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Halogenation Reactions of Phosphiniminocyclotrithiazenes: Search for New Inorganic Heterocycles

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Though the chemistry of tetrasulfur tetranitride is very well developed and studied, that of phosphiniminocyclotrithiazenes is not. Reactions of symmetrically substituted $R_3PN-S_3N_3$ [R = Ph, OC_4H_8N , $MeNC_4H_8N$, and $C_5H_{10}N$] with halogens and halogen sources (SO₂Cl₂, PhICl₂, Br₂, and I₂) gave rise to various products. In case of R = Ph, the ring-retained product, while for others, ring-degraded products were obtained. A novel cyclotrithiazene heterocycle, [Ph₃PN]₂S₃N₃⁺I₃⁻ containing a tetracoordinated sulfur atom with two phosphinimino substituents was obtained, which was further established by IR, NMR (¹H-, ¹³C-, and ³¹P-) and elemental analysis. Cyclic voltammetric studies indicated the redox behavior as well as the presence of triiodide. Theoretical calculations clearly indicate the residence of maximum positive charge (close to unity) on the tetracoordinated sulfur atom.

Keywords: halogenation, inorganic heterocycles, phosphiniminocyclotrithiazenes, cyclotrithiazenes, trisulfur trinitride, sulfur-nitrogen heterocycles

Introduction

To address the needs of the growing technology and demands for sophisticated and more advanced materials, the current research focus spans several sub-branches such as transition metal coordination, organometallic, theoretical, polymer, organic and inorganic chemistry.^[1,2] In these areas of research, inorganic heterocycles are known for a long period of time and their chemistry has been investigated for several decades. However, inorganic heterocyclic chemistry especially the search for new heterocycle systems is still pursued as one of the significant areas.^[3] Several research groups are involved in the inorganic heterocyclic chemistry mostly because of the complexity of the reactions that often require sophisticated experimental facilities. A quick, easy, and high yield synthesis are the current targets.^[4]

Phosphiniminocyclotrithiazenes, (R)(R')(R")P=N-S₃N₃, are π -electron rich six-membered inorganic heterocycles, prepared commonly and easily from a phosphine and tetrasulfur tetranitride, S₄N₄ (Eq. 1).^[5]

$$R_3P + S_4N_4 \xrightarrow[\text{Room temp.}]{\text{Solvent}} R_3P = N \cdot S_3N_3 + R_3P = S \quad (1)$$

The chemistry of S_4N_4 is well developed in terms of various reactions, namely, coordination, pyrolysis, halogenation, oxidation, reduction, and electro- and photochemical reactions, to name a few.^[6-9] In all these cases, the products resulted were quite unexpected and novel. On the contrary, despite the availability of many different kinds of substituents on phosphorus, very little reactivity aspects and chemistry are known for the -S₃N₃ derivatives: adduct formation, thermolysis, exchange, ring conversion, coordination, electrochemical, and hydrolytic degradation studies,^[10-13] and some are even in the infancy stage (Scheme 1). While acids and bases behave differently with -S₃N₃ systems leading to either ring degradation or ring expansion, the behavior of halogens, which are oxidants, would be of interest. Recent results, from our group, on the iodination reactions of phosphiniminocyclotrithiazenes suggest that the cyclotrithiazene ring reacts with iodine differently with different mole ratios of the reactants.^[14]

There are several reports on the use of all four halogens as well as interhalogen compounds in the reactions with S_4N_4 .^[8,15–18] The results suggest many unknown, unexpected as well as novel compounds by way of undergoing addition, ring contraction, fragmentation, and polymerization reactions (Scheme 2). Such vastness clearly indicates the very reactive nature of the heterocycle and the readiness to undergo the ring transformation reactions, and thus making it difficult to predict the reaction mechanisms.

