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

$$S:PF_2{\cdot}N:PF_2Cl + MeOH \rightarrow \underset{(I)}{S:PF_2{\cdot}N:PF_2OMe}, \quad \underset{(II)}{S:PF_2{\cdot}N(Me){\cdot}PF_2:O}, \quad \text{or } \underset{(III)}{MeS{\cdot}PF_2:N{\cdot}PF_2:O} + HCl$$

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.[2] In order to establish the chemical properties of these compounds we investigated the reaction with methanol. Hydrogen chloride was the 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 ^1H n.m.r. spectrum showed a doublet of triplets which was derived from coupling with one ^{31}P and two ^{19}F atoms; this excludes structure (II) where coupling with both phosphorus atoms would be expected. Compound (II) was prepared according to the following equation:[3]

$$S{:}PF_2{\cdot}N(Me){\cdot}SnMe_3 + (F_2PO)_2O \rightarrow \underset{(II)}{S{:}PF_2{\cdot}N(Me){\cdot}PF_2:O} + MeSn{\cdot}O{\cdot}PF_2:O$$

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

I.r. and ^{31}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^{-1} which are in the regions expected for $\nu(P{=}N)$ and $\nu(P{=}O)$ respectively. $MeS{\cdot}PFCl:N{\cdot}PF_2:O$ and $MeS{\cdot}PCl_2:N{\cdot}PF_2:O$ show $\nu(P{=}N)$ shifted *ca.* 20 cm^{-1} to lower frequency owing to replacement of fluorine by chlorine, and $\nu(P{=}O)$ at 1300 cm^{-1}. The ^{31}P n.m.r. spectrum has a 6-line signal for $-PF_2:O$ [J(P–F) 960 Hz, J(P–P) 106·6 Hz] and a 24-line signal for $MeS{\cdot}PF_2{=}$ [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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[1] For earlier work see U.S.P. 3,533,736, 1970.

[2] H. W. Roesky and L. F. Grimm, *Chem. Ber.*, 1969 **102**, 2319.

[3] H. W. Roesky and H. Wiezer, *Chem. Ber.*, in the press.