Phospha-alkenes as Intermediates in Polymer Synthesis

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THE aqueous hydrolysis of a compound that contains the group >CF·PH– leads to products which can best be explained by the formation of a phospha-alkene, $>C=P-$ or $>\overset{-}{C}\cdot\overset{+}{P}-$, as a reaction intermediate.[1] Further investigation has now shown that the phospha-alkene can be trapped by reaction with nucleophiles, such as alcohols or amines, without C–P fission. Thus, reaction between methanolic sodium methoxide and

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[1] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J.*, **1964**, **572**.

bistrifluoromethylphosphine gives methyl difluoromethyltrifluoromethylphosphinite (35% yield):

$$(CF_3)_2PH \xrightarrow{MeO^-,\ <0^\circ} (CF_3)_2P^- \xrightarrow{-F^-} CF_3{\cdot}P:CF_2 \xrightarrow{MeOH} CF_3{\cdot}P(OMe){\cdot}CHF_2$$

The p.m.r. spectrum of the last compound shows a doublet (τ6·08, $J_{CH_3{\cdot}P}$ = 13·8 c./sec.) and a triplet of doublets (τ3·72, J_{HF} = 50·4 c./sec. and $J_{H{\cdot}P}$ = 7·4 c./sec.) with an area ratio of 3 : 1, respectively, confirming the presence of the group $CHF_2{\cdot}P{\cdot}OCH_3$ in the compound.

At higher temperature (20—40°) the difluoromethyltrifluoromethylphosphinite reacts further, but relatively slowly:

$$CF_3{\cdot}P(OMe){\cdot}CHF_2 \xrightarrow{MeO^-,\ MeOH} CHF_3\ (100\%) + CHF_2{\cdot}P(OMe)_2$$

Treatment of bistrifluoromethylphosphine with ammonia similarly rapidly yields difluoromethyltrifluoromethylphosphinamide (64% yield):

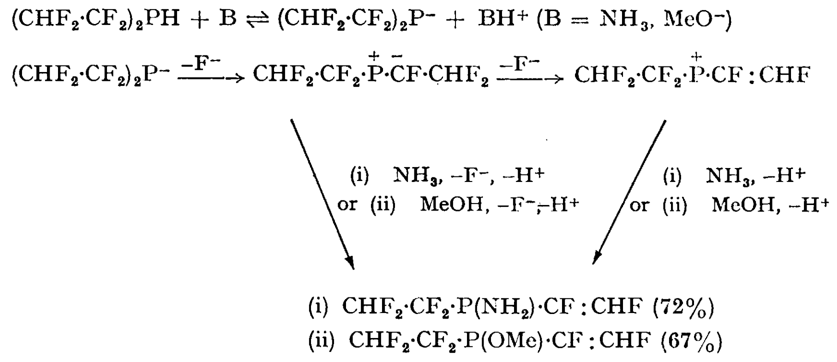
$$(CH_3)_2PH + NH_3 \longrightarrow NH_4F + CF_3{\cdot}P:CF_2 \xrightarrow{NH_3} CF_3{\cdot}P(NH_2){\cdot}CHF_2$$

The phosphinamide shows a C–H stretching frequency at 2960 cm.$^{-1}$, and the ready reaction with dry hydrogen chloride:

$$CF_3{\cdot}P(NH_2){\cdot}CHF_2 + 2HCl \longrightarrow CF_3{\cdot}PCl{\cdot}CHF_2\ (78\%) + NH_4Cl$$

shows the presence of a P–N bond and eliminates the possibility of the alternative formula $CF_3{\cdot}PH{\cdot}CF_2{\cdot}NH_2$.

Reaction of bis-(1,1,2,2-tetrafluoroethyl)phosphine with ammonia or with methanolic methoxide leads to the following products:



$$(CHF_2{\cdot}CF_2)_2PH + B \rightleftharpoons (CHF_2{\cdot}CF_2)_2P^- + BH^+\ (B = NH_3,\ MeO^-)$$

$$(CHF_2{\cdot}CF_2)_2P^- \xrightarrow{-F^-} CHF_2{\cdot}CF_2{\cdot}\overset{+}{P}{\cdot}\overset{-}{C}F{\cdot}CHF_2 \xrightarrow{-F^-} CHF_2{\cdot}CF_2{\cdot}\overset{+}{P}{\cdot}CF:CHF$$