Fluorination reactions with either fluorine or fluorinating agents afford to isolate three examples of fluorinated

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Sch. 1. Reported reactions of $(R)(R')(R'')P=N-S_3N_3$.

cyclothiazenes, *viz.* $S_4N_4F_4$, $S_4N_4F_2$ and $S_3N_3F_3$.^[16, 19] Chlorination reactions of S_4N_4 with Cl_2 or SO_2Cl_2 are one of the known routes for preparing cyclotrithiazyl chloride, (NSCl)₃. It was reported^[1] that this reaction proceeds through the formation of an unstable intermediate (NSCl)₄ that readily decomposes at room temperature to give (NSCl)₃. In such reactions, $S_4N_4Cl_2$, a novel disubstituted cyclotetrathiazene has been isolated and structurally characterized as well as its usefulness in synthesis has been demonstrated.^[15] On the contrary, serendipitous results have been obtained in the bromination reactions, for example, Br_2 in the vapor phase yields a highly conducting polymer of $[SNBr_{0,4}]_x$, and in the liquid phase an ionic product of $S_4N_3^+Br_3^{-[18]}$ and an unexpected product of $[CS_3N_2Br]^+Br_3^-$ in the presence of CS_2 solvent.^[20] Reaction between S_4N_4 and I_2 was found to give $S_3N_3I^{[17]}$ but was subsequently disproved.^[21] Reactions with the interhalogens ICl and IBr at room temperature produce conducting polymers such as $[(SN)(IX)_{0,4}]_x$ (X=Cl, Br),^[18] while at 100°C an ionic product $[S_4N_3]^+[ICl_2]^-$ is observed.^[17] On the contrary, when ClF was reacted with S₄N₄ monothiazyl halides NSX (X=Cl, F) are obtained.^[21] A variety of six membered S-N rings are established with or without one or more substituents, and among halogen substituted cyclotrithiazenes S₃N₃X₃ and S₃N₃X₂⁺ are known while S₃N₃X²⁺ is not known. A few attempts have been made to prepare S₃N₃ rings with a single exocyclic S-X bond^[22] but the efforts went in vain.

Reactions of phosphiniminocyclotrithiazenes with olefins such as norbornadiene gives 1:1 adducts wherein the heterocycle transforms from the π -electron rich (8π) to a π -electron precise (6π) system (Scheme 1). A similar



Sch. 2. Reactions of S_4N_4 with halogens and interhalogens.

reaction can also be assumed when the heterocycle is reacted with halogen, which certainly gives scope for the design and development of novel organo-inorganic hybrid heterocycles that could possibly have potential applications as molecular-based switches.^[2,3,23,24] An example is provided by taking 1,3-diaminopropane in Scheme 3. Search for new heterocycles for their further use as precursors to polymers and materials has also made this research to look into some of these aspects. Prompted by all these interesting reactions, especially considering the application potentials and simultaneously considering the highly ring-cleaving susceptibility of phosphiniminocyclotrithiazenes,^[25] herein attempts have been made to study the halogenation reactions on the selected examples of symmetrically substituted $R_3PN-S_3N_3$ under various reaction conditions and results are discussed.

Experimental

All manipulations were done in the inert atmosphere (dry N_2 or Ar gas) conditions. Br2, I2, and SO2Cl2, solvents (Caution! Benzene is carcinogenic) and other reagents were purified by standard methods.^[26] $C_6H_5ICl_2$ was prepared using the estab-lished procedure.^[27] $R_3PN-S_3N_3$, R = Ph (1); Mp, OC₄H₈N (2); NMP, MeNC₄H₈N (3); Pip, $C_5H_{10}N$ (4) was prepared by following the literature protocols.^[28, 29] Shimadzu UV-240 spectrophotometer is used for recording the UV-visible spectra in the range of 190-800 nm. IR spectra were recorded on a Perkin Elmer 1430 spectrophotometer using KBr windows as nujol mulls. Peaks in the finger print region (1600-400 cm⁻¹) alone are reported. ${^{1}H}^{31}P$ -NMR spectra (162 MHz) were recorded on JEOL JNM GSX-400 spectrometer in CH_2Cl_2 (provided with a D_2O insert) using 85% H_3PO_4 as external standard. Upfield shifts are negative. ¹H- and ¹³C-NMR spectra (400 and 100 MHz respectively) were recorded using the above spectrometer in CDCl₃ using tetramethylsilane as the internal standard. All the chemical shift values are quoted in ppm. Elemental analyses were done on Heraeus CHN rapid microanalyzer.

Halogenation Reactions

A typical reaction procedure for the reaction between 1 and iodine in 1:1 ratio in benzene is described below. Other reactions are summarized in Table 1.

