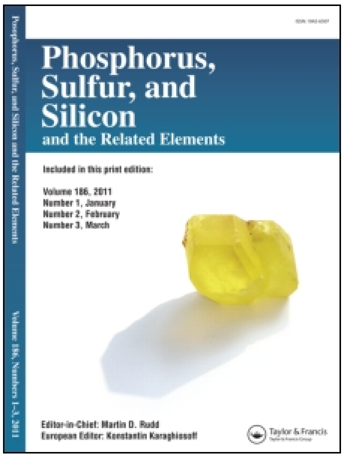

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REACTIONS OF AMINOPHOSPHAZENES (P-NH_2) WITH AND WITHOUT REARRANGEMENT

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Abstract 2,2-$N_3P_3(NH_2)_2Cl_4$ on complete alcoholysis in the NaOR/ROH system gave both rearranged 2,4-$N_3P_3(NH_2)_2(OR)_4$ and unrearranged 2,2-$N_3P_3(NH_2)_2(OR)_4$ (R = Me, CH_2CF_3), whilst for R = Et, Pr^n, Bu^n only the rearranged derivatives were observed. With NaOR in ether (R = Pr^n) only rearranged derivatives were obtained, whilst for R = CH_2CF_3, Ph only the unrearranged products were isolated. From the ROH/pyridine system only unrearranged derivatives (R = Me, Et, Pr^n, Pr^i) were obtained. Partial alcoholysis studies suggested that the rearrangement occurred with the introduction of the second alkoxy group. The alcoholysis of 2,2-$N_4P_4(NH_2)_2Cl_6$ and of 2,6-$N_4P_4(NH_2)_2Cl_6$ using NaOR/ROH (R = Me) yielded 2,2- and 2,6-derivatives $N_4P_4(NH_2)_2(OR)_6$ of the former and only the 2,6-isomers of the latter.

INTRODUCTION

Our earlier studies on the complete alcoholysis of $N_3P_3Cl_4(NH_2)_2$ (1) brought to light a geminal → nongeminal rearrangement of the amino groups. These findings can be summarised on follows: (i) The structure of the starting material (1) (hitherto controversial) has been shown by X-ray crystallography to be geminal. (ii) Reaction of (1) with an excess of NaOR in ROH (R = Me, Et, Pr^n, Bu^n) gave only cis and trans nongeminal rearrangement products, $N_3P_3(NH_2)_2(OR)_4$, (2), except for R = Me, where some unrearranged isomeric product, $N_3P_3(NH_2)_2(OR)_4$, (3), was also isolated. As this was the first geminal → nongeminal rearrangement reported in phosphazene chemistry, we undertook an investigation to discover under which conditions rearrangement takes place.

FACTORS AFFECTING REARRANGEMENT IN THE COMPLETE ALCOHOLYSIS OF TRIMER DERIVATIVES

(A) Variation in the grouping $P(NH_2)_2$. If this moiety was changed to $P(NHBu^t)_2$ no rearrangement took place. The products were $N_3P_3(NHBu^t)_2(OR)_4$ (R = Me, Et, Pr^n, Bu^n), (4). Change to the more electron releasing group $P(NH_2)(NPPh_3)$ slowed the alcoholysis reaction and gave only an unrearranged product, $N_3P_3(NH_2)(NPPh_3)(OR)_4$ (R = Me) (5). The even more powerful electron releasing moiety $P(NPPh_3)_2$ did not allow any alcoholysis to proceed under our reaction conditions and the starting material, $N_3P_3(NPPh_3)_2Cl_4$, (6), was recovered unchanged. Detailed comparison of the crystal structures of the starting molecules: (1), $N_3P_3(NHBu^t)_2Cl_4$, $N_3P_3(NH_2)(NPPh_3)Cl_4$ and (6) showed systematic structural changes in keeping with the above observations.[4]

(B) Variation in the nucleophilicity of the sodium alkoxide If in the system NaOR/ROH the nucleophilicity of the alkoxide ion was reduced, e.g. R = CH_2CF_3, unrearranged (3) and rearranged products (2) were isolated. Because phenol is a solid, the system for R = Ph was not investigated under these conditions.

(C) Change of solvent. On changing the solvent from an alcohol to an ether the reactivity of the sodium alkoxide, NaOR, was reduced. Thus for R = Pr^n, whilst no unrearranged compound (3) was obtained the rearranged cis and trans products, (2), were accompanied by a partially substituted derivative, $N_3P_3(NH_2)_2(OR)_3Cl$. The less powerful reagents (R = CH_2CF_3 and Ph) gave under these conditions only unrearranged products, (3).

(D) Change to alcohol/pyridine system. Replacing the alkoxide ion RO^-, by alcohol ROH, reduced the nucleophilicity and gave rise only to unrearranged derivatives (3), (R = Me, Et, Pr^n, Pr^i).

