This article was downloaded by: [University of Chicago Library]
On: 17 July 2013, At: 22:15
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Studies on Iodination Reactions of Phosphiniminocyclotrithiazenes

Akella Sivaramakrishna [a] [b] , U. Swarnalatha [a] & M. N. Sudheendra Rao [b]

[a] Chemistry Division, School of Advanced Sciences , VIT University , Vellore , 632 014 , Tamil Nadu , India

[b] Department of Chemistry, Indian Institute of Technology Madras , Chennai , 600 036 , Tamil Nadu , India

Accepted author version posted online: 03 Jun 2013.

To cite this article: Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry (2013): Studies on Iodination Reactions of Phosphiniminocyclotrithiazenes, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, DOI: 10.1080/15533174.2012.759231

To link to this article: http://dx.doi.org/10.1080/15533174.2012.759231

Disclaimer: This is a version of an unedited manuscript that has been accepted for publication. As a service to authors and researchers we are providing this version of the accepted manuscript (AM). Copyediting, typesetting, and review of the resulting proof will be undertaken on this manuscript before final publication of the Version of Record (VoR). During production and pre-press, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal relate to this version also.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Studies on Iodination Reactions of Phosphiniminocyclotrithiazenes

[1,2]Akella Sivaramakrishna*, [1]U. Swarnalatha, [2]M. N. Sudheendra Rao

[1]Chemistry Division, School of Advanced Sciences, VIT University, Vellore – 632 014,
Tamil Nadu, India

[2]Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600 036,
Tamil Nadu, India

ABSTRACT

Iodination reactions of various phosphiniminocyclotrithiazenes [$R_3PNS_3N_3$; R = (i) phenyl-, (ii) morpholino-, (iii) *p*-chlorophenyl-] have been studied under different experimental conditions. Iodination of $Ph_3PNS_3N_3$ yields interesting products such as $[(Ph_3PN)_2S_3N_3]I_3$, $((Ph_3PN)_3S)_2I_4$, $(Ph_3PNH_2)I_3$, $((Ph_3PSI_2)_2I_2$ and $[(Ph_3PN)_3SO]_2I_6$ depending on the experimental conditions. All the products have been isolated and characterized by the spectroscopic and analytical techniques.

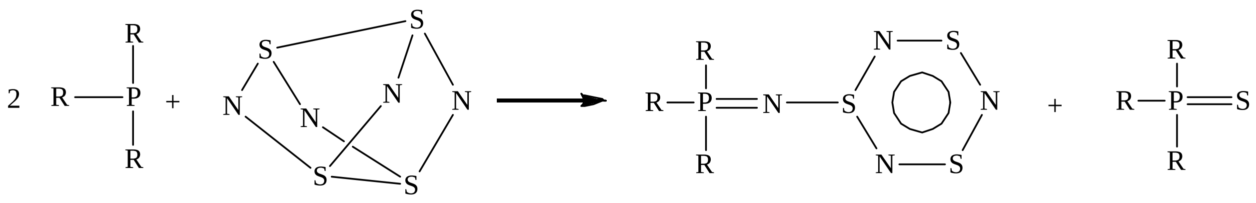
Keywords: phosphiminocyclotrithiazenes, iodination, oxidative addition; ring cleavage

*** To whom correspondence should be addressed: [asrkrishna@rediffmail.com]**

INTRODUCTION

Heterocyclic compounds are important and an active area of research in the contemporary inorganic chemistry.[1–6] Sulfur and nitrogen containing cyclothiazenes (e.g. S_4N_4, $S_3N_3Cl_3$, $S_3N_2Cl_2$, S_4N_3Cl, etc.) represent an interesting class among inorganic heterocycles and the chemistry of these cyclothiazenes is well developed and literature information available on them is fairly extensive.[7-13] Phosphiniminocyclotrithiazenes, R_3PN-S_3N_3 are a class of electron-rich inorganic heterocycles[10,11] having a phosphinimino moiety as the exocyclic substituent and have served as stable derivatives of monosubstituted cyclotrithiazenes (-S_3N_3).[14,15] In addition to the noticeable structural differences[16], some of the reactivity aspects of R_3PN-S_3N_3 heterocycles have also been demonstrated by redox reactions,[17] alkene adduct formation,[18] ring transformations,[19] electrochemical and coordination behavior,[20] substituent-dependent pyrolytic behavior,[21] and nucleophilic attack by ammonia, amines,[22] and phosphines.[23] These results suggested the preferential cleavage of the trithiazene ring skeleton over that of exocyclic substituent.

It has been believed that the presence of a relatively bulky phosphinimino moiety as an exocyclic part of the S_3N_3 ring skeleton and the possibility of substituent variation on phosphorus render them as interesting examples for further studies.[20] These observations prompted us to undertake this study to probe the studies on iodination reactions of R_3PN-S_3N_3 ring systems for the first time. In this paper, we have reported the preparation of R_3PN-S_3N_3 heterocycles with symmetrically substituted phosphines (Eq.1) and studied the tendency of these heterocyclic systems to oxidative cleavage by iodine.