To a stirred solution of the heterocycle 1 (1.20 g, 2.9 mmol) in benzene (20 mL) at room temperature, a solution of iodine (0.73 g, 2.9 mmol) in benzene (15 mL) was added in drops in 30 min. The solution turned brown gradually, and after ca. 5 h, the formation of a dark brown oily mass was observed. After 24 h of stirring, from the clear red brown benzene solution, the oily mass was separated by decantation and was then stirred in CH₃CN (25 mL) for 2 h and filtered to obtain the red brown solid which was recrystallized from CH₂Cl₂-CH₃CN (2:1, 15 mL) to get red brown crystals of $[Ph_3PN]_2S_3N_3^+I_3^-$ (5) (0.80 g, 30%). m.p.: 144– 45°C; IR (cm⁻¹): 1469(w), 1424(s), 1178(s), 1138(vs), 1107(s), 998(vs), 806(w), 736(m), 717(s), 688(s), 525(s) and 470(w). UV-Vis $[\lambda, \text{ nm } (\varepsilon, \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1})]$: 480 (0.03 × 10³), 363 (0.07 × 10³) and 293 (1.47 × 10³). ¹H-NMR (δ , ppm): 7.1– 7.3(m). ¹³C-NMR (δ, ppm): 124.0, 125.0, 130.0 and 134.0. ³¹P-NMR (δ, ppm): 22.2(s, 1P). Elemental Anal. Calcd. (%): C: 40.35, H: 2.83, N: 6.54, and I: 35.00. Found for C₃₆H₃₀N₅P₂S₃I₃: C: 39.92, H: 2.62, N: 6.31, and I: 34.89.

A further quantity (0.04 g) of **5** and pale yellow powdery solid (0.10 g) identified as $Ph_3PNH_2^{+}I^{-}$ (**6**) were isolated in successive crops by cooling the concentrated acetonitrile extract. m.p.: 224–26°C (Lit. 228°C^[30]). IR (cm⁻¹): 1430(vs), 1372(s), 1296(m), 1171(w), 1149(w), 1094(s), 1017(w), 992 (w), 910(vw), 749(s), 710(vs), 685(vs), 633(m), 611(vw) and 586(w). ³¹P-NMR (δ , ppm): 35.5(s, 1P). The original benzene solution was concentrated and cooled at *ca*. 5°C for a day to obtain **6** (0.25 g) and subsequently, S₄N₄ (0.10 g) as orange crystals.

Results and Discussion

The halogenation study has been prompted to verify (a) the possibility of oxidative addition reactions of $R_3PN-S_3N_3$



Sch. 3. Expected products of a halogenation reaction of Ph₃PNS₃N₃.

Compound	Halogen (source)	Mole ratio	Solvent	Addition period	Reaction conditions	Products obtained
1	I ₂	1:1	C_6H_6	30 min. at RT	Stirred at RT for 24 h	$ \begin{array}{c} [\text{Ph}_3\text{PN}]_2\text{S}_3\text{N}_3^+\text{I}_3^- (0.84 \text{ g}, 31.5\%) \\ \text{Ph}_3\text{PNH}_2^+\text{I}^- (0.35 \text{ g}) \text{S}_4\text{N}_4 \\ (0.10 \text{ g}) \end{array} $
		1:2	CH ₂ Cl ₂	30 min. at RT	Stirred at RT for 4 h	$[Ph_{3}PN]_{2}S_{3}N_{3}^{+}I_{3}^{-} (0.25 \text{ g}, 19\%) Ph_{3}PNH_{2}^{+}I^{-} (0.20 \text{ g}) S_{4}N_{4} (0.08 \text{ g}) I_{2} (0.05 \text{ g})$
		1:6	CH ₂ Cl ₂	30 min. at RT	Stirred at RT for 4 h	$[Ph_{3}PN]_{2}S_{3}N_{3}^{+}I_{3}^{-}(0.20 \text{ g}, 16\%)$ $Ph_{3}PNH_{2}^{+}I^{-}(0.26 \text{ g}) S_{4}N_{4}$ $(0.10 \text{ g}) I_{2}(0.25 \text{ g})$
		1:1	CH ₃ CN	30 min. at RT	Stirred at RT for 14 h	White solid ^a (0.11 g) $Ph_3PNH_2^+I^-$ (0.60 g) S_4N_4 (0.20 g)
	Br_2	1:1	CH ₂ Cl ₂	30 min. at 0°C	Stirred at RT for 17 h	$Ph_3PNH_2^+Br^-$ (0.42 g) S_4N_4 (0.02 g)
	$C_6H_5ICl_2$	1:1	CH_2Cl_2	1 h at 0°C	Stirred at 0°C for 4 h; RT for 2 h	$Ph_3PNH_2^+Cl^-$ (0.60 g) S_4N_4 (0.08 g)
2	I_2	1:1	CH ₃ CN	30 min. at RT	Stirred at RT for 12 h	White solid ^a (0.15 g) $Mp_3PNH_2^+I_3^{-d}$ (0.92 g) S_4N_4 (0.25 g)
		1:1	CH_2Cl_2	30 min. at RT	Stirred at RT for 20 h	$Mp_3PNS_3N_3$ (0.48 g) I_2 (0.18 g)
	Br_2	1:1	$CH_{3}CN$	30 min. at 0°C	Stirred at RT for 12 h	$Mp_3PNH_2^+Br^-$ (0.72 g)
3	I_2	1:1	CH_2Cl_2	30 min. at RT	Stirred at RT for 4 h	Brick red solid $(0.74 \text{ g})^{\text{b}}$
	SO_2Cl_2	1:1	CH_2Cl_2	30 min. at 0°C	Stirred at 0°C for 6 h	$(NMP)_3PNH_2^+Cl^{-c}$
4	I_2	1:1	CH_2Cl_2	30 min. at RT	Stirred at RT for 24 h	(Pip) ₃ PNS ₃ N ₃ (0.55 g) I ₂ (0.20 g)
	I ₂	1:1	CH ₃ CN	30 min. at RT	Stirred at RT for 24 h	White solid ^a (0.10 g) (Pip) ₃ PNH ₂ ⁺ I ⁻ (0.36 g) S_4N_4 (0.18 g)

