

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpss20>

Advances in Trifluoromethylating Phosphorus Compounds

Alexander Kolomeitsev , Michaela Görg , Uwe Dieckbreder , Enno Lork & Gerd-Volker Röschenthaler

^a Institute of Organic Chemistry, Ukrainian Academy of Sciences , Murmanskaya 6, 252660 Kiev-94, Ukraine

^b Institute of Inorganic and Physical Chemistry, University of Bremen , Leobener Straße, 28334 Bremen, Germany

^c Institute of Inorganic and Physical Chemistry, University of Bremen , Leobener Straße, 28334 Bremen, Germany

^d Institute of Inorganic and Physical Chemistry, University of Bremen , Leobener Straße, 28334 Bremen, Germany

^e Institute of Inorganic and Physical Chemistry, University of Bremen , Leobener Straße, 28334 Bremen, Germany

Published online: 06 Aug 2008.

To cite this article: Alexander Kolomeitsev , Michaela Görg , Uwe Dieckbreder , Enno Lork & Gerd-Volker Röschenthaler (1996) Advances in Trifluoromethylating Phosphorus Compounds, Phosphorus, Sulfur, and Silicon and the Related Elements, 109:1-4, 597-600, DOI: [10.1080/10426509608545224](https://doi.org/10.1080/10426509608545224)

To link to this article: <http://dx.doi.org/10.1080/10426509608545224>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising

directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

ADVANCES IN TRIFLUOROMETHYLATING PHOSPHORUS COMPOUNDS

ALEXANDER KOLOMEITSEV^a, MICHAELA GÖRG^b, UWE
DIECKBREDER^b, ENNO LORK^b and GERD-VOLKER
RÖSCHENTHALER^b

^aInstitute of Organic Chemistry, Ukrainian Academy of Sciences, Murmans-
kaya 6, 252660 Kiev-94, Ukraine; ^bInstitute of Inorganic and Physical Che-
mistry, University of Bremen, Leobener Straße, 28334 Bremen, Germany

Abstract The System $\text{CF}_3\text{I}/\text{Me}_3\text{P}$ is re-investigated and Me_2PCF_3 , $\text{Me}_4\text{P}^+\text{I}^-$, $(\text{CF}_3)_2\text{PMe}_3$, Me_3PI_2 , $[\text{Me}_3(\text{CF}_3)\text{P}]^+\text{I}^-$ are found as products. Using $\text{CF}_3\text{Br}/\text{P}(\text{NEt}_2)_3$ the phosphines R^1_2PCF_3 and $\text{R}^1\text{P}(\text{CF}_3)_2$ (e.g. $\text{R}^1 = \text{Me}$, $i\text{Pr}$, 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. $[\text{R}^1_2(\text{Me})\text{PCF}_3]^+\text{X}^-$ or $[\text{R}^1(\text{Me})\text{P}(\text{CF}_3)_2\text{X}]$). The latter are deprotonated to furnish methylene phosphoranes $\text{R}^1_2(\text{CH}_2=)\text{PCF}_3$ or $\text{R}^1(\text{CH}_2=)\text{P}(\text{CF}_3)_2$, reactive synthons. From $\text{CF}_3\text{Br}/\text{P}(\text{NEt}_2)_3/\text{P}(\text{OPh})_3$ the phosphine $\text{P}(\text{CF}_3)_3$ is available, which turned out to be a potent electrophile. Amido phosphites $\text{ROP}(\text{NEt}_2)_2$ and halides R^2X ($\text{R}^2 = \text{CCl}_2\text{CF}_3$, $\text{X} = \text{Cl}$; $\text{R}^2 = \text{CF}=\text{CFCF}_3$, $\text{X} = \text{F}$; $\text{R}^2 = \text{C}_6\text{F}_5$, $\text{X} = \text{Br}$, I ; $\text{R}^2 = \text{C}(\text{CF}_3)_3$, $\text{X} = \text{Br}$; $\text{R}^2 = \text{SCF}_3$, $\text{X} = \text{CF}_3$) 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 give¹ $\text{Me}_4\text{P}^+\text{I}^-$ and CF_3PMe_2 , which adds $(\text{CF}_3)_2\text{CO}$ or MeI to furnish an oxaphosphetane or the phosphonium salt $[\text{Me}_3\text{PCF}_3]^+\text{I}^-$, respectively². The latter is easily fluorinated yielding the phosphorane $\text{Me}_3(\text{F})\text{PCF}_3$. With $\text{P}(\text{NR}_2)_3$ ($\text{R} = \text{Me}$, Et) the compounds $\text{CF}_3\text{P}(\text{NR}_2)_2$, $(\text{R}_2\text{N})_4\text{P}^+\text{I}^-$ or $[\text{CF}_3\text{P}(\text{NR}_2)_3]^+\text{I}^-$ and $[(\text{R}_2\text{N})_3\text{PI}]^+\text{I}^-$ are observed depending on temperature and solvent^{3,4}. The system $\text{CF}_3\text{Br}/\text{P}(\text{NEt}_2)_3/\text{PCl}_3$ is found to yield $\text{CF}_3\text{P}(\text{NEt}_2)_2$ and the phosphonium salt, $[\text{CF}_3\text{P}(\text{NEt}_2)_3]^+\text{Br}^-$, as a by-product, which was investigated regarding its structure and reactivity^{5,6}. The amidophosphites $\text{ROP}(\text{NEt}_2)_2$ ($\text{R} = \text{CH}_2\text{Ph}$, $\text{CH}_2\text{CO}_2\text{Et}$, CHMeCOOEt) and CF_3SSCF_3 react to give⁷ $(\text{Et}_2\text{N})_2\text{P}(\text{O})\text{SCF}_3$ and RSCF_3 .

