

Convenient Synthesis and Ring Contraction *via* Thermolysis of 1,3-Dichloro-1,3,2,4,6-dithiatriazines

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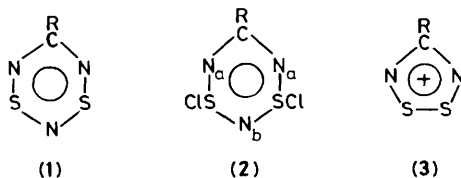
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The reaction of organic nitriles with $(\text{NSCl})_3$ at 23 °C, preferably under u.v. irradiation, produces the six-membered rings $\text{RCN}_3\text{S}_2\text{Cl}_2$ ($\text{R} = \text{Bu}^t, \text{CCl}_3, \text{Me}_2\text{N}, \text{Et}_2\text{N}, \text{Pr}_i_2\text{N}$), which are converted to the five-membered rings $\text{RCN}_2\text{S}_2^+\text{Cl}^-$ upon mild thermolysis.

The synthesis, structures, and properties of the eight π -electron 1,3,2,4,6-dithiatriazines (**1**; $\text{R} = \text{CF}_3$,¹ Ph ,^{2,3} *p*- ClC_6H_4 ,³ Et_2N ,⁴ Pr_i_2N ⁴) are of current interest.⁵ The phenyl derivative is a cofacial dimer,² whereas the properties of (**1**; $\text{R} = \text{Et}_2\text{N}, \text{Pr}_i_2\text{N}$) suggests a monomeric structure.⁴ The common route to (**1**) involves the reduction of the corresponding 1,3-dichloro-1,3,2,4,6-dithiatriazines, (**2**),^{1,2,4} and, in principle, the cycloaddition reaction (**1**) offers a general synthesis of (**2**). However, until now this reaction has only been successful for the preparation of (**2**; $\text{R} = \text{Me}_2\text{N}, \text{Et}_2\text{N}, \text{Pr}_i_2\text{N}$).⁶ By contrast, the treatment of other organic nitriles with $(\text{NSCl})_3$ at elevated temperatures gives modest yields of the corresponding 1,2,3,5-dithiazolium chloride, (**3**; $\text{R} = \text{Bu}^t, \text{CCl}_3, \text{Ph}$)⁷ or a mixture of both (**2**; $\text{R} = \text{CF}_3$) and (**3**; $\text{R} = \text{CF}_3$).¹ In order to reconcile these divergent results, we have investigated several $\text{RCN}-(\text{NSCl})_3$ systems under a variety of conditions using ¹⁴N n.m.r. spectroscopy to monitor the progress of reactions. We report here that reaction (**1**) occurs slowly at 23 °C, or more rapidly under u.v. irradiation, to give good yields of (**2**; $\text{R} = \text{Bu}^t, \text{CCl}_3, \text{Me}_2\text{N}, \text{Et}_2\text{N}, \text{Pr}_i_2\text{N}$), which undergoes a bimolecular ring contraction reaction to give (**3**) upon mild thermolysis.



For example, a mixture of $(\text{NSCl})_3$ (6.67 mmol) and an excess of trichloroacetonitrile (2 cm³) at 23 °C for 3 weeks under an inert atmosphere produced a yellow solid, after the removal of the excess of nitrile under vacuum, which was recrystallised from CH_2Cl_2 -hexane (1:3, 20 cm³) to give yellow needles of (**2**; $\text{R} = \text{CCl}_3$) in 71% yield. M.s.: *m/z* [electron ionisation (e.i.), 70 eV] 272 ($\text{CCl}_3\text{CN}_3\text{S}_2\text{Cl}^+$, 5), 237 ($\text{CCl}_3\text{CN}_3\text{S}_2^+$, 20), 118 (CS_2N_3^+ , 10), 92 (S_2N_2^+ , 15), 78 (S_2N^+ , 40), 64 (S_2^+ , 20), 46 (NS^+ , 100%); ¹³C n.m.r. (200 MHz, CDCl_3), 165.3 and 95.1. Similarly, (**2**; $\text{R} = \text{Bu}^t$) was obtained in 42% yield after a reaction time of 5 weeks.† Reaction (**1**) occurs more rapidly under the influence of u.v. radiation for $\text{R} = \text{CCl}_3, \text{Bu}^t$. A mixture of $(\text{NSCl})_3$ (3.35 mmol) and an excess of trichloroacetonitrile (1.5 cm³) in a water-cooled quartz tube (20 × 300 mm) under an inert atmosphere was irradiated (250 watt sun lamp) for 2 days to give (**2**; $\text{R} = \text{CCl}_3$) in 77% yield after recrystallisation. Compound (**2**; $\text{R} = \text{Bu}^t$) was obtained in 33% after 4 days irradiation.