Table 1. Reactions of $R_3PN-S_3N_3$ (1–4) with halogens/halogen sources at different reaction conditions

^aShowed broad bands in IR spectrum in the range $1000-1200 \text{ cm}^{-1}$; qualitatively answered for iodide.

^bCould not be further purified and characterized (M.pt. >250°C). Analogous reaction performed in C_6H_6 and CH_3CN as well as 1:1 bromination reaction gave only intractable pale coloured high melting solids (>250°C) which eluded from further characterization; the IR spectrum showed the presence of P=N bond.

^cFrom the oily mass, no other product could be isolated; IR spectrum indicated the presence of P=N bond and ³¹P-NMR spectrum showed the presence of $(NMP)_3PNH_2^+Cl^-$.

^d**Characterization data**: Dark red brown crystals. M.pt.: 210–12°C. IR (cm⁻¹): 3190(w), 3060(w), 2928(vs), 1560(m), 1440(vs), 1360(s), 1280(m), 1240(s), 1120 (s), 1080(s), 920(s), 830(m), 700(m), 590(m), and 450(m). UV-Vis [λ , nm (ϵ , dm³mol⁻¹cm⁻¹)]: 363 (1.9 × 10³) and 296 (3.7 × 10³). ³¹P-NMR (δ , ppm): 33.1 (s, 1P).

heterocycles (8π , electron-rich) with halogens (SO₂Cl₂ and PhICl₂ as chlorine source, liquid bromine and solid iodine) to produce electron-precise (6π) heterocycles with sulfur atoms containing mixed substituents (Scheme 3); and (b) the influence of nature of substituents attached on phosphorus center, where 1 has carbon groups (phenyl) attached while 2–4 have nitrogen groups (amino).

Three solvents C_6H_6 , CH_2Cl_2 and CH_3CN with differing polarity indices (2.7, 3.1, and 5.8, respectively), mole ratio of reactants (1:1, 1:2, and 1:6), reaction temperature (0°C and room temperature), and reaction period (4–24 h) have been used. It is known that in cyclothiazene chemistry chlorination and bromination reactions proceed more violently and pose problems due to their high reactivity and afford complex reaction mixtures, and that temperature plays a vital role in deciding the nature of the products thus formed.^[22] Hence, milder of the halogens in terms of reactivity, namely, iodine and a more stable one of the cyclotrithiazenes, namely $Ph_3PN-S_3N_3$ (1), were considered for a detailed study.

