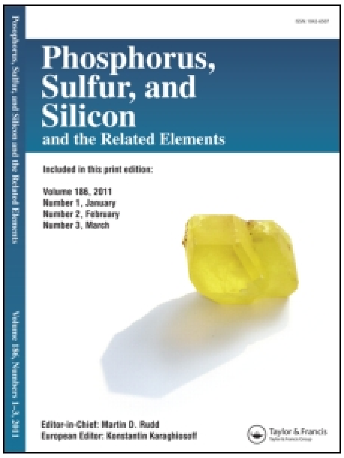

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Synthesis and Reactivity of Fluoro(Organyl)Phosphanes

Lothar Riesel[a]; Jürgen Haenel[a]
[a] Humboldt - Universität zu Berlin, Sektion Chemie, G.D.R.

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SYNTHESIS AND REACTIVITY OF FLUORO(ORGANYL)PHOSPHANES

LOTHAR RIESEL AND JÜRGEN HAENEL
Humboldt-Universität zu Berlin, Sektion Chemie, G.D.R.

Abstract A new method for producing fluoro(organyl) phosphanes is presented. They are prepared by Cl/F-exchange from the corresponding chloro compounds using $Et_3N.nHF$ as a fluorinating agent. Phosphanyl fluorophosphoranes, $R_2P\text{-}PR_2F_2$, are found to be intermediates of the disproportionation of fluoro(diorganyl)phosphanes. R_2PF react with aldehydes to form phosphinito phosphoranes, $R_2PF_2\text{-}CHR'\text{-}OPR_2$. Oxaphospholenes are formed in their reaction with α,β-unsaturated aldehydes. Furthermore, the reactions with 1.2-diketones, carboxylic acid derivatives, and covalent azides are described.

INTRODUCTION

So far the chemistry of fluoro(organyl)phosphanes, R_2PF and RPF_2, has been widely unknown caused by the considerable difficulties in preparing these substances as well as by their low stability. Especially the alkyl derivatives show a high tendency to undergo disproportionation and reduction reactions (eqs. 1-3).

$$3\ R_2PF \longrightarrow R_2PF_3 + R_2P\text{-}PR_2 \qquad (1)$$

$$2\ RPF_2 \longrightarrow RPF_4 + 1/n\ (RP)_n \qquad (2)$$

$$R_{3-n}PF_n + 2/3\ SbF_3 \longrightarrow R_{3-n}PF_{n+2} + 2/3\ Sb \qquad (3)$$

Therefore, fluoro(organyl)phosphanes, $R_{3-n}PF_n$ (n = 1, 2), usually cannot be produced from the corresponding chlorophosphanes using the common fluorinating agents.

PREPARATION

In connection with our studies on the application of $Et_3N.nHF$ adducts as a fluorinating agent we succeeded in developing a new very convenient method for preparing fluoro(organyl)-

phosphanes (eq. 4).

$$R_{3-x}PCl_x + x\ Et_3NHF \xrightarrow{Et_3N} R_{3-x}PF_x + x\ Et_3NHCl \qquad (4)$$

(x = 1, 2; R = n-Bu, t-Bu, Ph, $MeOC_6H_4$, a.o.)

Applying this process it is, however, extremely important to use a basic fluorinating agent ($n < 1$). Neither the neutral nor the acid composition ($n \geq 1$) of the fluorinating agent leads to the formation of fluoro(organyl)phosphanes. Depending on the reaction conditions disproportionation products, hydridofluorophosphoranes, $RPHF_3$, or hydridofluorophosphates, $RPHF_4^-$, resp., are obtained.

REACTION BEHAVIOUR

The disproportionation of fluoro(organyl)phosphanes is catalyzed by acids. It can be suppressed by adding Et_3N. Phosphanyl difluorophosphoranes, $R_2P\text{-}PR_2F_2$ (R = Ph, n-Bu), were detected by n.m.r. spectroscopy as intermediate products of the disproportionation of R_2PF. These phosphanyl phosphoranes react with unchanged R_2PF existing in equilibrium with the intermediate to the observed final products R_2PF_3 and $R_2P\text{-}PR_2$.[1]

Concluded from this knowledge on the disproportionation it has to be supposed that the reaction behaviour of fluoro(organyl)phosphanes is decisively determined by the dual nature of the phosphorus atom, i. e. by its nucleophilic as well as electrophilic character.

