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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### On Derivatisation Reactions of N-Phosphanyl-1.3.2-Oxaza- AND -1.3.2-Diazaphosphorinanes

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## ON DERIVATISATION REACTIONS OF N-PHOSPHANYL-1.3.2-OXAZA- AND -1.3.2-DIAZAPHOSPHORINANES

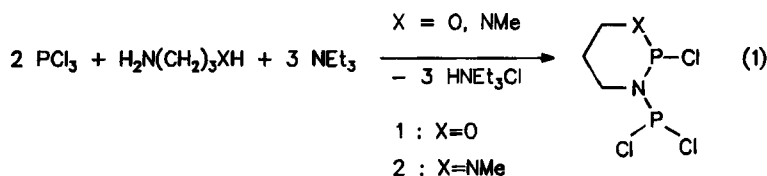
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**Abstract** Derivatisation reactions of N-phosphanylated oxaza- and diaza-phosphorinanes with protic nucleophiles are discussed.

### INTRODUCTION

The results of investigations concerning the derivatisation of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1** and 1-methyl-2-chloro-3-dichlorophosphanyl-1.3.2-diazaphosphorinane **2** formed by the reaction of  $\text{PCl}_3$  with propanolamine-1.3 and N-methyl-propanediamine-1.3 in the presence of  $\text{NEt}_3$  are represented <sup>1</sup>; Equation (1).



### RESULTS AND DISCUSSION

The reactions of **1** and **2** with protic nucleophiles like diethyl amine, methanol, ethanol, and  $\text{NEt}_3\text{HF}$  as a fluorinating agent were found to lead to a great variety of new heterocyclic compounds as shown in Figure 1. Whereas by the reactions of **1** and **2** with  $\text{HNEt}_2$  and with alcohols both the corresponding oxaza- and diazaphosphorinanes are formed, in the fluorination reactions of **1** only the 2-fluoro-3-difluorophosphanyl-1.3.2-oxazaphosphorinane and in the case of **2** only the double fluorinated compound were formed nearly quantitatively.

Concerning the reactivity of the endo- and exocyclic phosphorus atom in **1** and **2** it was of special interest on which of the two phosphorus atoms the nucleophilic attack

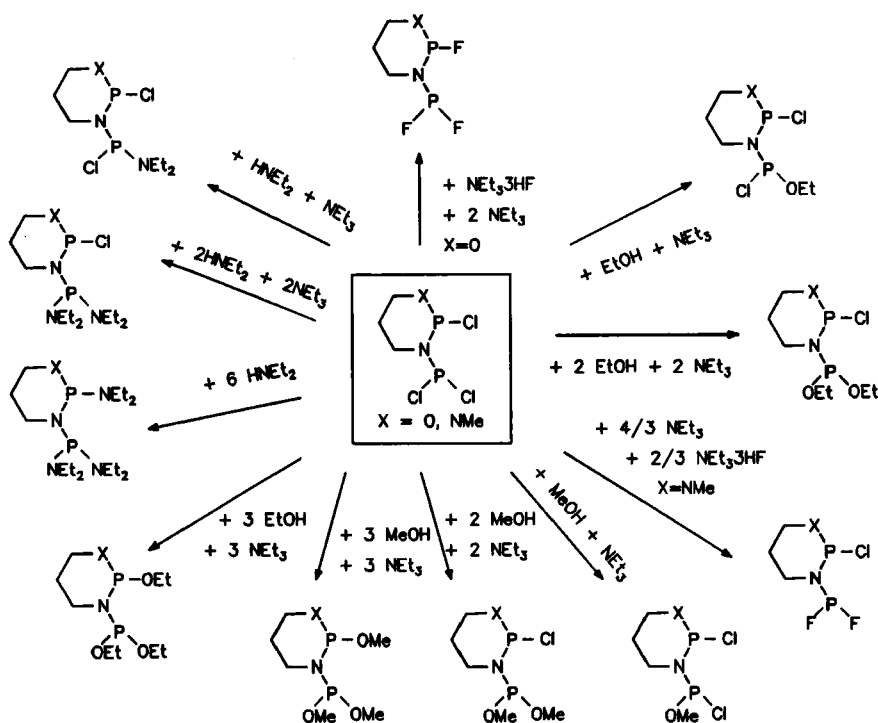


FIGURE 1 Derivatisation reactions of 1 and 2

preferentially occurs in partial replacement reactions.

Due to the splitting pattern of the  $^{31}\text{P}$ -NMR- and  $^{19}\text{F}$ -NMR-spectra of the double fluorinated derivative of 2 it was proved that the two fluorine atoms are bound on the exocyclic phosphanyl group, which was therefore recognized as the most reactive, electrophilic centre in 2. The comparison of the  $^{31}\text{P}$ -NMR- chemical shift values for the endo- and exocyclic phosphorus atoms of the amino and alkoxy derivatives of 2 led to the same conclusion. Furthermore in the case of the monoamidated and the monoalkoxylated derivative of 2 some evidence for a substitution taking place primarily on the exocyclic phosphorus atom was found by the NMR spectroscopic proof of the existence of diastereomers.

## REFERENCES

1. C. Mundt and L. Riesel, *Phosphorus, Sulfur, and Silicon*, **77**, 145 (1993)