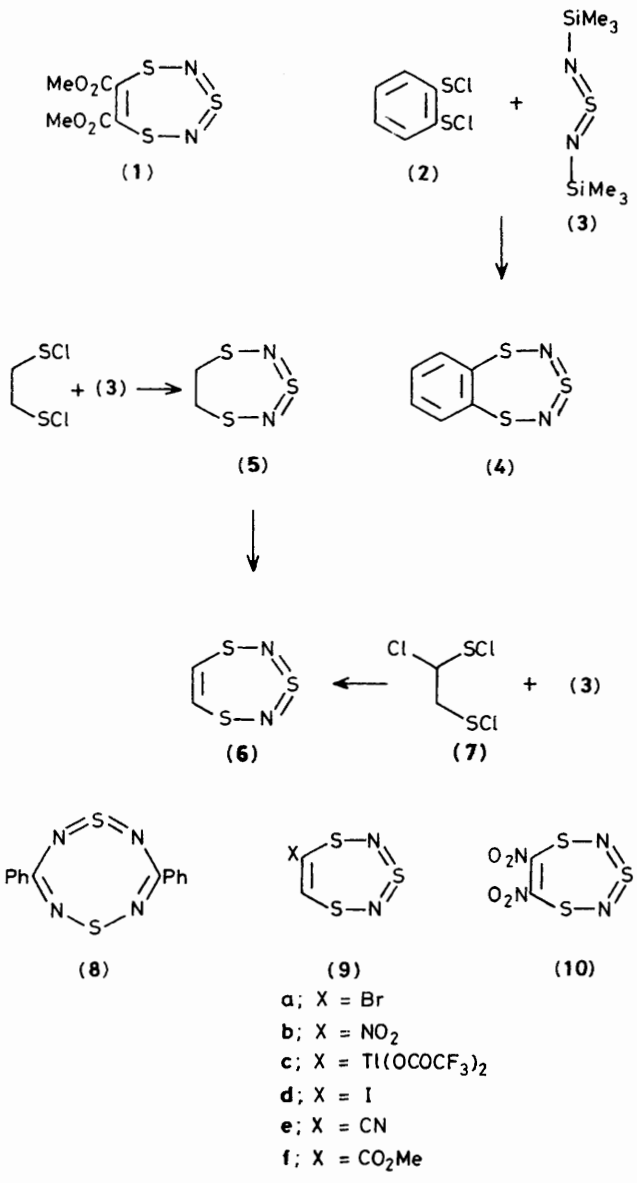
We have recently shown[1] that the reaction of tetrasulphur tetranitride with dimethyl acetylenedicarboxylate in boiling toluene yields small amounts (<10%) of the very stable dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (**1**), the first example of this novel aromatic system. With 10π electrons delocalized over seven atoms, the ring is electron-rich and is thus presumably stabilised by the ester groups. It was therefore of interest to determine the stability of the parent compound and to see if its chemical reactivity is comparable with that of simpler aromatic species.

In view of the low yields and general lack of predictability of the S_4N_4 reactions, a rational synthesis was clearly required; one was initially devised for benzo-1,3$\lambda^4\delta^2$,5,2,4-trithiadiazepine (**4**) based upon the reaction of arylsulphenyl chlorides with bis(trimethylsilyl)sulphurdiimide (**3**).[2] Dilute solutions in dichloromethane of benzene-1,2-bis(sulphenyl chloride) (**2**), prepared quantitatively from the dithiol and chlorine, and of sulphurdiimide (**3**), were added slowly and synchronously from mechanically driven syringes to a large volume of vigorously stirred dichloromethane under nitrogen. This gave benzotrithiadiazepine (**4**) as stable, bright yellow crystals, m.p. 78 °C (50%). The aromatic nature of (**4**) was supported by its spectral properties† and was confirmed by *X*-ray diffraction which showed the molecule to be planar and symmetrical, with delocalised ring bonds.[3]