This dual nature is especially clearly reflected in the interaction of fluoro(organyl)phosphanes with aldehydes. R_2PF react with various aldehydes in like manner forming phosphinito phosphoranes (eq. 5).

$$2\ R_2PF + R'CHO \longrightarrow R_2PF_2\text{-}CHR'\text{-}OPR_2 \qquad (5)$$

(R = Bu, Ph; R' = Ph, subst. aryl, thiophene, Et, i-Pr, Ph-CH=CH, CH_2=CH)

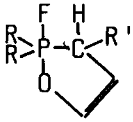
The reaction rate increases both with the nucleophilic power of the phosphane and the reactivity of the carbonyl compound. The molecular structure of the reaction products was derived from n.m.r. data and has been proved by X-ray structure analysis of the product of Ph_2PF with piperonal.[2]

In a recent publication[2] we explained the formation of these phosphinito phosphoranes by inserting the carbonyl compound into the P-P-bond of the phosphanyl phosphoranes appearing as intermediates of the disproportionation of fluoro(diorganyl)phosphanes. However, experiments with $n\text{-}Bu_2P\text{-}PF_2(n\text{-}Bu)_2$ as well as crossing experiments with equimolar mixtures of two phosphanes (Ph_2PF and $n\text{-}Bu_2PF$) showed that the reaction will occur between the aldehyde and the monomeric fluorophosphane. Treating $n\text{-}Bu_2P\text{-}PF_2(n\text{-}Bu)_2$ with aldehydes does not yield phosphinito phosphoranes and the crossing experiment yielded $n\text{-}Bu_2PF_2\text{-}CHR'\text{-}OPPh_2$ as main product and only small amounts of $n\text{-}Bu_2PF_2\text{-}CHR'\text{-}OP(n\text{-}Bu)_2$ (molar ratio 4 : 1).

Phosphinito phosphoranes are thermically fairly stable. Michaelis-Arbusov rearrangement into $R_2PF_2\text{-}CHR'\text{-}P(O)R_2$ has only been observed in the cases of R' = thiophene and PhCH=CH. The phosphinito phosphorus atom can easily be oxidized by sulfur and by covalent azides yielding thio or imido derivatives, resp., $R_2PF_2\text{-}CHR'\text{-}OP(X)R_2$ (X = S, NR"). Attempts to modify the phosphorus(V) part of the phosphinito phosphoranes by replacement reactions or elimination of HF failed. Always cleavage of the PCOP-bridge was observed.

In comparison with saturated aldehydes the reaction of fluoro(diorganyl)phosphanes with α,β-unsaturated aldehydes, R'CH=CH-CHO (R' = Ph, H), is more rapid. However, in competition with reaction (5) 1.4-cycloaddition is observed.

R_2PF + $R'\text{-}CH{=}CH\text{-}CHO \longrightarrow$



(6)

(R = n-Bu, Ph; R' = Ph, H)

The extent of this competitive reaction depends on the electronic nature of the reactants. By using acrolein or $n\text{-}Bu_2PF$ oxaphospholenes are already the main products.

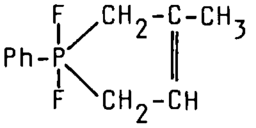
R_2PF don't react with carbonyl compounds possessing a less carbonyl activity than aldehydes. Even strongly activated ketones don't undergo a reaction with fluorophosphanes. 1.2-diketones, however, react by 1.4-cycloaddition forming dioxaphospholenes.

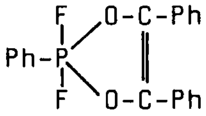
Carboxylic acid chlorides react with R_2PF under Cl/F-exchange. In the case of strong nucleophilic phosphanes, however, this exchange reaction is followed by an addition of the primarily formed carboxylic acid fluoride to the phosphane (eq. 7) yielding acyldifluorophosphoranes.

$$R_2PF + R'\text{-}C(O)F \longrightarrow R_2F_2P\text{-}C(O)R' \qquad (7)$$

$(R' = Ph, Me;\ R = Ph, n\text{-}Bu)$

The less nucleophilic difluoro(organyl)phosphanes, RPF_2, don't undergo similar reactions with aldehydes and other carbonyl compounds. $PhPF_2$ only reacts with benzil and isoprene forming cycloaddition products:





Both types of fluoro(organyl)phosphanes undergo the Staudinger reaction with aryl azides.[3] Fluoro-λ^5-monophosphazenes or fluorodiazadiphosphetidines are formed (eq. 8).

$$R_{3-n}PF_n + N_3Y \xrightarrow[-N_2]{} R_{3-n}PF_n{=}NY \rightleftharpoons 1/2\ [R_{3-n}PF\text{-}NY]_2 \qquad (8)$$

Whereas difluoro(organyl)phosphanes preferably form diazadiphosphetidines, fluoro(diorganyl)phosphanes only form monophosphazenes. In solution the diazadiphosphetidines dissociate into the monomeric phosphazenes.

REFERENCES

1. L. Riesel, J. Haenel, and G. Ohms, J. Fluorine Chem., 38, 335 (1988).
2. J. Haenel, B. Ziemer, L. Riesel, P. Leibnitz, and G. Ohms, Z. anorg. allg. Chem., 563, 173 (1988).
3. L. Riesel, D. Sturm, A. Nagel, S. Taudien, A. Beuster, and A. Karwatzki, Z. anorg. allg. Chem., 542, 157 (1986).