RESULTS AND DISCUSSION

The re-investigation of the system $\text{CF}_3\text{I} / \text{PMe}_3$ without a solvent showed that not only CF_3PMe_2 and PMe_4^+I^- , but also $[\text{CF}_3\text{PMe}_3]^+\text{I}^-$, $(\text{CF}_3)_2\text{PMe}_3$ ⁸ (Fig.1) and Me_3PI_2 ⁹ are being formed probably via a radical mechanism.

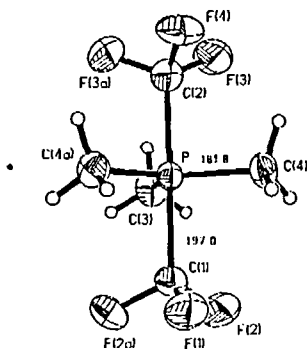


FIGURE 1 Molecular structure of $(\text{CF}_3)_2\text{PMe}_3$

The straightforward fluorination of $[\text{CF}_3\text{PMe}_3]^+\text{I}^-$ using the covalent $\text{F}_2\text{P}(\text{NEt}_2)_3$ (Fig. 2) give $\text{CF}_3(\text{F})\text{PMe}_3$ and $[\text{FP}(\text{NEt}_2)_3]^+$ (Fig.3).

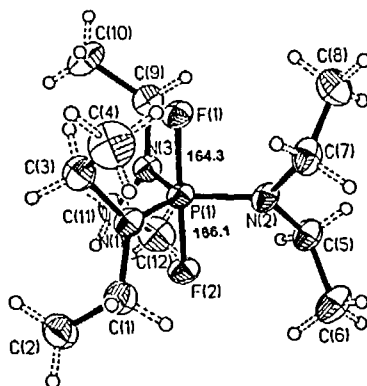


FIGURE 2 Molecular structure of $\text{F}_2\text{P}(\text{NEt}_2)_3$

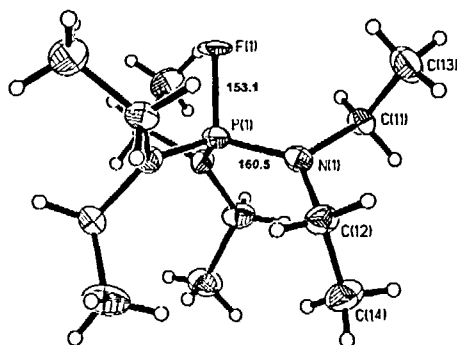
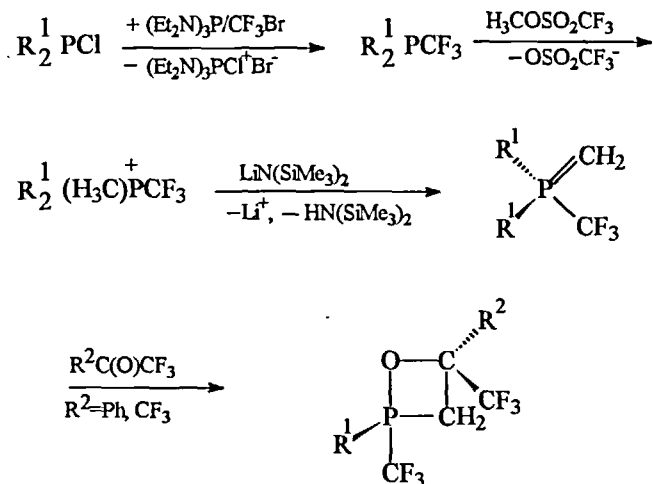
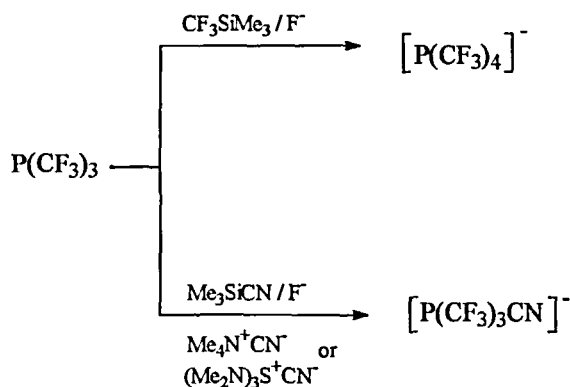