Iodination of 1

When the dark brown solution of iodine was treated with deep red dichloromethane of 1, no visual inference on the occurrence of the reaction could be assessed as the resulting solution was also dark red brown. However, the ³¹P-NMR spectrum revealed three peaks at 35.7, 31.2, and 21.4 ppm. The reaction mixture finally gave a dark red brown oily mass and a clear pale red brown filtrate. The oily mass with acetonitrile and dichloromethane yielded shining dark red brown crystals of [Ph₃PN]₂S₃N₃⁺I₃ (5). The other two products are phosphiniminium iodide, $Ph_3PNH_2^+I^-$ (6), and cyclotetrathiazene, S_4N_4 . They all have varying yields from all the reactions (1:1, 1:2, and 1:6) carried out either in benzene or dichloromethane, though with increasing iodine content, the yield of the triiodide product dropped from 31.5% to as low as 16%. Surprisingly, an equimolar reaction carried out in more polar acetonitrile solvent gave high yields of 6 and a white solid (which could not be characterized further), rather than 5. Such white solids are frequently

 Table 2. Cyclic voltammetric data for 5

	Peak poten	tial (mV)	Peak current (I _P)		
Species	Cathodic	Anodic	Cathodic	Anodic	
5	174	288	1.0589×10^{-4}	1.0540×10^{-4}	
I ₃ ⁻	155	290	1.4643×10^{-4}	1.5818×10^{-4}	

encountered in similar reactions^[12] and exhibited broad IR bands (in the $\nu_{\rm NH}$ and $\nu_{\rm SO}$ regions) suggesting their ionic and water-soluble nature. In the reaction of 1 with halogens / halogen sources, one of the definitive products obtained is the eight-membered heterocycle S₄N₄ that also formed during the halogenation reactions of six-membered cyclotrithiazene anion S₃N₃⁻.^[31] Reported data indicates that as many as five different types of products could be obtained in the case of R = Ph^[14] indicating the highly reactive nature of the ring in the formation of different products - ring retained and/or cleaved. In the present study, yet another novel product **5**, hitherto unreported, has been obtained suggesting the ring sensitivity towards mole ratios of the reactants, solvents and reaction periods.

Characterization of 5

Compound 5 is a dark red brown crystalline solid, air stable and more soluble in polar solvents like CH_2Cl_2 and CH_3CN . Its color clearly indicates the presence of the triiodide ion. Its melting point 144–45°C is higher, around 15°C, than the parent heterocycle 1 that melts at 126–28°C and shows deposition of iodine crystals in the sealed capillary during the determination of melting point. The IR spectral features of 5 are found to be very similar to those of 1.^[10] Upon comparing the UV-Visible spectra of 5, 1 and triiodide anion, it could be unambiguously concluded that 5 possesses: (a) triiodide anion, the strong absorption at 293 nm,^[32] thus confirming the ionic nature; and (b) the phosphiniminocyclotrithiazene moiety, the absorption at 480 nm.^[10] Subsequent, cyclic voltammetric studies on 5, at different sweep rates in the potential range -1500 to +1500 mV (Table 2), suggest that the values are in close comparison with those of triiodide ion,^[33] indicating the redox behavior of 5 as well as the presence of triiodide ion.

It is interesting to note that only a singlet is observed in the ³¹P-NMR spectrum at 22.2 ppm, emphasizing the identical stereochemical environment around the phosphorus centers in **5**. This value is quite close, but significantly different to that of the parent heterocycle **1** $(23.8 \text{ ppm}^{[10]})$ indicating a similar structure. The signals observed in its ¹H- and ¹³C-NMR spectra are consistent with the aromatic protons and phenyl carbons, respectively. Thus, it appears that the 8π -heterocycle **1** experiences one- or two- electron oxidation under the influence of the relatively mild oxidant iodine towards yielding the 7π - or 6π -heterocycle (Scheme 4). This hypothesis is consistent with the observation of stable 7π -heterocycle $S_3N_2^+AsF_6^-$ and the ionization of the substituted cyclotrithiazene $X_3S_3N_3$ in producing $N_3S_3X_2^+Y^-$.^[34, 35]

However, comparison of the analytical results indicates that the compound **5** is neither of the two compositions considered in Table 3, but it should be $[Ph_3PN]_2S_3N_3^+I_3^-$. Eight different trials have been conducted for estimating the iodine content^[36] and the results obtained (34.17–35.77%) undoubtedly suggest the formation of **5**.

