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ADVANCES IN TRIFLUOROMETHYLATING PHOSPHORUS COMPOUNDS

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Abstract The System CF_3I/Me_3P is re-investigated and Me_2PCF_3, $Me_4P^+I^-$, $(CF_3)_2PMe_3$, Me_3PI_2, $[Me_3(CF_3)P]^+I^-$ are found as products. Using $CF_3Br/P(NEt_2)_3$ the phosphines $R^1_2PCF_3$ and $R^1P(CF_3)_2$ (e.g. R^1 = Me, *i*Pr, NEt_2) can be obtained which are precursors either for phosphoranes (e.g. $1,2\lambda^5\sigma^5$-oxaphosphetanes) or phosphonium salts (e.g. $[R^1_2(Me)PCF_3]^+X^-$ or $[R^1(Me)P(CF_3)_2X^-]$. The latter are deprotonated to furnish methylene phosphoranes $R^1_2(CH_2{=})PCF_3$ or $R^1(CH_2{=})P(CF_3)_2$, reactive synthons. From $CF_3Br/P(NEt_2)_3/P(OPh)_3$ the phosphine $P(CF_3)_3$ is available, which turned out to be a potent electrophile. Amido phospites $ROP(NEt_2)_2$ and halides R^2X (R^2= CCl_2CF_3, X= Cl; R^2= $CF{=}CFCF_3$, X= F; R^2= C_6F_5, X= Br, I; R^2= $C(CF_3)_3$, X= Br; R^2= SCF_3, X= CF_3) undergo an ARBUZOV reaction.

Keywords: Trifluoromethylated phosphines, P-trifluoromethylated phosphonium salts and ylides, oxaphosphetanes, phosphoranides, ARBUZOV reaction.

INTRODUCTION

Trifluoroiodomethane, CF_3I and PMe_3 react to give[1] $Me_4P^+I^-$ and CF_3PMe_2, which adds $(CF_3)_2CO$ or MeI to furnish an oxaphosphetane or the phosphonium salt $[Me_3PCF_3]^+I^-$, respectively[2]. The latter is easily fluorinated yielding the phosphorane $Me_3(F)PCF_3$. With $P(NR_2)_3$ (R=Me, Et) the compounds $CF_3P(NR_2)_2$, $(R_2N)_4P^+I^-$ or $[CF_3P(NR_2)_3]^+I^-$ and $[(R_2N)_3PI]^+I^-$ are observed depending on temperature and solvent[3,4]. The system $CF_3Br/P(NEt_2)_3/PCl_3$ is found to yield $CF_3P(NEt_2)_2$ and the phosphonium salt, $[CF_3P(NEt_2)_3]^+Br^-$, as a by-product, which was investigated regarding its structure and reactivity[5,6]. The amidophosphites $ROP(NEt_2)_2$ (R=CH_2Ph, CH_2CO_2Et, CHMeCOOEt) and CF_3SSCF_3 react to give[7] $(Et_2N)_2P(O)SCF_3$ and $RSCF_3$.

RESULTS AND DISCUSSION

The re-investigation of the system CF_3I/ PMe_3 without a solvent showed that not only CF_3PMe_2 and $PMe_4^+I^-$, but also $[CF_3PMe_3]^+I^-$, $(CF_3)_2PMe_3$[8] (Fig. 1) and Me_3PI_2[9] are being formed probably via a radical mechanism.

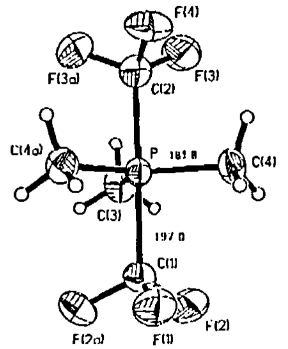


FIGURE 1 Molecular structure of $(CF_3)_2PMe_3$

The straightforward fluorination of $[CF_3PMe_3]^+I^-$ using the covalent $F_2P(NEt_2)_3$ (Fig. 2) give $CF_3(F)PMe_3$ and $[FP(NEt_2)_3]^+$(Fig.3).

