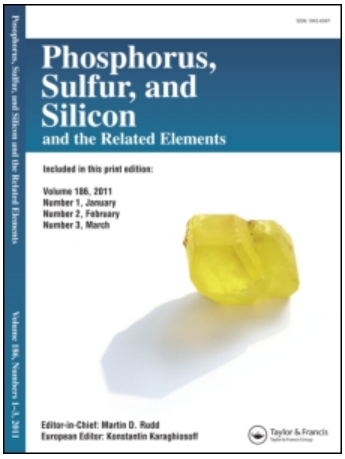

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INVESTIGATIONS ON THE COOPERATIVE EFFECTS OF PHOSPHINES: A CASE STUDY OF THE REACTIONS OF S_4N_4, Ph_3P AND Ph_2PR (R = p-$CH_3C_6H_4$-(I) AND OC_4H_8N-(II))

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Abstract *Reactions of tetrasulphur tetranitride and triphenylphosphine in presence of Phosphine (I) or (II) have been studied. In case of p-tolyldiphenylphosphine(I), in addition to the trisulphurtrinitride derivatives (III&VI) and compound (V), mixed phosphine derivatives (VII to IX) are obtained. In case of morpholinodiphenylphosphine(II), the corresponding trisulphurtrinitride derivatives (III&X) and compound (V) are the only cyclic products isolated. New products have been characterized by physical, spectroscopic and analytical data. The two phosphines seem to exert different effects.*

INTRODUCTION

The first report of the reaction of S_4N_4 and Ph_3P appeared in 1961.[1] A recent study of the same reaction has yielded many new results.[2] Similar detailed studies of S_4N_4 with other phosphines (eg.Ph_2PH[3], Ph_2PCl[4], etc.) have been reported since then. It has been proposed that the opening of S_4N_4 cage by the nucleophilic attack of S_4N_4 by phosphine is a necessary step in the formation of new compounds isolated from these reactions. We have studied the reaction of S_4N_4 and Ph_3P in presence of another phosphine to find out how far the course of this reaction is altered due to the second phosphine. Such a study, also offers scope to isolate compounds containing both phosphine moieties. As examples of second phosphine, we have considered i) (p-$CH_3C_6H_4$)$(C_6H_5)_2P$(I) and ii) $(OC_4H_8N)(C_6H_5)_2P$(II) and report here our findings.

EXPERIMENTAL

S_4N_4[5] and phosphine(II)[6] were synthesised using reported procedures.

Ph_3P and phosphine(I) were commercial samples. Dry and distilled solvents were used.

Typically, reactions were performed by adding S_4N_4(0.25g) as solid at r.t.(30±2°C) to a well stirred solution of the two phosphines in a specified ratio in CH_3CN (~20ml) in 15 minutes under nitrogen atmosphere. After 24hrs of stirring, the precipitate and filtrate portions were separately worked out to isolate pure products. (See Table(I)).

Products were characterized on the basis of their physical characteristics, spectroscopic data (IR,UV-VIS, ^1H& ^{31}P-nmr and MS) and CHN analysis.

RESULTS AND DISCUSSION

Independent reactions of S_4N_4 with phosphines(I)[7] and (II)[8] have been studied and only the results of ternary reaction systems are discussed here.

An equimolar reaction of S_4N_4 and Ph_3P in acetonitrile affords compound V, Ph_3PS and unreacted S_4N_4. However, in presence of one mole phosphine(I), this reaction gave the corresponding $S_3N_3^-$ derivatives (III and VI) in nearly equal amounts. It is noteworthy that Ph_3PN-S_3N_3(III) was not isolated from acetonitrile reaction by previous workers[2]. While a small amount of $S_4N_5^-$ with mixed phosphinimino sulphonium cation(IX) was obtained, no 1,5-disubstituted S_4N_4 derivative could be isolated. Interestingly, one equivalent of phosphine(II) in place of phosphine(I) in the above reaction gave $S_3N_3^-$ derivatives (III and X) and 1,5-$(Ph_3PN)_2S_4N_4$(V).