Scheme 5 highlights a possible mode of attack and the product formation, based on the nature of the compounds obtained thus far either through charged intermediates^[37] or radical intermediates as in solid state pyrolysis reactions.^[5] In the present study, as solvent has been used, the most likely mechanism could be through the charged intermediates. The observation of phosphiniminium salt formation is a clear indication of the attack of residual moisture available in the solvents on the more sensitive heterocycles and the intermediate products as well during the reaction. Thus, it appears that very often such salts are encountered^[31] in these reactions irrespective of the rigorous inert atmospheric manipulative conditions and the dry solvents. This presumption is supported by the ascertainment that larger quantities of salt were obtained in the presence of polar acetonitrile solvent (cf. Table 1). The phosphinimino substituent is highly susceptible for cleavage from the S₃N₃ ring as observed in the mass spectral fragmentation of such cyclotrithiazene heterocycles.^[25] The S-N ring cleaves the "NS" species^[11] and either polymerizes to the more stable S_4N_4 ,^[38] or combines with " S_3N_3 " to produce S_4N_4 . Despite the observation of phosphiniminium salt, no sign of SO₂ or SO₃ gas could be identified during the reaction, though their occurrence was reported for such similar reactions.^[31] From the structure of 5, as shown in Scheme 5, it is clear that the low-energy empty 3d orbitals of the tetracoordinated S-atom are involved in the



Table 3. Comparison of analytical data

Compound	С %	Η%	N %	I %
$\frac{Ph_{3}PNS_{3}N_{3}^{+}I_{3}^{-} \text{ (calcd.)}}{[Ph_{3}PNS_{3}N_{3}]^{2+} 2I_{3}^{-} \text{ (calcd.)}}$ $[Ph_{3}PN]_{2}S_{3}N_{3}^{+}I_{3}^{-} \text{ (calcd.)}$ $Dark \text{ red brown crystals (obsvd.)}$	27.17	1.91	7.05	47.92
	18.37	1.29	4.77	64.80
	40.35	2.83	6.54	35.00
	39.92	2.62	6.31	34.89



Sch. 5. Proposed mode of attack for the formation of 5.

bond formation. In fact, compound **5** appears to be the first example of a cyclotrithiazene to contain a tetracoordinated sulfur atom while the other two sulfur centers are dicoordinated.

Theoretical Calculations on 1,1-Bis(triphenylphosphinimino)-1,3,5-trithia-2,4,6-triazenium triiodide, $[Ph_3PN]_2S_3N_3^+I_3^-$ (5)

Scheme 6 highlights the possible seven resonance structures for 5. These delocalized structures indicate the residence of mono-positive charge on all the six endocyclic atoms (3 sulfur + 3 nitrogen atoms) and the four exocyclic atoms (2 nitrogen + 2 phosphorus atoms) of the two substituents. Based on these findings, it can be assumed that different resonating structures (I–VII) contribute towards bonding, where delocalization starts from the phosphorus atom on the left and extends up to the other phosphorus atom on the right passing through the cyclotrithiazene ring (structure VIII), with varying degrees of bond elongation and shortening.^[39]

The main idea of undertaking the theoretical study was to determine: (a) the total charge, (b) the atomic charge densities, and (c) the site of preference for the positive charge on the heterocyclic cation. Using the available structural information of the molecule,^[39] semiempirical calculations were performed with different modes of parameterization, namely, MNDO and PM3 and the results are given in the Table 4. The numbering of endocyclic atoms is as given in structure VIII of the Scheme 6.

The data analysis and conclusions drawn from MNDO calculations clearly reveal that the maximum positive charge resides on the tetracoordinate sulfur atom and the overall charge of the heterocyclic cation is close to unity (as shown in structure I, Scheme 6). The results further substantiate that other resonance structures (II–VII) do not contribute to any appreciable extent to the resonance hybrid.

Iodination of 2–4

The behavior of the other $R_3PNS_3N_3$ ring systems, 2–4 for iodination reaction was found to be quite different to that of 1. For example, in dichloromethane solvent, an equimolar reaction of 3 and iodine gave an insoluble brick red precipitate that did not melt even at 250°C, while 2 and 4 did not react at all. Although these observations underscore the importance of the substituents, the complex nature of the obtained results is difficult to explain easily. Analogous reactions carried out in CH₃CN showed differences compared to CH₂Cl₂ reactions, suggesting that the choice of solvent is vital for halogenation reactions. For example, a 1:1 reaction of 3 and iodine in three different solvents C₆H₆, CH₂Cl₂ and CH₃CN gave substantial amounts of high melting solids (nearly 60% of the weight of reactants) with colors of brick red, yellow and white, respectively. The



Sch. 6. Resonance structures of 5.