(i) $CHF_2{\cdot}CF_2{\cdot}P(NH_2){\cdot}CF:CHF$ (72%)

(ii) $CHF_2{\cdot}CF_2{\cdot}P(OMe){\cdot}CF:CHF$ (67%)

It will be noted that only one of the tetrafluoroethyl groups becomes vinylic, and this is consistent with the phospha-alkene mechanism advanced for the aqueous alkaline hydrolysis of bis-(1,1,2,2-tetrafluoroethyl)phosphine to give 1,2-difluoroethylene (50%) and 1,1,2,2-tetrafluoroethane (50%).[1] An equimolar mixture of the last two compounds is formed on hydrolysis of the compounds $CHF_2{\cdot}CF_2{\cdot}PX{\cdot}CF:CHF$ (X = NH_2 or OMe).

Use of primary αα-dihalogeno-phosphines leads to novel polymers considered to arise *via* phospha-alkene formation. Thus, 1,1,2,2-tetrafluoroethylphosphine reacts rapidly with liquid ammonia at −78° to give a solid polymer containing a P–N network and of empirical formula $C_6H_9F_6N_2P_3$; the polymer has good thermal stability (400°), and is unattacked by aqueous alkali or by non-oxidising acids. The empirical formula suggests a polymer $[(CHF_2{\cdot}CH_2{\cdot}P)_3N_2]_n$ containing linear or cyclic units or both, in which it will be seen that both fluorines α to phosphorus have been replaced by hydrogen; other evidence[2] is consistent with the presence of the $CHF_2{\cdot}CH_2$ group. The

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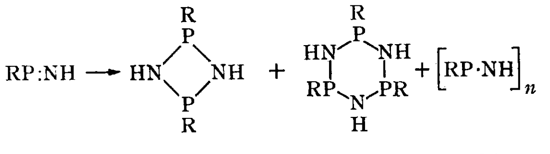
[2] M. Green, R. N. Haszeldine, and B. R. Iles, unpublished results.

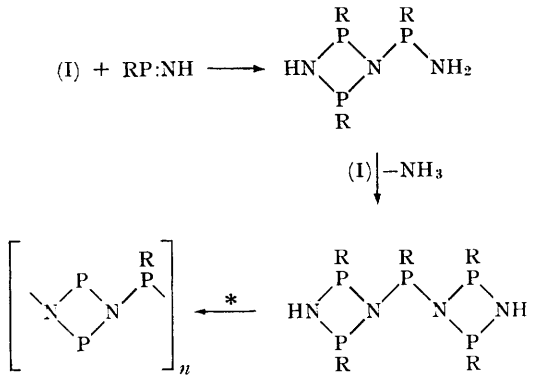
following scheme, in which it should be noted that the phospha-alkene becomes converted first into a –P : N– intermediate, is suggested:

$$\begin{tikzcd}[column sep=large]
\mathrm{CHF_2{\cdot}CF_2{\cdot}PH_2} \arrow[r, "\mathrm{NH_3}"] & \mathrm{CHF_2{\cdot}CF:PH} \arrow[r, "\mathrm{NH_3}"] & \mathrm{CHF_2{\cdot}CHF{\cdot}PH{\cdot}NH_2} \\
\mathrm{CHF_2{\cdot}CHF{\cdot}PH{\cdot}NH_2} \arrow[r, "\mathrm{NH_3}"] & \mathrm{CHF_2{\cdot}CH:P{\cdot}NH_2} \arrow[r, "\mathrm{NH_3}"] \arrow[dr, "\text{H shift}"] & \mathrm{CHF_2{\cdot}CH_2{\cdot}P(NH_2)_2} \arrow[d, "-\mathrm{NH_3}"] \\
 & & \mathrm{CHF_2{\cdot}CH_2{\cdot}P:NH}
\end{tikzcd}$$

then, where $R = CHF_2{\cdot}CH_2$,



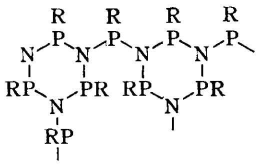
(I) (II) (III)



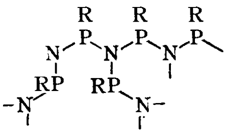
(IV)

* RP:NH; (I); –NH$_3$

Reaction of RP : NH with each of the NH groups in (II) or (III) affords lattice or cross-linked structures (V) or (VI):



(V)



(VI)

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