Compound IV in 16% yield and V in 41% yield were isolated from a 1:2 reaction of S_4N_4 and Ph_3P in CH_3CN[2]. This reaction which we were able to reproduce, in presence of two equivalents of phosphine(I) gave V and mixed phosphinimino derivatives of S_4N_4 and $S_4N_5^-$ rings (VII and VIII). To our knowledge, compound VII, ((p-tolyl)Ph_2PN)(Ph_3PN)S_4N_4 is the first example of a 1,5-disubstituted S_4N_4 derivative carrying two different substituents.

TABLE (I): Reactions of S_4N_4, Ph_3P and Phosphine (I) or (II)

Ph_3P	(I) or (II)	Stoichiometry $S_4N_4/Ph_3P/$ (I) or (II)	Products isolated[b,d]
0.36g (1.35mmol)	(I) 0.38g (1.35mmol)	1:1:1	III (0.26g, 46%) VI (0.22g, 38%) IX (0.04g, 5%)
0.72g (2.70mmol)	(I) 0.76g (2.70mmol)	1:2:2	V (0.05g, 8%) VII (0.17g, 25%) VIII (0.15g, 20%)
0.36g (1.35mmol)	(I) 0.76g (2.70mmol)	1:1:2[a]	VI (0.05g, 8%) VII (0.08g, 12%) IX (0.21g, 28%)
0.72g (2.70mmol)	(I) 0.38g (1.35mmol)	1:2:1[a]	V (0.25g, 39%) VI (0.02g, 4%) VII (0.10g, 14%) VIII (0.10g, 13%)
0.36g (1.35mmol)	(II) 0.37g (1.35mmol)	1:1:1	X (0.18g, 31%) III (0.04g, 7%) V (0.12g, 18%)
0.72g (2.70mmol)	(II) 0.74g (2.70mmol)	1:2:2	V (0.30g, 44%)
0.36g (1.35mmol)	(II) 0.74g (2.70mmol)	1:1:2[c]	X (0.26g, 46%) III (0.11g, 19%) V (0.09g, 13%)
0.72g (2.70mmol)	(II) 0.37g (1.35mmol)	1:2:1	III (0.08g, 12%) V (0.41g, 63%)

III - $Ph_3PN\text{-}S_3N_3$; IV - $(Ph_3PN)_3S^+S_4N_5^-$; V - 1,5-$(Ph_3PN)_2S_4N_4$; VI - (p-tolyl)$Ph_2PN\text{-}S_3N_3$; VII - 1,5-((p-tolyl)Ph_2PN)(Ph_3PN)S_4N_4 ; VIII - ((p-tolyl)Ph_2PN)$(Ph_3PN)_2S^+S_4N_5^-$; IX - ((p-tolyl)$Ph_2PN)_2$ $(Ph_3PN)S^+S_4N_5^-$; X - (Morpholino)$Ph_2PN\text{-}S_3N_3$

a - refers to reaction carried out at 20°C.

b - In all the reactions, sulphides of both phosphines are formed.

c - 10 to 20 mg of S_4N_4 was also isolated.

d - Percentage yield reported is based on nitrogen.

It may be mentioned that no S_3N_3- derivative was isolated, from this reaction. Surprisingly, the corresponding reaction of S_4N_4, Ph_3P and phosphine(II) afforded 1,5-$(Ph_3PN)_2S_4N_4$ in good yield as the only isolable cyclic product. Similar differences in the nature of products isolated and their yields were also found in the other reactions studied. (See Table (I)).

These results reveal that the course of the reaction of S_4N_4 and Ph_3P is considerably affected due to the second phosphine and the nature and magnitude of this variation seem to be dependent not only on the choice of the phosphine system and reaction conditions but also on the stabilities of the analogous compounds.

Also, the synthetic approach employed in this study appears to be promising for obtaining a variety of unsymmetrically disubstituted S_4N_4 derivatives. This aspect is currently under investigation.

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