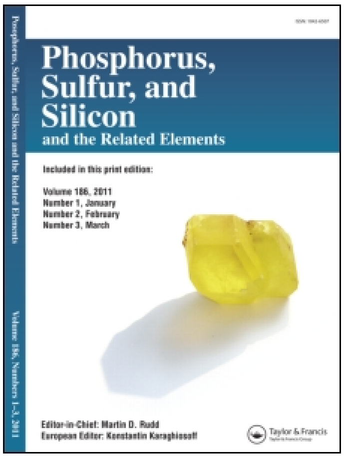

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CYCLOADDITION REACTIONS OF $(NSCl)_3$ WITH ORGANIC NITRILES

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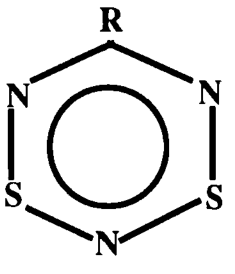
Abstract The six-membered ring system $RCN(NSCl)_2$ (R= ${}^tBu$, CCl_3, Me_2N, Et_2N, ${}^iPr_2N$) can be prepared by a cycloaddition reaction of the free nitrile, RCN, with cyclo-$(NSCl)_3$ at room temperature. This reaction is slow for R= ${}^tBu$ and CCl_3, but it can be accelerated by UV light. The six-membered rings are converted to five-membered rings $RCN_2S_2^+$ Cl^- by thermolysis. By varying the conditions of the cycloaddition reaction, 1,3-$(RCN)_2(NSCl)_2$ (R= Me_2N, Et_2N) and 1,5- $RCN(NSN)_2SCl$ can be obtained.

INTRODUCTION

There is current interest in the synthesis, structure, and properties of the 8 π -electron 1,3,2,4,6-dithiatriazines 1. When R= phenyl 1 has been demonstrated to have a cofacial dimeric structure,[1] but a monomeric structure is indicated for the dialkylamino derivatives.[2] The trifluoromethyl derivative, 1 (R= CF_3) has been reported but it is not well characterized.[3] Therefore the preparation of 1 with other R groups is of considerable importance.

In principle 1 can easily be prepared by the reduction of the corresponding 1,3-dichloro derivatives 2. However, 2 has only be obtained in high yield for R= Me_2N, Et_2N, ${}^iPr_2N$ by the cycloaddition of RCN and $(NSCl)_3$ in carbon tetrachloride at 60°C.[4] By contrast, the reaction of other organic nitriles with $(NSCl)_3$ at elevated temperatures leads to modest yields (<50 %) of the five-membered ring 1,2,3,5-dithiazolium chloride 3 (R= ^{t}Bu, CCl_3, Ph)[5,6] or a mixture of 2 (21 %) and 3 (45 %) for R= CF_3.[3] These divergent results suggest that for all nitriles the initial cycloaddition reaction leads to the six-membered ring 2, which can be subsequently converted to the five-membered ring by thermolysis.



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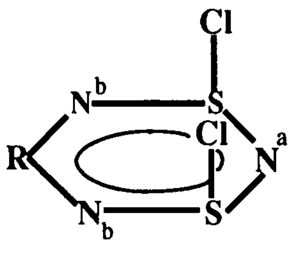

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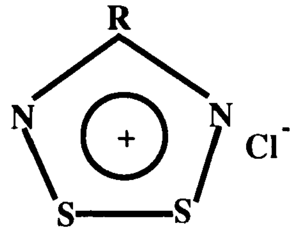

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PREPARATION OF RCN(NSCl)$_2$

We find that the six-membered ring 2 (R= ^{t}Bu, CCl_3) can be prepared by employing milder reaction conditions. For example a mixture of $(NSCl)_3$ (6.67 mmol) and an excess of trichloroacetonitrile (2 ml) at 23°C for three weeks produced a yellow solid after removal of the excess nitrile. Recrystallization from 1:3 CH_2Cl_2: hexane gave yellow needles of 2 (R=CCl_3) in 71 % yield. Similarly, 2 (R= ^{t}Bu) was obtained in 42% yield after a reaction time of 5 weeks.

These reactions can be accelerated by irradiation with UV light. A mixture of $(NSCl)_3$ (3.35 mmol) and an excess of trichloroacetonitrile in a water-cooled quartz tube under an inert atmosphere was irradiated for two days (250 watt sun lamp) to give 2 (R=CCl_3) in 77 % yield after recrystallization. Similarly compound 2 (R=

^tBu) was obtained in 33% yield after 4 days irradiation [this reaction also produced 3 (R= ^tBu)]

The known dialkylamino derivatives of 2 (R= Me_2N, Et_2N, $^iPr_2N$) can also be prepared at room temperature by treatment of the nitrile with $(NSCl)_3$ in carbon tetrachloride. The rate of reaction was found by ^{14}N NMR to depend on the steric bulk of the R group.The reaction is complete in 12 hours, 48 hours, and 1 week, for R= Me_2N, Et_2N,and $^iPr_2N$, respectively.