R = Phenyl (**1**); Morpholino (**2**); p-Chlorophenyl (**3**)

Eq.1

EXPERIMENTAL

Apparatus

Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls (NaCl windows) on a Shimadzu 470 spectrophotometer. Electronic spectra were recorded by JASCO –V-550 UV/Vis Spectrophotometer. Spectra for ^{1}H, ^{13}C and ^{31}P–NMR were collected on a Jeol JNM GSX – 400 (160 MHz) NMR spectrometer and all ^{1}H chemical shifts are reported relative to residual proton resonance in the deuterated solvents. Heraeus CHNS rapid micro analyzer was used for elemental analysis.

Materials

All the reactions and subsequent work up were done under an inert atmosphere of dry nitrogen gas using Schlenk line technique. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen atmosphere. Melting points were determined with an apparatus using samples in one side sealed capillaries. Tetrasulfur tetranitride was synthesized by the reported procedure and crystallized from toluene[24] (Caution: S_4N_4 may cause an explosion!!. Recommended safety procedures should be strictly observed).[25] Morpholine ($HNC4H_8O$), PPh_3 and (*p*-chlorophenyl)$_3$P

(Aldrich) were used as received. The tris(morpholino)phosphine was prepared by the reaction of PCl_3 with the respective amine.[26] $Ph_3PNS_3N_3$ (**1**),[27] $(OC_4H_8N)_3PNS_3N_3$ (**2**) and (*p*-$ClC_6H_4)_3PNS_3N_3$ (**3**)[20] were synthesized using reported procedures. Freshly sublimed iodine sample was used.

Preparation of $[(Ph_3PN)_2S_3N_3]I_3$ (5)

To a stirred solution of **1** (2.002 g, 4.836 mmol) in 30 mL of toluene at 0 °C, a solution of iodine (0.365 g, 1.35 mmol) in 20 mL of toluene was added by a dropping funnel for 30 min. The reaction mixture was allowed to room temperature and after 5 h stirring, a dark brown oily mass was formed. At the end of 6h, the oily mass was separated by decantation from clear red brown filtrate. The oily mass was then stirred in 10 mL of CH_3CN for 2 h and filtered to obtain a red brown solid which was recrystallized from a solvent mixture of CH_3CN-CH_2Cl_2 (1:1, 20 mL) to afford 184 mg (8 %) of red brown crystals of the title compound, $[(Ph_3PN)_2S_3N_3))I_3]$; m.p. 174-176 ºC. Anal. Calcd for $C_{36}H_{30}I_3N_5P_2S_3$: C, 40.35; H, 2.82; N, 6.54; S, 8.98. Found: C, 40.54: H, 3.15: N, 6.72: S, 9.06. The ^{1}H-NMR spectrum δ_{TMS} ($CDCl_3$): 7.26-8.16 (m, 30H, Ph); ^{13}C–NMR: δ 124.62, 125.43, 126.96, 128.46, 129.06, 129.75, 131.09, 134.64 and ^{31}P–NMR: δ 15.6.

Preparation of $((Ph_3PN)_3S)_2I_4$ (6)

A solution of iodine (0.651 g, 1.44 mmol) in 20 mL of toluene was added to a stirred solution of **1** (1.06 g, 2.56 mmol) in 15 mL of toluene at room temperature. A similar procedure was followed as given above to afford 122 mg of the dark red brown crystals of the compound $((Ph_3PN)_3S)_2I_4)$ (**6**) (6 **%)**; m.p 174-176 ºC. Anal. Calcd for calculated for $C_{108}H_{90}P_6N_6S_2I_4$: C, 58.18: H, 4.07: N, 3.77: S, 2.88. Found: C, 58.26: H, 4.26: N, 3.84: S, 2.91.The NMR spectrum δ_{TMS} ($CDCl_3$): δ 7.12-7.96 (m, 90H, Ph); ^{13}C–NMR: δ 124.12, 125.36, 129.56, 130.78 and 134.18. ^{31}P NMR: δ 15.6.

Preparation of (Ph_3PNH_2)I_3 (7)

Iodine (0.338 g, 1.33 mmol) in toluene (20 mL) was added to a stirred solution of **1** (0.5028 g, 1.21 mmol) in toluene (10 mL) and 0.5 mL of water. After the addition was complete (approx. 30min.), the reaction mixture was refluxed for 6h. The formed oily mass was separated by decantation of the filtrate. The same procedure was adopted for working up of the reaction mixture further as given in the above to afford 345 mg of compound **7** (43 **%)**; m.p. 98-100 ºC. Anal. Calcd for calculated for $C_{18}H_{17}PNI_3$: C, 32.8: H, 2.58: N, 2.12. Found: C, 32.5: H, 2.67: N, 2.18. The NMR spectrum δ_{TMS} ($CDCl_3$): δ 7.16-7.88 (m, 15H, Ph), 1.54 (br, 2H, NH); ^{13}C–NMR: δ 124.88, 125.32, 127.40, 128.22, 129.11, 129.84, 131.44, 134.24; ^{31}P–NMR: δ 35.5.