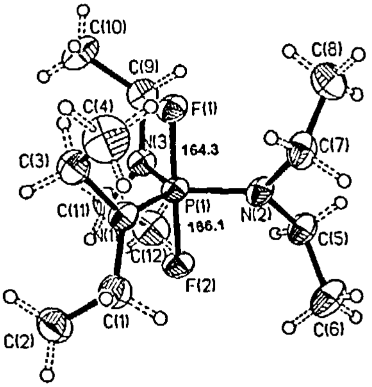


FIGURE 2 Molecular structure of $F_2P(NEt_2)_3$

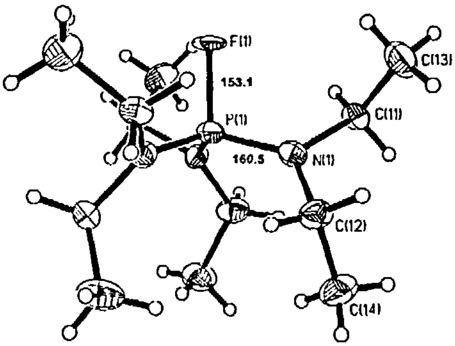
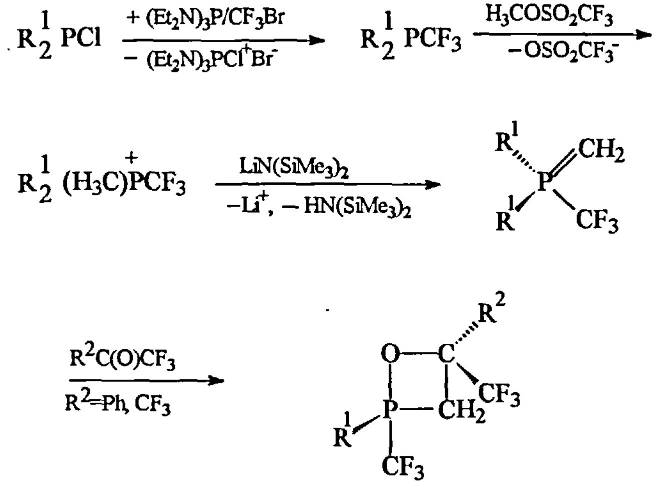
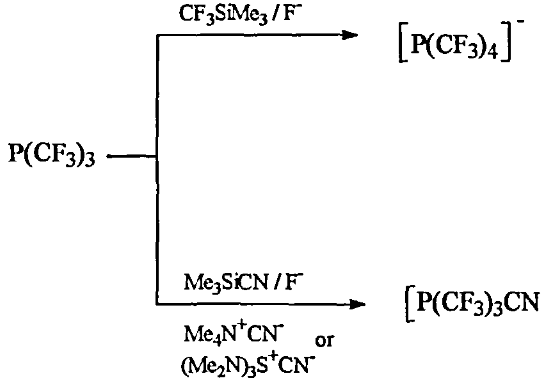


FIGURE 3 Molecular structure of $[FP(NEt_2)_3]^+$

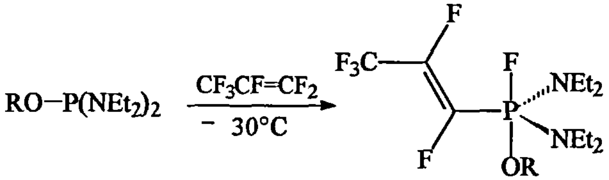
The chlorophosphines R^1_2PCl and R^1PCl_2 (R^1=Me, *i*Pr, NEt_2) are trifluoromethylated using the RUPPERT reagent to yield $R^1_2PCF_3$ and $R_1P(CF_3)_2$. Both types of phosphines are methylated and the resulting phosphonium salts deprotonated to give methylene phosphoranes which can be stabilized adding activated ketones to furnish oxaphosphetanes.

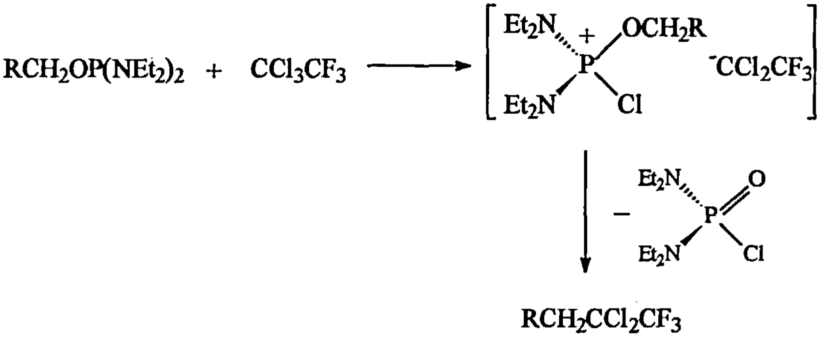


From $CF_3Br/P(NEt_2)_3/P(OPh)_3$ the tertiary phosphine $P(CF_3)_3$ is prepared in very good yield. Addition of F^-, CN^-, $[CF_3^-]$ leads to phosphoranides $[FP(CF_3)_3]^-$, $[NCP(CF_3)_3]^-$ and $[P(CF_3)_4]^-$.



Amidophosphites $ROP(NEt_2)_2$(R= CH_2Ph, CH_2CF_3, $CH(CF_3)_2$) and hexafluoropropene form monofluorophosphoranes which decompose in the case of R= CH_2Ph, CH_2CF_3 under formation of FR and an amidophosphonate. The ARBUZOV reaction with CCl_3CF_3 results in the formation of $(Et_2N)_2P(O)Cl$ and $RCH_2CCl_2CF_3$. The latter compound is dehydrochlorinated to yield $RC{\equiv}CCF_3$, (R=Ph, CF_3) using $(Et_2N)_3P{=}NMe$.





A similar transfer of a benzyl group is observed in the case of $PhCH_2OP(NEt_2)_2$ and $XC(CF_3)_3$ and XC_6F_5 (X=Br, I)

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