MECHANISM OF CYCLOADDITION REACTION

The cycloaddition reaction of Me_2NCN with $(NSCl)_3$ occurs on a convenient time scale to be studied in detail by ^1H and ^{14}N NMR. Upon addition of Me_2NCN to a solution of $(NSCl)_3$ the original yellow solution becomes mint green indicating that monomerization of the $(NSCl)_3$ is occurring. After 15 minutes the solution begins to turn an intense red color which then fades slowly over a period of 4 hours to the yellow - orange color of 2 (R= Me_2N). The red intermediate has ^{14}N NMR chemical shifts of 209, -154, and -340 ppm (relative to nitromethane) and a signal in the ^1H NMR spectrum at 3.54 ppm. After 5 minutes reaction time 2 could already be detected by NMR along with free nitrile and the intermediate. Free nitrile did not disappear until 1.5 hours reaction time. In the early part of the reaction the ^{14}N NMR signals for NSCl monomer and the NSCl unit of the intermediate (see Figure 1) were exchange-broadened and coalesced into one peak whose shift varied with time, as the NSCl monomer was consumed. Finally this peak became a sharp singlet at the position observed for the red intermediate (a change from 301 ppm at 5 minutes to 209 ppm after 2 hours). No back reaction from the intermediate to the nitrile and NSCl was detected and the data indicate that the rate determining step is the cyclization of the intermediate with another NSCl unit. A mechanism that is consistant with this information is shown in Figure1.

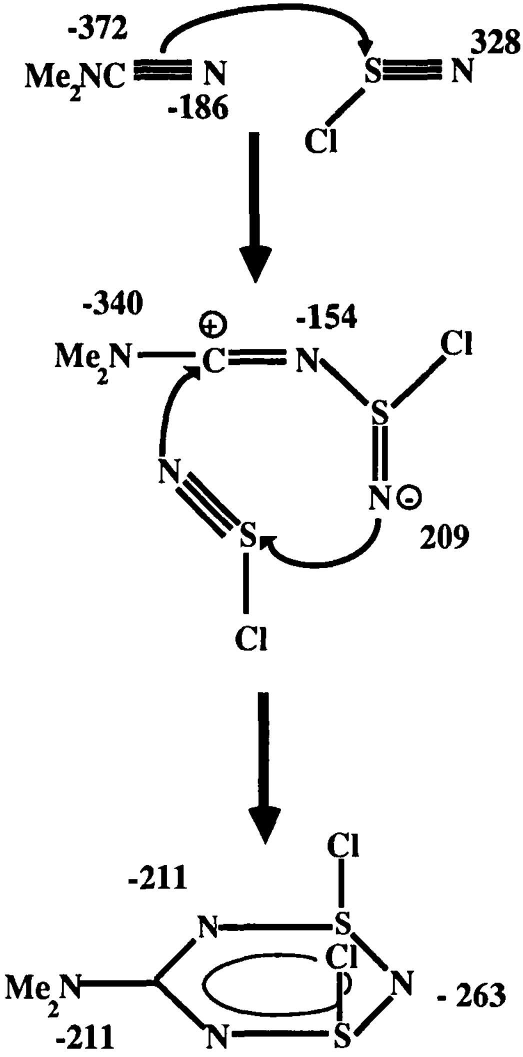


FIGURE 1 Mechanism of the cycloaddition reaction and^{14}N NMR chemical shifts for Me_2NCN + $(NSCl)_3$.

THERMOLYSIS OF $RCN(NSCl)_2$

The thermolysis of the heterocycles 2 produces 3 in good yields at temperatures which vary greatly depending on the R group. Yellow solutions of 2 (R= Me_2N,

Et_2N) in toluene at reflux for 24 hours gave purple crystals of 3 in 91% and 74% yield, respectively. This is a considerable improvement on the existing synthesis of 3 from 2 (R= Et_2N) and sodium azide.[2]

The thermolysis of the trichloromethyl derivative of 2 occurs at 80 °C and yields the corresponding five membered ring in 87% yield, whereas the thermolysis of 2 (R= ^tBu) occurs at ca. 40 °C. Brief mention has been made of the conversion of 2 into 3 for R= CF_3 at 120 °C.[3] NMR data for various derivatives of 2 and 3 are summarized in Tables 1 and 2 respectively.

TABLE 1 ^1H, ^{13}C, and ^{14}N NMR chemical shifts of $RCN(NSCl)_2$.[a]

R	$\delta(^{14}N)$ N^A	$\delta(^{14}N)$ N^B	$\delta(^{14}N)$ N^R	$\delta(^{13}C)$ C^{ring}	$\delta(^{13}C)$ C^R	$\delta(^1H)$
Me_2N	-263	-211	-211	152.3	36.7 (CH_3)	3.24
Et_2N	-229	-216	-242	151.5	13.3 (CH_3)	1.28
					42.8 (CH_2)	3.63
$^iPr_2N$	-257	-221		151.7	20.5 (CH_3)	1.39
					48.5 (CH)	4.41
Cl_3C	-248	-195	----	165.3	95.1 (CCl_3)	----
^tBu	-213	-133	----	161.0	29.8 (CH_3)	1.72
					43.8 (CMe_3)	

a. ^1H and ^{13}C chemical shifts are relative to Me_4Si while those for ^{14}N are relative to $MeNO_2$. The superscript R indicates shifts for the R group.