This synthesis could not be extended directly to the monocyclic compound because of the instability of *Z*-ethene-1,2-dithiol and the associated difficulties of its chlorination. However, ethane-1,2-dithiol was readily and quantitatively converted into the bis(sulphenyl chloride), with chlorine (−20 °C) or sulphuryl chloride (20 °C) in tetrachloromethane. Reaction of this with sulphurdiimide (**3**) in dichloromethane, as above, gave the orange dihydro derivative (**5**)† (20%), m.p. 30 °C, b.p. 45 °C/0.3 mm Hg, which was readily dehydrogenated with dichlorodicyanobenzoquinone in boiling dioxane to give the desired 1,3$\lambda^4\delta^2$,5,2,4-trithiadiazepine (**6**) (70%) as *colourless* volatile crystals, m.p. 57 °C. In view of the low yield of the cyclisation step, this procedure was modified by allowing chlorination of the ethanedithiol to proceed to the trichloro stage (Cl_2 in CCl_4 at 0 °C; monitored by n.m.r. spectroscopy). When the trichloride (**7**) was treated with sulphurdiimide (**3**) as before, the trithiadiazepine, (**6**) was formed directly, with spontaneous loss of hydrogen chloride, in 30% overall yield from ethanedithiol. The spectral properties† and *X*-ray diffraction[3] of (**6**) support a fully delocalised structure; the molecule is planar, symmetrical, and has the intermediate bond lengths expected for an aromatic structure. The chemical properties of trithiadiazepine (**6**) are equally in accord with this.

Compound (**6**) is thermally stable, being unchanged in boiling 1,2-dichlorobenzene (180 °C) for over 2 days, but is

† Satisfactory spectral and analytical data were obtained for all new compounds. Representative data for selected compounds are as follows: (**4**), $\lambda_{max.}$ (EtOH) 252 (log ε 4.25), 292 (4.02), 365 nm (3.63); $\nu_{max.}$ ($CHCl_3$) 1455, 1150 cm^{-1}; δ_H (250 MHz, $CDCl_3$) AA'BB' multiplet (18 lines detected) δ_A 7.78, δ_B 7.29, $J_{AA'}$ 0.54, $J_{AB'}$ 1.17, $J_{BB'}$ 6.80, J_{AB} 8.70 Hz; δ_C ($CDCl_3$) 121.8, 123.0, 147.2; *m/z* 200 (M^+), 154 (M − NS). (**5**), $\lambda_{max.}$ (EtOH) 208 (log ε 3.26), 260 (3.15), 305 (2.76), 408 nm (3.26); $\nu_{max.}$ (film) 1390, 1138 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 3.71 (s); δ_C ($CDCl_3$) 55.9; *m/z* 152 (M^+), 124 ($M - C_2H_4$), 106 (M − NS). (**6**), $\lambda_{max.}$ (EtOH) 224 (log ε 3.76), 330 nm (3.64); $\nu_{max.}$ (KBr) 1410, 1150 cm^{-1}; δ_H (90 MHz, $CDCl_3$), 7.70 (s); δ_C ($CDCl_3$) 127.8; *m/z* 150 (M^+), 124 ($M - C_2H_2$), 104 (M − NS).



decomposed on irradiation (300 nm) in light petroleum. It is inert towards protic and Lewis acids (acetic acid, aqueous hydrochloric acid,‡ $AlCl_3$, BF_3), and towards triethylamine, but it is instantly destroyed by aqueous sodium hydroxide. It is only very slowly consumed by triphenylphosphine in boiling toluene or by *m*-chloroperbenzoic acid in boiling dichloromethane; in marked contrast the benzo derivative (4) is rapidly decomposed by these two reagents at room temperature. Compound (**6**) shows no tendency to undergo cycloaddition reactions with a range of electron-rich and electron-poor 2π and 4π components nor, more surprisingly, to form charge transfer complexes with picric acid, tetracyanoethylene, or 2,4,7-trinitro-9-fluorenylidenemalononitrile.

