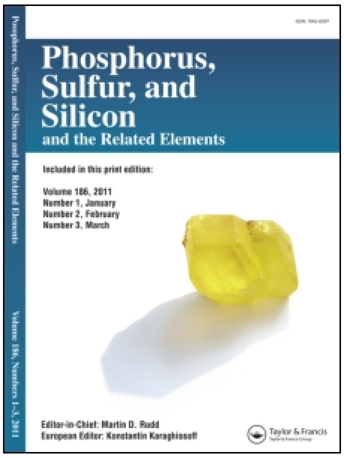

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On Derivatisation Reactions of N-Phosphanyl-1.3.2-Oxaza- AND -1.3.2-Diazaphosphorinanes

Cornelia Mundt[a]; Lothar Riesel[a]
[a] Humboldt-Universität zu Berlin, Berlin, Germany

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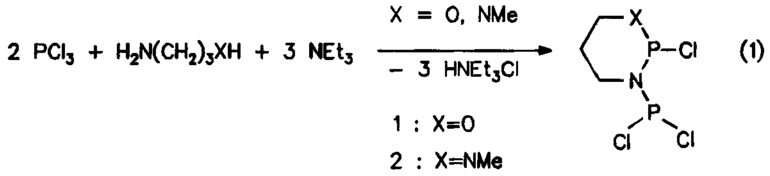
ON DERIVATISATION REACTIONS OF N-PHOSPHANYL-1.3.2-OXAZA- AND -1.3.2-DIAZAPHOSPHORINANES

CORNELIA MUNDT* AND LOTHAR RIESEL
Humboldt-Universität zu Berlin, Hessische Str.1/2, 10115 Berlin, Germany

Abstract Derivatisation reactions of N-phosphanylated oxaza- and diazaphosphorinanes 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 PCl_3 with propanolamine-1.3 and N-methyl-propanediamine-1.3 in the presence of NEt_3 are represented [1]; Equation (1).



(1)

RESULTS AND DISCUSSION

The reactions of **1** and **2** with protic nucleophiles like diethyl amine, methanol, ethanol, and NEt_33HF 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 $HNEt_2$ 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

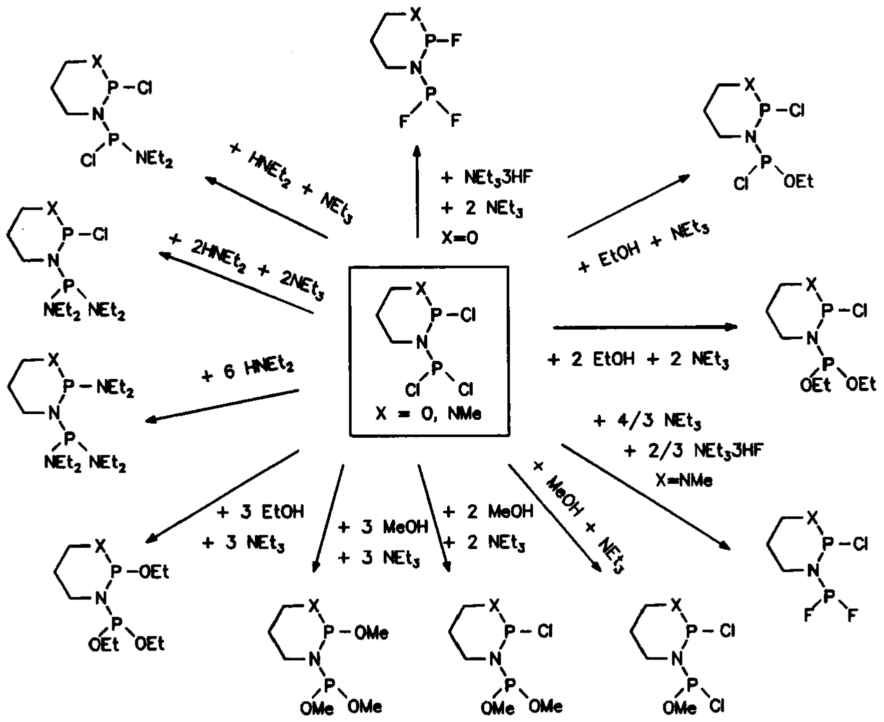


FIGURE 1 Derivatisation reactions of **1** and **2**

preferentially occurs in partial replacement reactions.

Due to the splitting pattern of the ^{31}P-NMR- and ^{19}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}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.

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