Table 4. Atomic charges of ring atoms for 5

Atom	MNDO	PM3
S ₁	0.5731	0.7601
S_2 (tetracoordinated)	1.7992	1.4678
S ₃	0.6120	0.9048
N ₁	-0.8765	-0.9184
N ₂	-0.4323	-0.8567
N ₃	-0.8601	-0.6641

corresponding IR spectra suggested the presence of N-methylpiperazino group and P=N bond as well as the absence of trithiazene ring. Subsequent qualitative analyses of the solids revealed the presence of iodide, sulfur, and phosphorus that in turn suggests that these compounds are mixtures of products. In general, the corresponding phosphiniminium salts, $R_3PNH_2^+I^-$ and S_4N_4 are the only isolable products from these reactions. Interestingly, in the case of morpholino derivative, a triiodide salt $(OC_4H_8N)_3PNH_2^+I_3^-$ was isolated.

Bromination and Chlorination of 1–4

Though bromination and chlorination reactions were carried out under relatively mild conditions (1:1 ratio, 0°C and short reaction time) in CH₂Cl₂ and CH₃CN solvents, they progressed far more rapidly and revealed more complex pathways. This is further supported by the ³¹P-NMR data of the filtrates of the reactions that clearly revealed the presence of many phosphorus-based products. For example, the filtrate of the reaction between 3 and SO₂Cl₂ exhibited signals at 74.3, 35.7, 24.6, 22.6, 19.9, and 13.3 ppm. However, the complexity gradually decreases from chlorination to bromination to iodination, which very well correlates with their oxidizing ability. Expectedly, in almost all the cases, the starting heterocycle was found to be absent and the presence of corresponding iminium salt, $R_3PNH_2^+X^-$, as evidenced by the presence of a strong signal at around 35 ppm.^[40] Strikingly, in all these spectra, a signal around 74 ppm that could be attributable to the aminophosphine sulfide $R_3PS^{[40]}$ has been observed stressing the thiophilic nature of the phosphorus atom.^[41] This observation further exemplifies the more complex nature of these reactions. Considerable amounts of colored precipitate (yellow or red brown) or oily mass (yellow) are obtained and are found to be mixtures of corresponding phosphiniminium bromide or chloride salts. In some cases, relatively pure samples of these salts could as well be isolated along with small amounts of S_4N_4 . Overall, our results suggest that though tris (amino)phosphiniminium halide salts are difficult to prepare due to the formation of highly air and moisture sensitive pentavalent phosphorus intermediates, by judicially involving R_3PX_2 compounds in the reaction sequence pure crystalline solids of these halides could be prepared easily, as demonstrated in the present study (Scheme 7).

Conclusions

The quest for novel π -electron systems has paved the way to explore many new heterocyclic systems, and cyclic SN systems (e.g., S₄N₄ and S₃N₃) stand out as special examples. Importantly, their synthesis, chemistry, and structure elucidation offer several favorable opportunities. In addition, the continuing interest in these systems has motivated us to undertake a systematic investigation on the cyclic SN systems, especially to gain better insights on the bonding and conformation. Herein, we demonstrated that upon reacting iodine with Ph₃PNS₃N₃, a novel inorganic heterocycle could be obtained wherein one of the sulfur atoms is tetracoordinated while the other two are dicoordinated. Subsequent spectroscopic characterization along with the theoretical calculations suggest the structure as $[Ph_3PN]_2S_3N_3^+I_3^-$. In general, the halogenation reactions of phosphiniminocyclotrithiazenes proceed at different rates and at variable complexities depending on: (a) the nature of halogen used for the reaction, (b) the nature of substituent (whether P-C or P-N bonded) on the P-atom, (c) the nature of solvents used, and (d) the mole ratio of the reactants. However, more cyclic SN systems need to be synthesized to tap their complete potential and functionality.

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Sch. 7. Ways of producing phosphiniminium halide salts.

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