Trithiadiazepine (**6**) undergoes some standard electrophilic aromatic substitution reactions. Thus it forms the 6-bromo compound (**9a**), m.p. 31 °C (88%), with *N*-bromosuccinimide (1 equiv.) in acetonitrile at room temperature, and the 6,7-dibromo compound, m.p. 89 °C (50%), with excess of the same reagent; it also forms the yellow 6-nitro compound (**9b**), m.p. 84 °C (90%), with copper(II) nitrate trihydrate in acetic anhydride at 0 °C, and the yellow 6,7-dinitro compound (**10**), m.p. 60 °C (54%), with excess of nitronium tetrafluoroborate in acetonitrile. However, attempts to acetylate and formylate (**6**) have so far failed.

6-Aminotrithiadiazepine would be particularly interesting since it would show the interaction between the electron-rich ring and an electron-releasing substituent.§ Unfortunately 6-nitrotrithiadiazepine (**9b**) has resisted all our attempts to reduce it to the amine. It does not undergo catalytic hydrogenation (Pd/C, $Pd/C/H_2SO_4$, PtO_2) presumably because its sulphur-rich ring is an effective catalyst poison. Indeed trithiadiazepine (**6**) was found to inhibit totally the catalytic hydrogenation of *p*-nitroacetophenone which was complete in its absence. Chemical reduction of (**9b**) has so far been no more successful.

The bis(trifluoroacetoxy)thallium derivative (**9c**) was formed from trithiadiazepine (**6**) and thallium(III) trifluoroacetate in refluxing acetonitrile (3 h). Without isolation (**9c**) was directly converted into the pale yellow 6-iodo compound (**9d**), m.p. 93 °C (80%), with aqueous potassium iodide, into the 6-cyano compound (**9e**), m.p. 71 °C (85%), with copper(I) cyanide in boiling acetonitrile,[5] and into methyl trithiadiazepine-6-carboxylate (**9f**), m.p. 111 °C (70%), with carbon monoxide and methanol in the presence of palladium chloride, lithium chloride, and magnesium oxide.[6] Ester (**9f**) is identical with a minor product previously obtained from the reaction of S_4N_4 with methyl propiolate and assigned an incorrect structure;[7] structure (**9f**) is to be expected for this product in the light of our earlier work.[1]

Thus, in spite of the predominance of heteroatoms, the trithiadiazepine (**6**) and its derivatives are stable aromatic compounds which, with a closely related trithiatriazepine also produced from S_4N_4,[1] are being further investigated.

Received, 16th October 1984; Com. 1461

References

1 S. T. A. K. Daley, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1984, 55.
2 J. Kuyper and G. B. Street, *J. Am. Chem. Soc.*, 1977, **99**, 7848.
3 R. Jones, J. L. Morris, A. W. Potts, C. W. Rees, D. J. Rigg, H. S. Rzepa, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1985, following communication.
4 I. Ernest, W. Holick, G. Rihs, D. Schomburg, G. Shoham, D. Wenkert, and R. B. Woodward, *J. Am. Chem. Soc.*, 1981, **103**, 1540.
5 E. C. Taylor, A. H. Katz, and A. McKillop, *Tetrahedron Lett.*, 1984, **25**, 5473.
6 R. C. Larock and C. A. Fellows, *J. Org. Chem.*, 1980, **45**, 363.
7 S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, 1979, **16**, 1009.

‡ The properties of (**6**) are broadly similar to those of the 10π aromatic dithiatetrazocine (**8**),[4] though the latter was readily hydrolysed by hydrochloric acid as well as by potassium hydroxide.

§ For example, replacement of the phenyl groups in (**8**) by dimethylamino groups transforms the planar aromatic ring into a non-planar structure folded along the S–S axis.[4]