Synthesis and Interconversion of 5-Phenyl-1,3,2,4,6-dithiatriazine Derivatives; Crystal and Molecular Structure of the Bicyclic Molecule $PhCN_5S_3$

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Novel synthetic routes to heterocycles based on the 1,3,2,4,6-dithiatriazine framework are described;the *X*-ray crystal structure determination of the bicyclic derivative $PhCN_5S_3$ is reported.

Considerable interest has been demonstrated in the chemistry of heterocyclic thiazyl compounds, *i.e.* compounds that incorporate one or more unsaturated carbon atoms into an otherwise binary SN framework.[1—8] Most of the preparative routes to molecules of this type involve the reactions of nitriles and amidines (or their salts) with $S_3N_3Cl_3$, $S_3N_2Cl_2$, or SCl_2.[2—8] However, these methods generally lead to a mixture of products, the composition of which is difficult to anticipate. Following our recent study[2] of the reaction of benzamidine with $S_3N_3Cl_3$ we have examined the use of *N,N,N'*-tris(trimethylsilyl)benzamidine $PhC(NSiMe_3)N(SiMe_3)_2$[9] as a milder, more specific reagent. We report herein that the reaction of this compound with $S_3N_3Cl_3$ provides a simple, efficient, and rational synthesis of the bicyclic molecule $PhCN_5S_3$ (**1**).

Compound (**1**) was prepared by the slow addition of a solution of $PhC(NSiMe_3)N(SiMe_3)_2$ (6.89 g, 20.5 mmol) in 100 ml CH_2Cl_2 to a stirred solution of $S_3N_3Cl_3$ (5.00 g, 20.5 mmol) in 100 ml CH_2Cl_2 at 0 °C. Subsequent removal of the solvent and recrystallization of the residue from hot acetonitrile afforded golden air-stable plates of (**1**) {3.20 g, 12.5 mmol, 61%, decomp. 136 °C;† *m/z* [electron impact (E.I.), 70 eV] 195 ($PhCN_3S_2^+$, 23%), 181 ($PhCN_2S_2^+$, 75), 149 ($PhCN_2S^+$, 29), 135 ($PhCNS^+$, 30), 103 ($PhCN^+$, 100)}.

The crystal and molecular structures of (**1**) have been determined by *X*-ray crystallography.‡ An ORTEP drawing of the molecule and pertinent structural information are provided in Figure 1. The molecule can be described in terms of a 1,3,2,4,6-dithiatriazine skeleton loosely bridged by a NSN fragment across the 1,3-sulphur atoms. As such the molecule has many structural features in common with the phosphorus containing molecule $F_2PS_3N_5$.[10] In particular we note that the bonds to the NSN bridge in (**1**) [mean of S(1)–N(3) and S(2)–N(2) = 1.728(2) Å] are even longer than the corresponding linkages in $F_2PS_3N_5$ [1.692(8) Å].

Oxidation of (**1**) (4.00 g, 15.7 mmol) in 100 ml CCl_4 with chlorine yields (in addition to small amounts of

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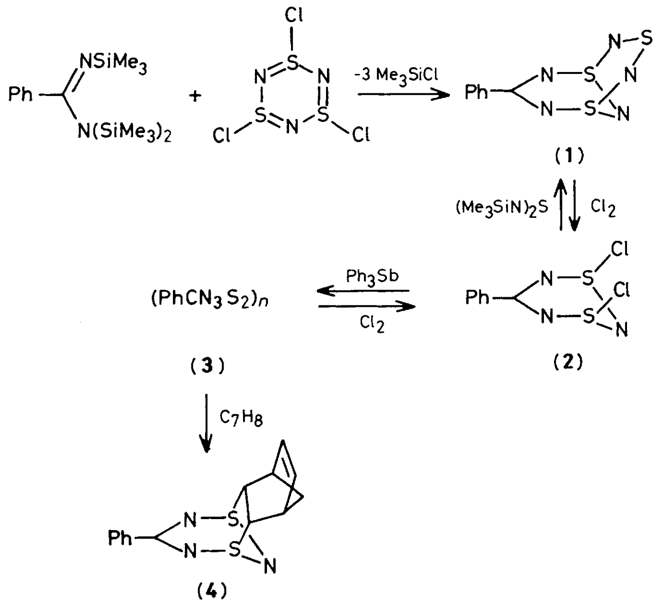
† The elemental compositions of (**1**), (**2**), (**3**), and (**4**) have been confirmed by chemical analysis.

‡ *Crystal data:* $C_7H_5N_5S_3$, $M = 255.3$, monoclinic, space group $P2_1/_n$ $a = 5.958(1)$, $b = 22.955(2)$, $c = 7.427(1)$ Å, $\beta = 106.25°$, $Z = 4$, $U = 975.2$ Å^3, and $D_c = 1.740$ g cm^{-1}. Data were collected on an Enraf–Nonius CAD-4 automated diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) using ω–2θ scans ($\theta_{max.}$ of 50°), and were corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares to an *R*-value of 0.030 for 1364 independent reflections ($I > 3\sigma_I$) and 156 parameters. All hydrogen atom positions were located from Fourier difference maps and were refined isotropically. The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



