

## Formation of an *S*-Methyl Derivative from the Reaction of Methanol with Compounds of the Type $S:PX_2 \cdot N:PF_2Cl^1$

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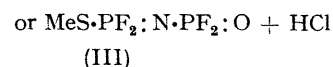
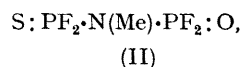
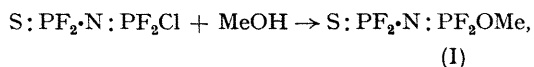
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**Summary** The compounds  $S:PX_2 \cdot N:PF_2Cl$  ( $X = F$  or  $Cl$ ) react with methanol to form the *S*-methyl derivatives  $MeS \cdot PX_2 \cdot N \cdot PF_2 \cdot O$ .

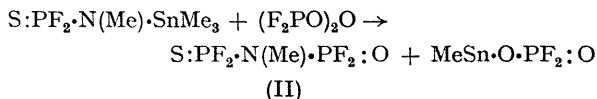
THE novel compounds  $S:PX_2 \cdot N:PF_2Cl$  ( $X = F$  or  $Cl$ ) have recently been prepared from the reaction of the amides  $S:PX_2 \cdot NH_2$  with an excess of  $PF_3Cl_2$ .<sup>2</sup> In order to establish the chemical properties of these compounds we investigated the reaction with methanol. Hydrogen chloride was the

It is a distillable liquid and shows no tendency to rearrange.

I.r. and <sup>31</sup>P n.m.r. spectra show unambiguously that the product is compound (III). The i.r. spectrum shows two strong absorptions at 1380 and 1305 cm<sup>-1</sup> which are in the regions expected for  $\nu(P=N)$  and  $\nu(P=O)$  respectively.  $MeS \cdot PFC_2 \cdot N \cdot PF_2 \cdot O$  and  $MeS \cdot PCl_2 \cdot N \cdot PF_2 \cdot O$  show  $\nu(P=N)$  shifted *ca.* 20 cm<sup>-1</sup> to lower frequency owing to replacement of fluorine by chlorine, and  $\nu(P=O)$  at 1300 cm<sup>-1</sup>. The <sup>31</sup>P n.m.r. spectrum has a 6-line signal for  $-PF_2 \cdot O$  [ $J(P-F)$



only volatile product formed; therefore the first step of the reaction occurred at the chlorine atom of the  $-N:PF_2Cl$  group. This reaction produced only one of the three possible isomers (I)—(III). The <sup>1</sup>H n.m.r. spectrum showed a doublet of triplets which was derived from coupling with one <sup>31</sup>P and two <sup>19</sup>F atoms; this excludes structure (II) where coupling with both phosphorus atoms would be expected. Compound (II) was prepared according to the following equation:<sup>3</sup>



960 Hz,  $J(P-P)$  106.6 Hz] and a 24-line signal for  $MeS \cdot PF_2 \cdot O$  [ $J(P-F)$  1133 Hz,  $J(P-H)$  20 Hz]. We suggest that structure (III) is favoured by the high tendency for the formation of the phosphorus-oxygen double bond.

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<sup>1</sup> For earlier work see U.S.P. 3,533,736, 1970.

<sup>2</sup> H. W. Roesky and L. F. Grimm, *Chem. Ber.*, 1969 **102**, 2319.

<sup>3</sup> H. W. Roesky and H. Wierzer, *Chem. Ber.*, in the press.