Preparation of ((Ph_3PSI_2)$_2$$I_2$ (9)

A solution of iodine (1.229 g, 4.84 mmol) in toluene (25 mL) was added dropwise to a solution of **1** (0.5012g, 1.21mmol) in toluene (10 mL). Then the reaction mixture was subjected to refluxing for 18 h. The same procedure was adopted for working up of the reaction mixture further as given in the above to afford 156 mg of compound **9** (19 **%)**; m.p. 142-144 ºC. Anal. Calcd for calculated for $C_{36}H_{30}P_2S_2I_6$: C, 32.00: H, 2.24: S, 4.74. Found: C, 32.02: H, 2.42: S, 4.78. The NMR spectrum δ_{TMS} ($CDCl_3$) δ 7.20-8.14 (m, 30H, Ph); ^{13}C–NMR: δ 124.53, 125.48, 128.30, 128.92, 131.64, 133.94; ^{31}P–NMR: δ 42.2.

Preparation of $((Ph_3PN)_3SOI_6$ (10)

A solution of iodine (1.485 g, 5.85 mmol) in toluene (25 mL) was added dropwise to a solution of **1** (0.606 g, 1.462 mmol) in toluene (10 mL) and 0.5 mL of water. Then the reaction mixture was subjected to refluxing for 18 h. The same procedure was adopted for working up of the reaction mixture further as given in the above to afford 118 mg of compound **10** (15 **%)**; m.p. 168-170 ºC. Anal. Calcd for calculated for $C_{54}H_{45}P_3N_3SOI_6$: C, 39.56: H, 2.77: N, 2.56: S, 1.95. Found: C, 39.52: H, 2.81: N, 2.56: S, 1.97. The NMR spectrum δ_{TMS} ($CDCl_3$): δ 7.02-7.68 (m, 45H, Ph); ^{13}C–NMR: δ 125.17, 128.58, 129.96, 131.60, 134.23; ^{31}P–NMR: δ 19.4. In all the above reactions, varying amounts of pale yellow precipitate, removed by filtration, was identified as a known $[Ph_3PNH_2]I$ (**8**).[28]

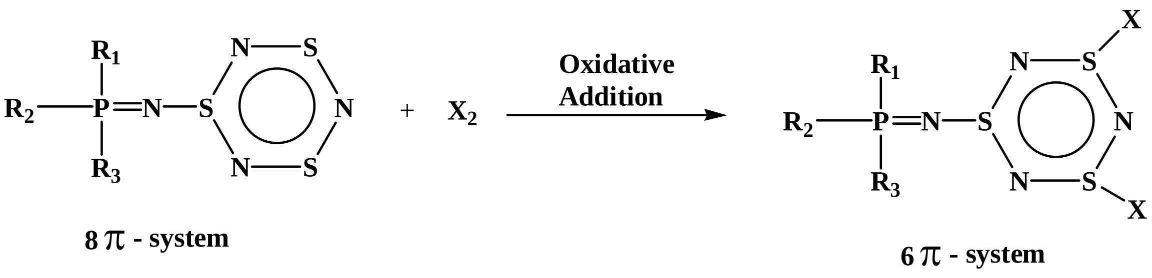
Preparation of $((p\text{-}ClC_6H_5)_3PNH_2)I_3$ (11b)

Iodine (0.245 g, 0.97 mmol) in toluene (20 mL) was added to a stirred solution of **3** (0.5024 g, 0.97 mmol) in toluene (15 mL) at room temperature. The reaction mixture was refluxed for 8 h. The obtained red brown precipitate was filtered and washed with toluene (2 x 5 mL) and recrystallized from a solvent mixture of CH_2Cl_2-CH_3CN (1:1) to afford 392 mg of compound **11b** (53 %); m.p. 102-104 ºC. Anal. Calcd for calculated for $C_{18}H_{14}PNCl_3I_3$: C, 28.33: H, 1.85: N, 1.84. Found: C, 28.45: H, 1.90: N, 1.86. The NMR spectrum δ_{TMS} ($CDCl_3$): 7.14-7.78 (m, 12H, Ph), 1.56 (br, 2H, NH); ^{13}C–NMR: δ 124.0, 125.0, 130.0 and 134.0; ^{31}P–NMR: δ 35.5.

RESULTS AND DISCUSSION

Halogenation of sulfur-nitrogen compounds is important because of the influence of halogens on the electronic properties of $(SN)_x$ species and their ability to cause spontaneous polymerization of cyclothiazine compounds.[29-32] The preparation of various halogenated cyclothiazenes of the type $S_3N_2Cl_2$[30] and S_4N_3Cl[31] and their chemistry have been reported.[32] It is also interesting to note that the halogenation does not proceed analogously with all halogens.

In light of this, the present halogenation study has been prompted by the desire to verify the possibility of oxidative addition reactions of $Ph_3PNS_3N_3$ heterocycles (8π to 6π) with iodine and isolation of hitherto unknown cyclotrithiazine systems with mixed substituents on sulfur centers through the formation of **4** as shown in Eq.2. The reactions of halogens like chlorine and bromine with $Ph_3PNS_3N_3$ did not yield any new products because of their strong oxidizing capacity to cleave the heterocycle ring. Hence we focused our further studies with iodine, which is a mild oxidant.