The known derivatives (**2**; $\text{R} = \text{Me}_2\text{N}, \text{Et}_2\text{N}, \text{Pr}_i_2\text{N}$) can also be prepared at room temperature in high yields by treatment of R_2NCN with $(\text{NSCl})_3$ in carbon tetrachloride. The rate of these reactions was shown by ¹⁴N n.m.r. spectroscopy to depend on the size of the R group. The reaction is complete in 12 h, 48 h, and 1 week for $\text{R} = \text{Me}_2\text{N}, \text{Et}_2\text{N}$ and Pr_i_2N , respectively. The characteristic ¹⁴N n.m.r. chemical shifts for (**2**) are given in Table 1.

The thermolysis of (**2**) produces (**3**) in high yields. For example, a yellow solution of (**2**; $\text{R} = \text{Et}_2\text{N}$) in boiling toluene (10 cm³) for 24 h gave dark purple needles of (**3**; $\text{R} = \text{Et}_2\text{N}$)⁴ in 74% yield. Under similar conditions, (**3**; $\text{R} = \text{Me}_2\text{N}$) was obtained in 91% yield from (**2**; $\text{R} = \text{Me}_2\text{N}$). This synthesis of (**3**; $\text{R} = \text{Me}_2\text{N}, \text{Et}_2\text{N}$) is a marked improvement over the existing procedure.⁴ The thermolysis of (**2**; $\text{R} = \text{CCl}_3$) occurs at 80 °C to give (**3**)⁷ in 87% yield, whereas the conversion of (**2**; $\text{R} = \text{Bu}^t$) into (**3**)⁷ takes place at 40 °C. The transformation of (**2**) into (**3**) ($\text{R} = \text{CF}_3$) at 120 °C has been reported without details.¹

The ring contraction reaction (**2**) → (**3**) can be conveniently monitored by ¹⁴N n.m.r. spectroscopy (Table 1). The two signals attributed to the inequivalent nitrogen atoms, N_a and N_b , of the six-membered ring, (**2**), are replaced by the characteristic singlet of the five-membered ring, (**3**), during the course of the reaction.

The transformation of (**2**; $\text{R} = \text{Me}_2\text{N}$), λ_{max} 360 nm into (**3**; $\text{R} = \text{Me}_2\text{N}$), λ_{max} 530 nm was monitored by u.v.-vis. and ¹H n.m.r. spectroscopy. A red intermediate (λ_{max} 500 nm), which could not be isolated, was observed and the reaction was found to be second order in (**2**). This suggests that the ring contraction occurs *via* the initial ring opening dimerisation of (**2**), possibly to give a twelve-membered ring, a process that has been observed for other heterocyclothiazines.^{8,9}

In summary, the initial product of the reaction of organic nitriles with $(\text{NSCl})_3$ is the six-membered ring (**2**). The conversion of (**2**) into (**3**) upon thermolysis accounts for the

Table 1. ¹⁴N n.m.r. chemical shifts for $\text{RCN}_3\text{S}_2\text{Cl}_2$ (**2**), and $\text{RCN}_2\text{S}_2^+\text{Cl}^-$ (**3**).

Compound ^a	$\delta(^{14}\text{N})^b$			
	N_a	N_b	R_2N	N
$\text{Me}_2\text{NCN}_3\text{S}_2\text{Cl}_2$	-211	-263	-211	
$\text{Et}_2\text{NCN}_3\text{S}_2\text{Cl}_2$	-216	-229	-242	
$\text{Pr}_i_2\text{NCN}_3\text{S}_2\text{Cl}_2$	-221	-257	-221	
$\text{Bu}^t\text{CN}_3\text{S}_2\text{Cl}_2$	-193	-245		
$\text{CCl}_3\text{CN}_3\text{S}_2\text{Cl}_2$	-195	-248		
$\text{Me}_2\text{NCN}_2\text{S}_2^+\text{Cl}^-$			-318	-133
$\text{Et}_2\text{NCN}_2\text{S}_2^+\text{Cl}^-$			-296	-127
$\text{Bu}^t\text{CN}_2\text{S}_2^+\text{Cl}^-$				-135
$\text{CCl}_3\text{CN}_2\text{S}_2^+\text{Cl}^-$				-181

^a In CH_2Cl_2 . ^b In p.p.m. rel. to MeNO_2 .

† Satisfactory C, H, N analyses were obtained for new compounds.

early reports that this reaction yields (3) directly at elevated temperatures. This simple synthesis of (2) should facilitate investigations of the corresponding eight π -electron systems, (1).

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