FIGURE 3 Molecular structure of $[\text{FP}(\text{NEt}_2)_3]^+$

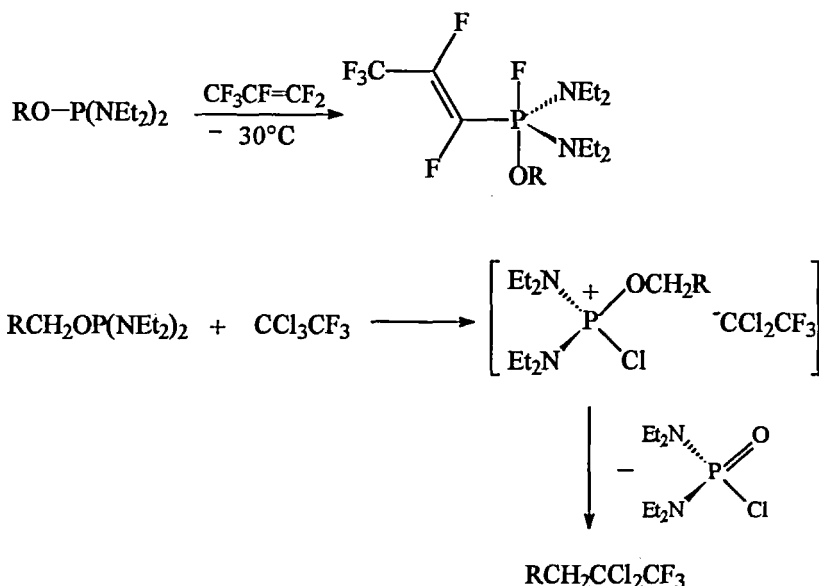
The chlorophosphines R^1_2PCl and R^1PCl_2 ($R^1=Me, iPr, NEt_2$) are trifluoromethylated using the RUPPERT reagent to yield $R^1_2PCF_3$ and $R^1P(CF_3)_2$. Both types of phosphines are methylated and the resulting phosphonium salts deprotonated to give methylene phosphoranes which can be stabilized 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 $\text{PhCH}_2\text{OP(NEt}_2)_2$ and $\text{XC(CF}_3)_3$ and XC_6F_5 ($\text{X}=\text{Br, I}$)

REFERENCES

1. R.N. HASZELDINE and B.O. WEST, *J. Chem. Soc.* **1956**, 3631.
2. A.A. KOLOMEITSEV, YU.L. YAGUPOLSKIY, A. GENTZSCH, E. LORK and G.-V. RÖSCHENTHALER, *Phosphorus, Sulfur & Silicon* **92**, 179 (1994).
3. H.A. ANG, G. MANOUSSAKIS and Y.O. EL-NIGUMI, *J. Inorg. Nucl. Chem.* **30**, 1715 (1968).
4. L. RIESEL, K. LAURITSEN and H. VOGT, *Z. Anorg. Allg. Chem.* **620**, 1099 (1994).
5. W. VOLBACH and I. RUPPERT, *Tetrahedron Lett.* **24**, 5509 (1983).
6. A. N. CHERNEGA, A.A. KOLOMEITSEV, YU.L. YAGUPOLSKIY, A. GENTZSCH and G.-V. RÖSCHENTHALER, *J. Fluorine Chem.* **70**, 271 (1995).
7. A.A. KOLOMEITSEV, K. YU. CHABANENKO, G.-V. RÖSCHENTHALER and YU.L. YAGUPOLSKIY, *Synthesis* **1994**, 145.
8. R.G. CAVELL, J.A. GIBSON and K.I. THE, *J. Am. Chem. Soc.* **99**, 7841 (1977).
9. N. BRICKLLBANK, ST. M. GODFREY, A.G. MACKIE, CH. A. MCAULIFFE, R.G. PRITCHARD, P.J. KOBRUN, *J. Chem. Soc. Dalton Trans.* **1993**, 101.