4

Eq.2: Expected halogenation reaction

When a dark solution of iodine (1:1) was treated with deep red toluene solution of $Ph_3PNS_3N_3$ (**1**) at 0 °C did not go to completion as the unreacted precursor **1** (δ 22.0) was observed by ^{31}P-NMR spectrum. However, the reaction mixture finally gave a dark red-brown oily mass and a clear red-brown filtrate after 5 h stirring at room temperature. The oily mass upon treatment with CH_3CN gave a red brown powdery solid which can be recrystallized from CH_3CN-CH_2Cl_2 solvent mixture. The characterization data of this solid revealed the formation of a novel iodinated cyclotrithiazene compound, $[(Ph_3PN)_2S_3N_3]^+[I_3]^-$, which has an I_3^- unit confirmed by elemental analysis. The IR spectrum showed a strong band for S-N at 1325 cm^{-1} in nujol. It is found that the product **5** is sensitive to the air- and moisture. It was difficult to separate other products from the reaction mixture. However, our efforts to identify **4** in the reaction mixtures were completely failed.

On refluxing, an iodine solution (1:1) of **1** in toluene for 6 h yielded **6** by cleaving the –S_3N_3 ring. The IR bands of **6** were almost identical to the known $(R_3PN)_3S^+$ Cl^- (R = Me, Et, Ph) salts.[33] The same reaction in wet toluene either on refluxing or at room temperature produced traces of **6** and the corresponding phosphonium salts, **7** and **8** in high yields (Scheme 1).

Reaction of 4-fold excess of iodine with **1** gave **6** at room temperature. But the formation of **9** was observed when the same reaction mixture is refluxed for 18 h. The product **9** $[(Ph_3PSI_2)_2I_2]$ is an iodine adduct and has been the only isolated product from the crude reaction mixture. The compound **9** consists of two Ph_3PSI_2 units interacting with an iodine molecule. The characterization data of **9** is in good agreement with the earlier work.[34] It appears that the oxidative degradation of cyclotrithiazene occurs by the initial separation of phosphazene unit and then the formation of P-S-I species through the cleavage of a P-N as well as S-N bonds in the presence of iodine.

A new cationic product, **10** was isolated from the iodination of **1** (iodine in 4-fold excess) in a refluxing wet solution of toluene. The other products in this reaction were found to be **7** and **8**. ^{31}P-NMR of **10** (δ 19.4) shows a sharp singlet which is slightly downfield shift compared to **6** (δ 15.6).

The IR spectra of the crude reaction mixture show several S-N stretching bands indicating a mixture of iodinated cyclothiazene species. The iodination of $R_3PNS_3N_3$ always conceded a cyclothiazene cation ($S_4N_3^+$) in varying yields depending on the experimental conditions as the evidence for the $S_4N_3^+$ cation is obtained by the IR data of the crude reaction mixtures. A band at 1320 cm^{-1} appears in the region expected for S-N stretching frequency due to the formation of $S_4N_3^+$, which is consistent with the literature.[35] This was further confirmed by mass spectral data. The ready formation and stability of S-N cationic compounds is of particular significance in view of the apparent role of I_3^- ions[36] in enhancing the conductivity and superconductivity of $(SN)_x$.

It is surprising to observe that the iodination reactions of **2** and **3** always yielded **11** and **12** respectively (Eq.3). This could be due to the hydrolysis of products during the work-up of the reaction mixtures.

$$R_3PN{-}S_3N_3 \xrightarrow{I_2} [(R_3PNH_2)]^+I_3^- + [(R_3PNH_2)]^+I^-$$

11a, R = morpholino;
11b, R = *p*-chlorophenyl

12a, R = morpholino;
12b, R = *p*-chlorophenyl

Eq.3

It is found that this iodination reaction is dependent on several factors such as temperature, iodine concentration, mode of addition of iodine, nature of solvents, time of reaction and remote substituent R (Scheme 1). Further, it is also possible that the iodinated products formed during the reaction may undergo a side reaction to cleave –S_3N_3 ring completely. Prolonged heating of the reaction mixture resulted by the cleavage of P-N bond as well as formation of P-S bond.

