The Preparation of Benzo-1,3-dithia-2,4-diazine, a Novel Electron-rich Heterocycle

Hans Koenig and Richard T. Oakley*

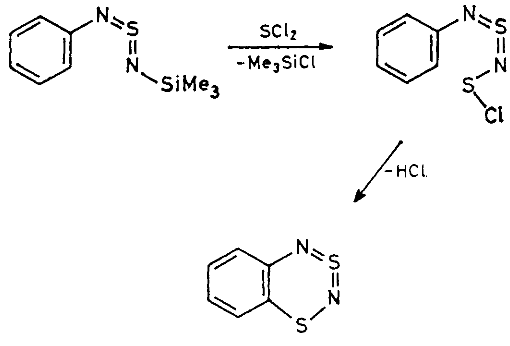
Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

The reaction of *N*-phenyl-*N*′-trimethylsilyl sulphur di-imide with sulphur dichloride yields benzo-1,3-dithia-2,4-diazine, a novel twelve π-electron heterocycle.

The coupling of silylated sulphur di-imides with sulphur dichloride is a widely-used method for producing conjugated sulphur–nitrogen oligomers[1] and polymers[2] (equations 1 and 2). However, if the R group of (**1**) is an aromatic ring, an alternative reaction to that shown in equation 2 is possible. Instead of the metathetical elimination of trimethylsilyl chloride to form an N–S bond, electrophilic attack of the sulphenyl chloride group of (**2**) at the *ortho*-position of the aromatic ring can occur, yielding a novel six-membered 1,3-dithia-2,4-diazine ring (equation 3).

$$\underset{(\mathbf{1})}{\text{R–NSN–SiMe}_3} \xrightarrow[-\text{Me}_3\text{SiCl}]{\text{SCl}_2} \underset{(\mathbf{2})}{\text{R–NSN–SCl}} \qquad (1)$$

$$(\mathbf{1}) + (\mathbf{2}) \xrightarrow[-\text{Me}_3\text{SiCl}]{} \text{R–NSN–S–NSN–R} \qquad (2)$$



(3)

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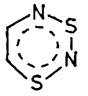
As a typical example, the slow addition of *N*-phenyl-*N*′-trimethylsilyl sulphur di-imide (2.57 g, 12.0 mmol) in 100 ml of methylene chloride to a solution of sulphur dichloride (1.26 g, 12.0 mmol) in 300 ml of methylene chloride affords benzo-1,3-dithia-2,4-diazine (**3**) (245 mg, 1.5 mmol, 12%). The product can be purified by vacuum sublimation at 30 °C/ 10^{-2} Torr and recrystallization from pentane to give deep blue fibrous needles, m.p. 48—50 °C {mass spectrum (70 eV): 168 ($C_6H_4S_2N_2$, 100%), 136 ($C_6H_4SN_2$, 17%), 122 (C_6H_4SN, 17%), and 108 (C_6H_4S, 17%); u.v.-visible spectrum (CH_2Cl_2), λ_{max} (log ϵ): 617 (2.7), 371 (3.0), 291 (4.3), and 283 nm (4.3); ^{13}C n.m.r. [$CDCl_3$ 10^{-2} M Cr(acac)$_3$(Hacac = acetylacetone)], δ: 138.8, 133.4, 130.7, 124.3, 123.2, and 115.5 p.p.m.}. The appearance of six resonances in the ^{13}C n.m.r. spectrum of (**3**) and the observed fragmentation pattern for the molecule confirm the proposed structure.†

The annelation reaction (equation 3) represents the first example of a potentially general method for preparing electron-rich heterocycles based on the novel 1,3-dithia-2,4-diazine unit (**4**). Although benzo-1,3-dithia-2,4-diazine (**3**) possesses a naphthalene-like framework, the π-manifold contains two extra electrons (12π *vs.* 10π for napthalene). Similarly (**4**) is an 8π-electron system, and as such is intermediate between benzene (6π) and the $S_3N_3^-$ anion (**5**) (10π).[3]



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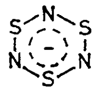

(5)

The formation of (**3**) demonstrates that planar rings containing conjugated S–N units can exist with 4*n* as well as 4*n* + 2 π-electrons. The stability of these electron-rich π-systems is made possible by the high effective nuclear charge of their constituent atoms, which supports a larger number of π-electrons/atomic centre than in carbocyclic systems.[4,5] A diverse redox chemistry for molecules such as (**3**) is to be expected. The u.v.-visible spectrum of (**3**) exhibits a number of low-energy absorptions. While the detailed nature of these bands is not yet established, they are likely to involve π → π* and π* → π* excitations.

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† The elemental composition of (**3**) has been confirmed by chemical analysis and high resolution mass measurement.