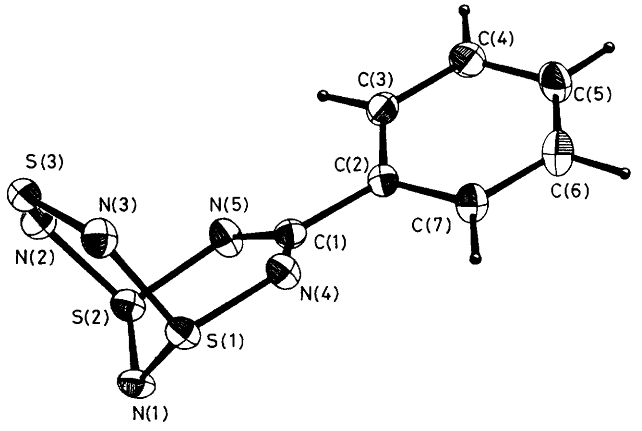


Figure 1. ORTEP drawing (30% probability ellipsoids) of $PhCN_5S_3$ (**1**). Selected bond lengths (in Å) and angles (in °) are: S(1)–N(1) 1.630(2), S(1)–N(3) 1.728(2), S(1)–N(4) 1.622(2), S(2)–N(1) 1.630(2), S(2)–N(2) 1.728(2), S(2)–N(5) 1.621(2), S(3)–N(2) 1.547(2), S(3)–N(3) 1.547(2), N(4)–C(1) 1.337(3), N(5)–C(1) 1.333(3), C(1)–C(2) 1.486(3); N(1)–S(1)–N(3) 106.1(1), N(1)–S(1)–N(4) 109.5(1), N(3)–S(1)–N(4) 102.5(1), N(1)–S(2)–N(2) 105.1(1), N(1)–S(2)–N(5) 110.2(1), N(2)–S(2)–N(5) 102.4(1), N(2)–S(3)–N(3) 119.0(1), S(1)–N(1)–S(2) 111.8(1), S(2)–N(2)–S(3) 119.7(1), S(1)–N(3)–S(3) 121.5(1), S(1)–N(4)–C(1) 118.8(2), S(2)–N(5)–C(1) 120.8(2), N(4)–C(1)–N(5) 129.9(2), N(4)–C(1)–C(2) 115.6(2), N(5)–C(1)–C(2) 114.5.

$PhCN_2S_2^+Cl^-$)[4] the 1,3-dichloro-5-phenyl-1,3,2,4,6-dithiatriazine (**2**), which can be recrystallised from CH_2Cl_2–hexane as yellow moisture-sensitive plates [2.52 g, 9.47 mmol, 60%, m.p. 119—121 °C; m/z (E.I., 70 eV) 230 ($PhCN_3S_2Cl^+$, 2%), 195 ($PhCN_3S_2^+$, 39), 181 ($PhCN_2S_2^+$, 11), 149 ($PhCN_2S^+$, 46), 135 ($PhCNS^+$, 13), 103 ($PhCN^+$, 50), 46 (NS^+, 100)]. Treatment of (**2**) with N,N'-bis(trimethylsilyl)sulphur diimide reforms the bicyclic structure (**1**). We note that the isolation of (**2**) completes the series of heterocycles $(PhC)_x(SCl)_{3-x}N_3$ (for x = 2, see ref. 2).

Reduction of (**2**) (0.50 g, 1.87 mmol) with triphenylstibine (0.66 g, 1.87 mmol) in 50 ml chloroform yields a buff-coloured air-stable microcrystalline precipitate of 5-phenyl-1,3,2,4,6-thiatriazine (**3**) [0.28 g, 0.15 mmol, 78%, m.p. 115 °C; m/z (E.I., 70 eV) 195 ($PhCN_3S_2^+$, 19%), 181 ($PhCN_2S_2^+$, 6), 149 ($PhCN_2S^+$, 21), 135 ($PhCNS^+$, 3), 103 ($PhCN^+$, 25), 92 ($S_2N_2^+$, 12), 78 (S_2N^+, 11), 76 (?, 12), 64 (S_2^+, 9), 46 (SN^+, 100)]. We have confirmed the structural integrity of the six-membered CN_3S_2 ring in (**3**) by its reconversion into (**2**) (in 85% yield) upon treatment with chlorine and through formation of the norborna-1,3-diene adduct (**4**). The adduct is obtained (in 63% yield) by reacting a slurry of (**3**) (0.45 g, 2.3 mmol) in 10 ml acetonitrile with an excess of norbornadiene. The product can be recrystallized from acetonitrile as colourless plates [m.p. 179—180 °C; m/z (E.I., 70 eV) 287 ($PhCN_3S_2 \cdot C_7H_8^+$, 1%), 259 ($PhCNS_2 \cdot C_7H_8^+$, 2), 195 ($PhCN_3S_2^+$, 100), 149 ($PhCN_2S^+$, 41), 103 ($PhCN^+$, 21), 91 ($C_7H_7^+$, 19); ^1H n.m.r. (400 MHz, $CDCl_3$) δ 7.3—7.9 (m, 5H, Ph), 6.24 (s, 2H, $H_{5,6}$), 4.48 (d, 2H, $H_{1,4}$, J 1.5 Hz), 3.24 (t, 2H, $H_{2,3}$, J 1.7 Hz), 2.08 and 1.16 (d, 1H, H_7 and H_8, $J_{7,8}$ 9.8 Hz)].[11]

The colour of (**3**) and its low solubility in organic media set it apart from the formally isoelectronic 8π-heterocycles $R_2PN_3S_2$ and $S_3N_3O_2^-$ that we have prepared.[11,12] The CF_3-substituted dithiatriazine $CF_3CN_3S_2$ has been reported recently, but no details were provided.[5b] The behaviour of (**3**) leads us to suggest that the compound is not monomeric.

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