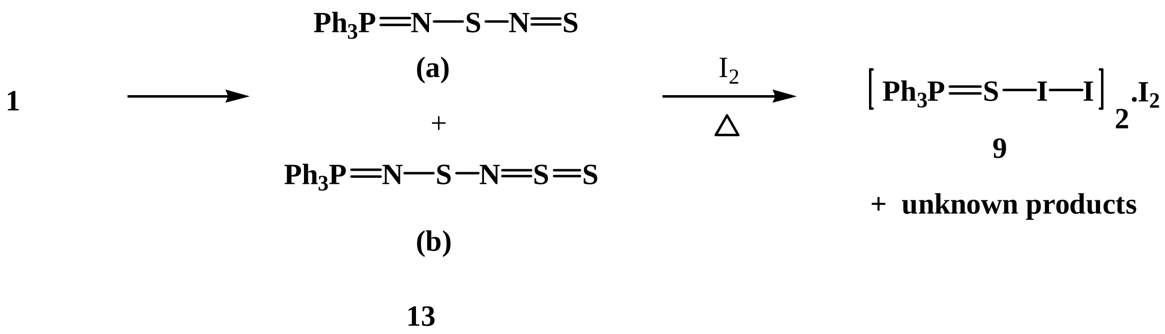
In all the reactions, $[R_3PNH_2]I$ is the most common product in varying amounts. All the isolated products except the yellow crystalline $R_3PNH_2^+I^-$ salts are obtained as dark red brown crystalline solids that are found to be soluble in both dichloromethane as well as acetonitrile. Though $R_3PNH_2^+I^-$ and $R_3PNH_2^+I_3^-$ salts show similar spectral properties, the compounds can be easily identified by their color and melting points from their respective reaction mixtures. All the products show high melting point (> 170 ºC), which was quite different to that of $Ph_3PNS_3N_3$ (126 ºC) and the triiodide salts showed deposits of iodine crystals in the sealed capillary used for melting point determination.

A sharp singlet with ^{31}P chemical shift value revealed that all phosphorus atoms are in the same environment. ^{1}H-NMR spectra showed the presence of aromatic protons in the region of δ 7.02-8.16 as well as ^{13}C- NMR spectra also indicated the phenyl carbons at δ 124-134 as expected for compounds **5-7**, **9** and **10**. The other products, **11a** and **12a** derived from **2** clearly show the ^{1}H-NMR and ^{13}C-NMR signals for morpholine ring in the region of δ 3.15 (N-CH_2), 3.78 (O-CH_2) and δ 43.5 (N-CH_2), 66.4 (O-CH_2) respectively[37]. The compounds **11b** and **12b** show the signals in ^{1}H- and ^{13}C-NMR spectra for the aromatic phenyl rings.

The isolated iodinated products containing I_3^- anionic units display the UV-visible absorption (λ_{max}) at 478, 351, 288 nm (**5**), 364, 294 nm (**6**), 351, 288 nm (**7**) and 362, 294 (**11**) respectively, where the precursor **1** shows a characteristic λ_{max} at around 480 and 330 nm (Fig.1).[38] Apart from the presence of cyclotrithiazene ring (λ_{max} at 478 nm), an additional absorption for **5** around 351, 288 nm indicates the presence of I_3^-. On comparison of the electronic spectra of the compounds **5-7**, **10** with $Ph_3PNS_3N_3$ (**1**) and products having I_3^- anion, it is clearly found that the compound has triiodide ion and thus confirming the ionic nature of the compound (Fig.1). All the products with I_3^- anion showed similar absorption patterns having λ_{max} around 360 and 288 nm which are completely different from the precursor.

The mass spectra of these crude reaction mixtures derived from different experiments showed a mixture of products containing $[(Ph_3PN)_2(S_3N_3)]^+$, $[Ph_3PNH_2]^+$, $[(Ph_3PN)_3S]^+$, $S_4N_3^+$, $S_3N_3^+$ and the less intense mass fragments of smaller S-N species i.e. S_2N, S_2N_2, S_3N_2, S_3N_3 and S_8. The spectra clearly showed that there is no evidence of the higher mass species in the mass spectra. The formation of elemental sulfur could be due to thermal decomposition of S-N compounds. These results were consistent with the literature reports.[33] It was interesting to note that the relative stability of iodinated products strongly dependent on the nature of ligand: PPh_3 > (*p*-chlorophenyl)$_3$P > $(OC_4H_8N)_3P$. The presence of excess of iodine is believed to cause the formation of I_3^-. It is observed that the wet solvents change the product distribution and yield several additional products of the type $PR_3NH_2^+I^-$, $PR_3NH_2^+I_3^-$ and $[(PR_3N)_3SO]^{2+}(I_3^-)_2$.

It has been reported that solid state pyrolysis of **1** leads to the formation of acyclic derivatives (**13**) from a thermally prompted and controlled ring fragmentation reaction.[39] But the same thermolysis of **1** in the presence of solid iodine at 175 °C yielded **9** in 20% yield by the cleavage of S-N and P-N bonds (Eq.4).



Eq.4

Conclusions

The electron-rich symmetrical heterocycles, $R_3PNS_3N_3$ undergo a smooth oxidative addition with iodine to give various new and interesting halogenated products. The products are characterized by various spectroscopic and analytical techniques. The product distribution strongly depends on the experimental conditions. The iodination reactions can be influenced by various factors such as iodine concentration, mode of addition of iodine, temperature, nature of solvent, and nature of substituent R. Iodination of $Ph_3PN\text{-}S_3N_3$ serves as a source of the “$S(NP)_3$” species while $(OC_4H_8N)_3PN\text{-}S_3N_3$ and $(p\text{-}ClC_6H_4)_3PN\text{-}S_3N_3$ offer good yields of the corresponding phosphonium triiodide salts.

Acknowledgements. The authors (ASRK and MNSR) thank DST, India for the financial assistance.