TABLE 2 ^{14}N NMR chemical shifts of $[RCN_2S_2]^+$ Cl^-.[a]

R	$\delta(^{14}N)$ N^{ring}	$\delta(^{14}N)$ $N^{R\ group}$
Me_2N	-133	-318
Et_2N	-127	-296
^tBu	-135	----
Cl_3C	-181	----
Ph	-122	----

a. Relative to $MeNO_2$

MECHANISM OF RING CONTRACTION REACTION

The transformation of 2 into 3 (R= Me_2N, Et_2N) was monitored by UV-Visible and ^1H NMR spectroscopies. A red intermediate [λ_{max} 500 nm, δ (^1H) 3.51 ppm], which could not be isolated, was observed and the reaction was found to be second order in 2 (Figure 2). This indicates that the ring contraction occurs via initial dimerization of 2 to give a twelve-membered ring (a process observed for other heterocyclothiazenes).

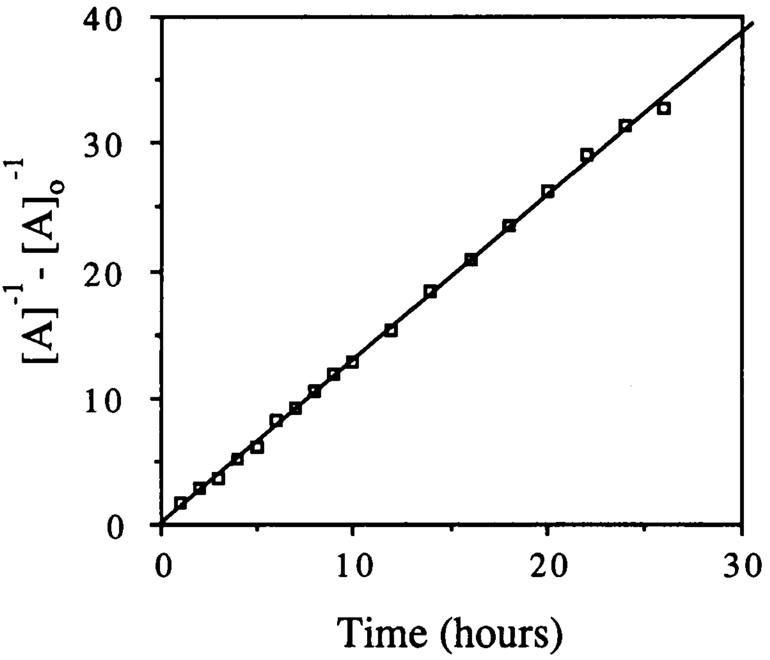
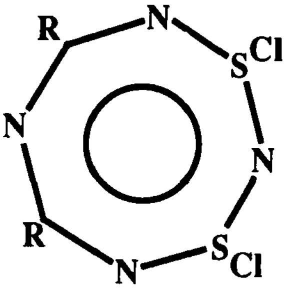


FIGURE 2 Kinetic plot of thermolysis of $Me_2NCN(NSCl)_2$ (A) (from ^1H NMR data)

OTHER CYCLOADDITION PRODUCTS FROM RCN AND $(NSCl)_3$

Two eight-membered rings can be prepared by the cycloaddition of nitriles with $(NSCl)_3$. One of these, 1,3-$(RCN)_2(NSCl)_2$, 4, (R=Me_2N) was originally prepared by the addition of an 8-fold excess of nitrile to $(NSCl)_3$ in CCl_4.[4] However 4 can be more conveniently prepared by the stoichiometric reaction of RCN (R= Me_2N, Et_2N) and one NSCl unit in CCl_4. Compound 4 exists in the solid state as an eight-membered ring but dissociates in solution to 2 and RCN.

The same reaction performed in nitromethane yielded approximately equal amounts of 4 and 1,5- $Me_2NC(NSN)_2SCl$, 5. The latter compound was previously obtained from 2 (R= Me_2N) and Me_3SiNSO as a minor product.[7]



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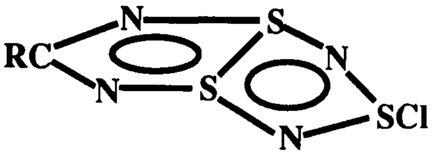

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CONCLUSION

In summary, the initial product of the reaction of nitriles with $(NSCl)_3$ is the six-membered ring 2. The conversion of 2 into the five-membered ring 3 upon heating accounts for the early reports that the RCN-$(NSCl)_3$ reactions yield 3 directly at elevated temperatures. The simple synthesis of 2 should facilitate studies of the corresponding 8π electron systems 1. Under appropriate conditions the RCN-$(NSCl)_3$ reaction produces chloro derivatives of the 1,3- dithiatetrazocine and 1,3,5-trithiatetrazocine ring systems, 4 and 5 respectively . The chemistry of these eight-membered rings has yet to be investigated.

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