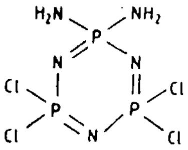
PARTIAL ALCOHOLYSIS OF $N_3P_3(NH_2)_2Cl_4$

In our studies of the $NaOR/ROH/N_3P_3(NH_2)_2Cl_4$ system, we had inadvertently isolated two partially alcoholysed products, $N_3P_3(NH_2)_2(OR)_2Cl_2$ (R = Et, Pr^i), whose structures were shown to be rearranged (7). We therefore investigated in more detail the partial alcoholysis of (1) in the NaOR/ROH system. When treating (1) with one equivalent of NaOR (R = Me), we obtained a monoalkoxy derivative,

$N_3P_3(NH_2)_2(OR)Cl_3$, (8); no rearrangement had taken place at that stage. Three bis derivatives $N_3P_3(NH_2)_2(OR)_2Cl_2$, were observed. Two were the rearranged cis and trans isomers (7) (R = Me); the third may be an unrearranged derivative. A rearranged tris derivative, $N_3P_3(NH_2)_2(OR)_3Cl$ (R = Me) was also obtained. From the NaOR system (R = Et) we isolated two rearranged bis isomers (7) (R = Et). The above data suggest that rearrangement takes place on forming the bis alkoxy derivatives, $N_3P_3(NH_2)_2(OR)_2Cl_2$. As no nongeminal $N_3P_3(NH_2)_2Cl_4$ is known we were unable to test whether the reverse rearrangement nongeminal → geminal could take place in the trimer system.

THE ALCOHOLYSIS OF 2,2- AND 2,6-$N_4P_4(NH_2)_2Cl_6$

2,6-$N_4P_4(NH_2)_2Cl_6$ (9) has been known for a long time[5] and its structure deduced more recently by derivatisation and ^{31}P nmr spectroscopy.[6] Its 2,2-isomer (10) was isolated only very recently.[7] Complete alcoholysis of (9) using the NaOR/ROH (R = Me) method gave two isomeric cis and trans derivatives, $N_4P_4(NH_2)_2(OR)_6$, (11) (R = Me). No compound containing a geminal $P(NH_2)_2$ grouping was isolated. Hence no nongeminal → geminal rearrangement occurs under these conditions. Complete alcoholysis of the 2,2-isomer (10),



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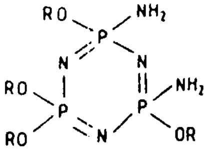

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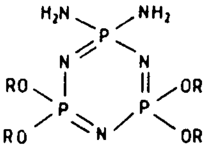

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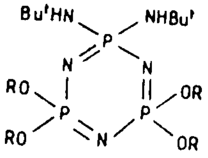

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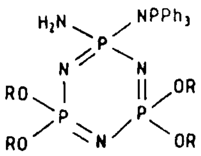

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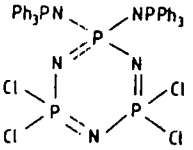

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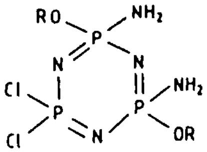

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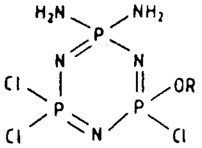

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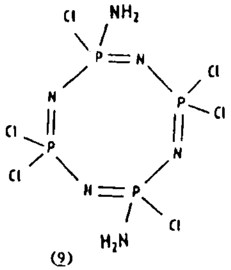

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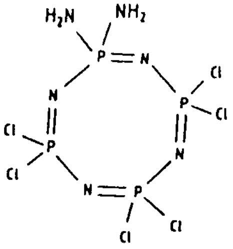

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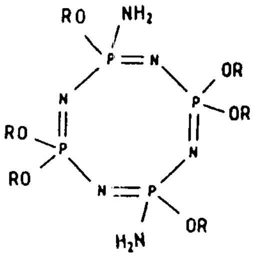

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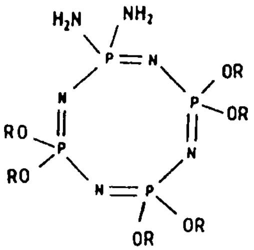

(12)

gave in addition to a 2,6-derivative (11)(R = Me), also some geminal unrearranged alkoxide (12) (R = Me).

2,2-$N_4P_4(NH_2)_2Cl_6$ (10), thus parallels in its behaviour that of its lower homologue 2,2-$N_3P_3(NH_2)_2Cl_4$ (1).

SUMMARY In our studies of the alcoholysis of aminophosphazenes we observed geminal → nongeminal rearrangements for compounds containing $P(NH_2)_2$ moieties. If one or both of the NH_2 groups were replaced by other groups no rearrangement was noted. The ease of rearrangement was related to the nucleophilicity of the reagent: NaOR/ROH R = Alk > R = CH_2CF_3, Ph > ROH.

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