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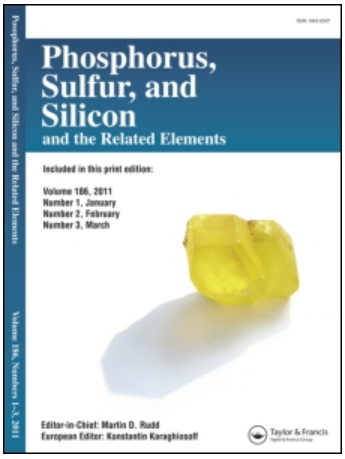

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CYCLIC S-N COMPOUNDS AND PHOSPHORUS REAGENTS: III[1]

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CYCLIC S–N COMPOUNDS AND PHOSPHORUS REAGENTS: III[1]

REACTIONS OF TRIPHENYLPHOSPHINIMINO-CYCLOTRITHIAZENE WITH AMMONIA AND AMINES—OBSERVATION OF RING EXPANSION REACTIONS LEADING TO 1,5-BIS(TRIPHENYL-PHOSPHINIMINO)CYCLOTETRATHIAZENE

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Reactions of Ph_3PN-S_3N_3 (*I*) with ammonia and various amines (primary, secondary and tertiary) have been studied in CH_3CN-C_6H_6 mixture (5:1) at 50°C. In the case of ammonia, t-butylamine, morpholine, pyrrolidine and triethylamine, the eight membered heterocycle 1,5-$(Ph_3PN)_2S_4N_4$ (*II*) was isolated in better yields compared to earlier methods. Bis(morpholino) sulfide was also isolated from reactions of morpholine. However pyrrole, pyridine, diphenylamine and urea gave no reaction with (*I*).

Key words: Triphenylphosphiniminocyclotrithiazene, 1,5-Bis(Triphenylphosphinimino)cyclotetra-thiazene, Ring expansion.

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INTRODUCTION

The eight membered sulfur-nitrogen ring S_4N_4 has been the source of a number of ring transformations[2] including the recent preparations of PNS[3] and CNS[4] heterocycles. The first example of a stable, fully characterized 1,5-disubstituted S_4N_4 derivative, $(Ph_3PN)_2S_4N_4$ (*II*) was obtained from the reaction of Ph_3P and S_4N_4 in CH_3CN in Ca. 40% yield.[5] It has been established that the two phosphinimino substituents of this compound are non-equivalent both in the solid and solution phases.[6,7] Roesky *et al.* reported the isolation of this compound in approximately the same yield from the reactions of Ph_3PN–$SiMe_3$ with $S_4N_4O_2^8$. We have studied the reactions of Ph_3PN–S_3N_3, the first stable monosubstituted S_3N_3 ring to be isolated,[9] with ammonia and various amines and have isolated the ring expansion product (*II*) in improved yield. The details of this study are reported here.

RESULTS AND DISCUSSION

Although different methods are now available[6,10] to prepare the six-membered heterocycle(*I*) in good yield, relatively little in known about the chemistry of this

ring system. Only three reactions: i) Cycloaddition with norbornadiene[11] yielding a S_3N_3 ring retained product, ii) thermal degradation resulting in an acylic species, Ph_3PNS_3N[12] and iii) exocyclic substituent exchange reaction[10] have been studied so far. In this study we have investigated the chemical response of this ring system to various amines and ammonia and find that the attempted reactions either give 1,5-$(Ph_3PN)_2S_4N_4$ as the product [Equation (1)] or are unsuccessful.

$$2\ Ph_3PN{-}S_3N_3 \xrightarrow{\text{Amines, Ammonia}} 1,5\text{-}(Ph_3PN)_2S_4N_4 + \text{`}S_2N_2\text{'} \qquad (1)$$

Ammonia, t-butylamine, morpholine, pyrrolidine and triethylamine afford the eight-membered S-N ring, (*II*) whose yield varies in the range 35 to 75%. A maximum yield of Ca. 75% was obtained in the case pyrrolidine. The reaction with morpholine also afforded a small amount of its sulfide.

On the contrary, amines like pyrrole, pyridine, diphenylamine and urea did not react and allowed only the isolation of the starting material (*I*). The pK_a values of the former set of amines lie in the range 8.70 to 11.27 while that of the latter set lie in ther range −0.27 to 5.17. The difference in their behaviour observed, presumably reflect their differing basicities. Also, it may be noted that the reactions performed in benzene or at room temperature or with no nucleophile, led to the recovery of the starting material only, (see Table I).

With this report on easy and high yield preparation of (*II*) we hope to contribute to the chemistry of this interesting heterocycle, which is practically not known.

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TABLE I

Reactions of $Ph_3PN{-}S_3N_3$(I) with amines and ammonia

S. No.	Nuclophile (pk_a)[14]	Stoichio-metry	Reaction period at 50°C	Products isolated
1.	NH_3(9.27)	excess	3h	II 35%$^+$
2.	t-$C_4H_9NH_2$(10.68)	1:3	6h	II 65%$^+$
3.	OC_4H_8NH(8.70)	1:3	6h	II 50%$^+$ + $(OC_4H_8N)_2S$(70 mg)
4.	C_4H_8NH(11.27)	1:3	6h	II 75%
5.	$(C_2H_5)_3N$(10.87)	1:3	7h	II 65%$^+$
6.	C_5H_5N(5.17)	1:3	7h	I 68%
7.	$(C_6H_5)_2NH$(0.90)	1:3	7h	I 60%
8.	$OC(NH_2)_2$(0.18)	1:3	7h	I 60%
9.	C_4H_4NH(−0.27)	1:3	7h	I 75%
10.	$(C_2H_5)_3N$	1:3	7h@	I 82%
11.	—	—	7h	I 65%
12.	$(C_2H_5)_3N$	1:10	7h	II 16%$^+$
13.	t-$C_4H_9NH_2$	1:3	36h*	I 80%

A mixture of $CH_3CN{-}C_6H_6$ (5:1) was used as the solvent to improve the solubility of (*I*). Yield of (*II*) is calculated on the basis of Equation (1).

@ In this reaction, benzene (25 ml) alone was used as the solvent.

$^+$ In all these reactions, (*I*) also was isolated in 15 to 28% yield.

* This reaction was done at room temperature.

EXPERIMENTAL

All the reactions were performed under an atmosphere of dry, oxygen free nitrogen. $Ph_3PN–S_3N_3$ was prepared by the literature method and recrystallized from $CH_3CN–C_6H_6$ before use.

Dry and distilled samples of amines and ammonia were used for the reactions. CH_3CN was twice distilled over P_2O_5 and then distilled and stored over CaH_2. Benzene (AR) was distilled and stored over sodium before use. Identification of compounds (*I*) and (*II*) were done by comparing their physical characteristics (colour, m.p, solubility etc.) and IR spectral data with those reported.[6] Bis(morpholino)sulfide, $(OC_4H_8N)_2S$ was characterized by comparing its m.p, IR and ^1H nmr spectral data with those reported on the authentic sample.[13] Reactions performed in this study have been given in Table I.

Typically the reactions were performed by taking (*I*), (0·25 g) and the amine in 1:3 molar ratio in 25 ml of $CH_3CN–C_6H_6$ (5:1) and stirring it under nitrogen for about 7 hours at 50°C. It was then brought to room temperature and stirred for another 3 hours when compound (*II*) precipitates out. In some cases, small amounts of (*II*) was also recovered from the filtrate portion.

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