References

1) a) Bowman, W. R.; Burchell, C. J.; Kilian, P.; Slawin, A. M. Z.; Wormald, P.; Woollins, J. D.; *Chem. Eur. J.,* **2006**, *12*, 6366-6381; b) Bridgeman, A. J.; Cavigliasso, G.; and Ireland, L. R.; Rothery, J.; *J. Chem. Soc. Dalton Trans.,* **2001**, 2095-2108; c) Hass, A.; *J. Organomet. Chem.*, **2001**, *623*, 3-13; d) Datta, A.; *Phys. Chem. Chem. Phys.* **2009**, *11*, 11054-11059; e) Nagy, V.; Benltifa, M.; Vidal, S.; Berzsényi, E.; Teilhet, C.; Czifrák, K.; Batta, G.; Docsa, T.; Gergely, P.; L. Somsák, L.; Praly, J. P.; *Bioorg. Med. Chem.* **2009**, *17*, 5696.
2) a) Ali, T. E. S.; Ibrahim, M. A.; Magdy, A.; and Abdel-Kariem, S. M.; *Phosphorus Sulfur Silicon Relat. Elem.,* **2009**, *184*, 2358-2392; b) Steudel (ed.), R.; *The Chemistry of Inorganic Ring Systems,* Elsevier Science, Amsterdam, 1992.

3) a) Mahdavian, M.; and Ashhari, S.; *Electrochim. Acta*, **2010**, *55*, 1720-1724*; b)* Allen, C. W.; *Chem. Rev.*, **1991**, *91*, 119-135.

4) a) Cox, P. J.; Psomas, G.; and Bolos, C. A.; *Bioorg. Med. Chem.*, **2009**, *17*, 6054-6062; b) Woolins, J. D.; *Non-Metal Rings, Cages and Clusters*, John Wiley and Sons, New York, **1988**.

5) a) Zhang, G. H.; Zhao, Y, F.; Wu, J. I.; and Schleyer, P. V. R.; *Inorg. Chem.*, **2009**, *48*, 6773-6780; b) Haiduc, I.; and Sowerby (eds), D. B.; The Chemistry of Inorganic Homo- and Heterocycles, Academic Press, London, 1987, vols I and II; c) Pflantz, R.; Sluiter, J.; Krička, M.; Saak, W.; Hoenke, C.; and Christoffers, J.; *Eur. J. Org. Chem.*, **2009**, 5431-5436.

6) a) Borisov, A. V.; Osmanov, V. K.; Borisov, G. N.; Matsulevich, Z. V.; and Fukin, G. K.; *Mendeleev Commun.*, **2009**, *19*, 49-51; b) Allock, H. R.; Desorcie, J. L.; and Riding, G. H.; *Polyhedron*, **1987**, *6*, 119-157; c) Roesky, H. W.; *Rev. Inorg. Chem.* **1982**, *4*, 36-52.

7) Gmelins Hand Book Series, *Sulphur–Nitrogen Compounds*, **1987**, Part 3.

8) Morris, J. L.; Rees, C. W.; *Chem. Soc. Rev.* **1986**, *15*, 1-16.

9) Roesky, H. W.; *Chem. Soc. Rev.*, **1986**, *15*, 309-334.

10) Chivers, T.; *Chem. Rev.*, **1985**, *85*, 341-365.

11) Chivers, T.; *Acc. Chem. Res.*, **1984**, *17*, 166-171.

12) Roesky, H. W.; and Witt, M.; *Comments Inorg. Chem.*, **1981**, *1*, 183-192.

13) The Inorganic Heterocyclic Chemistry of Sulphur, Nitrogen and Phosphorus, Academic Press, London, **1980**.

14) a) Chivers, T.; and Rao, M. N. S.; *Can. J. Chem.*, **1983**, *61*, 1957; b) Chivers, T.; Oakley, R. T.; Coats, A. W.; and Pennington, W. T.; *J. Chem. Soc. Chem. Commun.*, **1981**, *1214*.

15) Rao, M. N. S.; *Curr. Sci.*, **2000**, *78*, 479-485 and the references therein.

16) a) Srinivas, J.; Srinivasamurthy, G.; Thomas, C. J.; and Rao, M. N. S.; *J. Chem. Crystallogr.*, **1996**, *26*, 403-406; b) Janarthanan, G.; Srinivas, J.; Srinivasamurthy, G.; and Rao, M. N. S.;*Polyhedron*, **1997**, *16*, 1089-1094.

17) Liblong, S. W.; Oakley, R. T.; Cordes, A. W.; Noble, M. C.; *Can. J. Chem.*, **1983**, *61*, 2062-2067.

18) Srinivas, J.; Rao, M. V.; Murthy, G. S.; Thomas, C. J.; and Rao, M. N. S.; *J. Chem. Cryst.*, **2004**, *34*, 19-24.

19) a) Elias. A. J.; and Rao, M. N. S.; *Phosphorus Sulfur Silicon Relat. Elem.*, 1989, **41**, 367; b) Appel, R.; Ruppert, I.; Milker, R.; and Bastian,V.; *Chem. Ber.*, **1974**, *107*, 380-384.

20) Swarnalatha, U.; Sivaramakrishna, A.; Venkatachalam, C. S.; Rao, M. N. S.; Inoue, T.; Ueda, T.; and Hojo, M.; *Can. J. Chem.*, **2002**, *80*, 1428-1434.

21) a) Swarnalatha, U.; Rao, M. N. S.; and Udupa, M. R.; *Thermochim. Acta*, **1997**, *297*, 139-142; b) Elias,A.J.; and Rao, M.N.S.; *Phosphorus Sulfur Silicon Relat. Elem.*, **1988**, *37*, 179-184.

22) a) Thomas, C. J.; and Rao, M. N. S.; *Indian J. Chem. Sect. A: Inorg. Phys. Theor. Anal.*, **1990**, *29A*, 450-454.

23) a) Akhtar, M.; Chiang, C. K.; Heeger, A. J.; and MacDiarmid, A. G.; *J. Chem. Soc. Chem. Commun.* 1977, 846; b) Wolmershaeuser, G.; Krueger, C.; and Tsay, Y. H.; *Chem. Ber.*, **1982**, *115*, 1126-1128.

24) Blanco, M. V.; and Jolly, W. L., *Inorg. Synth.*, **1967**, *9*, 98.

25) Bannister, A. J.; *Inorg. Synth.*, **1977**, *17*, 197.

26) Ewart, G.; Payne, D. S.; Porte, A. L.; and Lane, A. P.; *J. Chem. Soc.*, **1962**, 3984.

27) Bransford, J. W. ; Meyers, E. A. ; *Cryst. Stru. Commun.*, **1978**, *7*, 697.

28) Vogt, H.; Fischer, A.; and Jones, P. G.; *Z. Naturforsh. B: Chem. Sci.*, **1996**, *51*, 865.

29) Zalkin, A.; Hopkins, T. E.; and Templeton, D. H.; *Inorg. Chem.*, **1966**, *5*, 1767.

30) Gillespie, R.T.; Sawyer, J. F.; Slim, D. R.; and Tyrer, J. D.; *Inorg. Chem.*, **1982**, *21*, 1296.

31) a) Banister, A. J.; and Smith, N. R. M.; *J. Chem. Soc. Dalton Trans.* 1980, 937; b) Irsen. H.S.; and Dronskowski, R.; *Z. Naturforsch. B: Chem. Sci.* **2002**, *57*, 1387.

32) a) Kunkel, F.; Folkerts, H.; Wocadlo, S.; Kang, H. C.; Massa, W.; Dehnicke, K. Z.; *Z. Natuforsch.*, **1995**, *50*, 1455; b) Bojes, J.; Chivers, T.; Cordes, A.W.; McLean, G. and Oakley, R.T.; *Inorg. Chem.*, **1981**, *20*, 16; c) Kunkel, F.; Harms, K.; Kang, H.-C.; Massa, W.; and Dehnicke, K.; *Z. Anorg. Allg. Chem.* **1997**, *623*, 962; d) Chitsaz, S.; Neumuller, B.; Dehnicke, K.; *Z. Anorg. Allg. Chem.* **2000**, *626*, 1535.

33) a) Schweikert, W. W.; and Meyers, E. A.; *J. Phys. Chem.*, **1968**, *72*, 1561; b) Arca, M.; Demartin, F.; Devillanova, F.A.; Garau, A.; Isaia, F.; Lippolis, V.; Verani, G.; *J. Chem. Soc. Dalton Trans.* **1999**, 3069.

34) Wolmershäuser, G.; and Street, G. B.; *Inorg. Chem.*, **1978**, *17*, 2685.

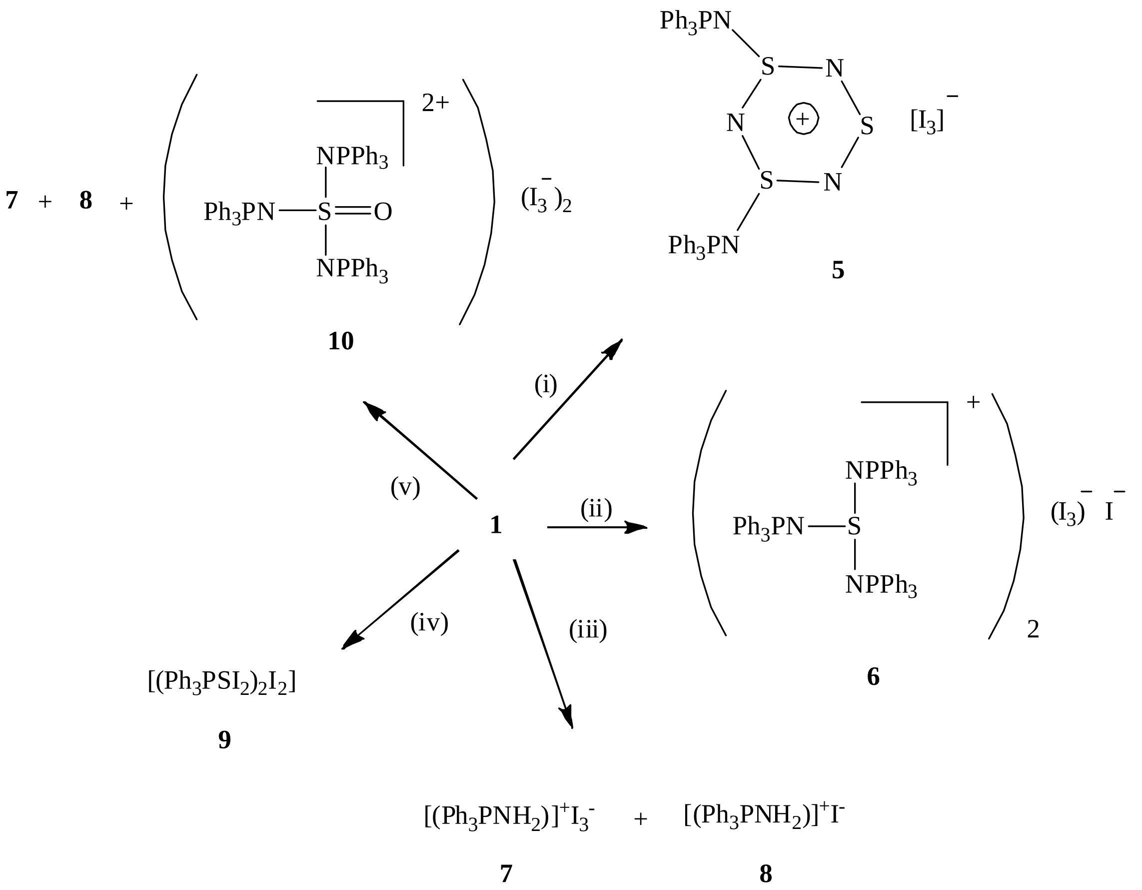
35) a) Temkin, H.; and Street, G. B.; *Solid State Commun*., **1978**, *26*, 455; b) W. Eyer, W.D. Gill and G.B. Street, *Solid State Commun*., **1978**, *27*, 343.

36) Swarnalatha. U.; Rao, M. N. S.; Srinivas, J.; and Murthy, G. S.; Kristallog, Z.; **1997**, *212*, 241

37) a) Bojes, J.; Chivers, T.; Cordes, A.W.; MacLean, G.; and Oakley, R.T.; *Inorg. Chem.*, **1981**, *20*, 16; b) Sivaramakrishna, A.; Rao, M. N. S.; *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, **2011,** *41*, 147.

38) Smith, R. D.; Street, G. B.; *Inorg. Chem.*, **1978**, *17*, 938.

39) Mohan, T.; and Rao, M. N. S.; *Heteroatom Chem*., **1997**, *8*, 225.



Scheme-1: (i) RT, toluene, 5 h, iodine (1:1); (ii) Reflux, toluene, 6 h, iodine (1:1); (iii) Reflux, toluene (wet), 6 h, iodine (1:1); (iv) Reflux, toluene, 18 h, iodine (1:4); (v) RT, toluene (wet), 18 h, iodine (1:4)

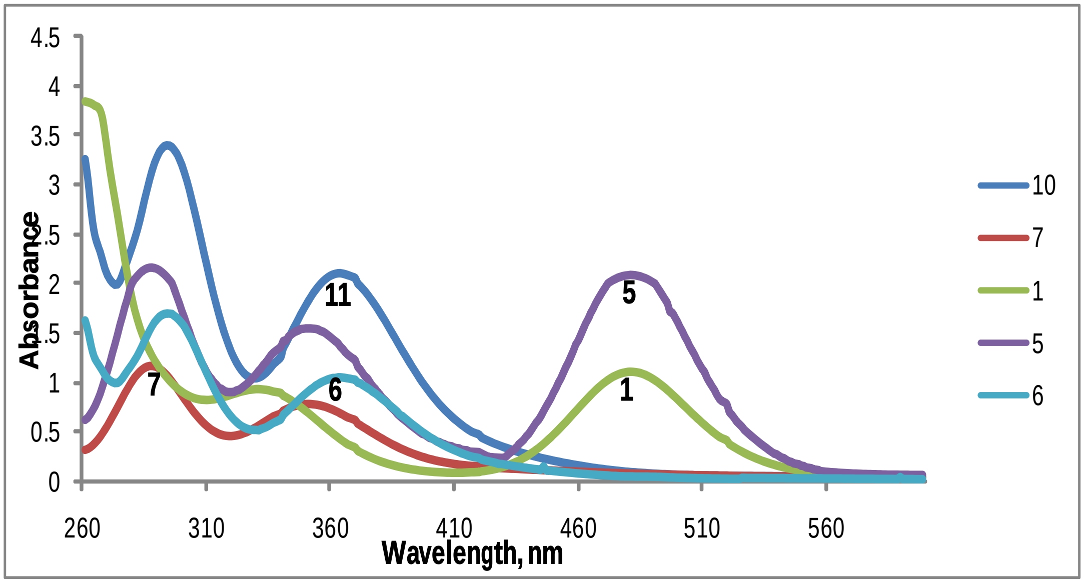


Fig.1: UV-Vis absorption spectra in CH_2Cl_2