Russian Chemical Reviews

January 1982

Translated from *Uspekhi Khimii*, 51 3-22 (1982)

U.D.C. 547.221 : 547.241

Fluorine-containing Phosphorus Ylids

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The methods of preparation and properties of phosphorus ylids containing fluorine atoms in the "alkylidene" component are considered with the exception of halogenomethylenephosphoranes and ylids which contain fluorine atoms only at an appreciable distance from the carbanionic centre.
The bibliography includes 87 references.

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I. INTRODUCTION

A review dealing with fluorine-containing halogenomethylenephosphoranes was published previously[1]. In contrast to these, other fluorine-containing phosphorus ylids are characterised by a wide variety of properties, are frequently entirely stable, and can be isolated and characterised. However, in certain instances, for example, when triphenylphosphine interacts with perfluoroisobutene, the intermediate formation of fluorine-containing phosphorus ylids is only postulated.

The Wittig reaction ("carbonyl-olefination"), which represents the main synthetic application of phosphorus ylids[2-7], has been less thoroughly investigated in relation to fluorine-containing phosphorus ylids. At the same time the chemistry of these compounds involves many interesting reactions, which are frequently unusual.

This review describes the methods of preparation and properties of phosphorus ylids containing fluorine atoms in the "alkylidine" component†. Fluorine-containing halogenomethylenephosphoranes have been excluded from consideration[1]. Phosphorus ylids containing fluorine atoms only at a considerable remove from the carbanionic centre, for example, $Ph_3P{=}CHC_6H_4CF_3$ [8] or $Ph_3P{=}CH(CH_2)_3CF_3$,[9] have also been disregarded, because in this case the influence of these atoms on the properties of the ylids is insignificant.

† The AIPS-FTOR (VINITI) automated information-seeking system was used in selecting the literature.

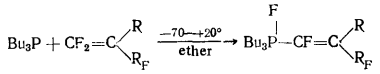
II. PREPARATION

The commonest methods of synthesising fluorine-containing phosphorus ylids are based on the reactions of tertiary phosphines with various fluorine-containing compounds—fluoro-olefins, fluoroalkyl halides, fluorothioketones, etc. Furthermore, it is possible to make use of methods involving the introduction of fluorine-containing groups into non-fluorinated phosphorus ylids.

1. Interaction of Tertiary Phosphines with Fluoro-olefins

The ability of fluoro-olefins to react with nucleophilic tertiary phosphines is due to the electrophilic properties of the former[10]#. The result then depends on the structure of the initial compounds and sometimes on the reaction conditions.

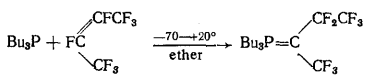
Substituted vinylfluorophosphoranes (I) have been obtained by the reaction of perfluoropropene and other terminal fluoro-olefins with tributylphosphine under mild conditions[11,12]§:



(I)

R	F	F	F	Ph	Ph
R_F	CF_3	n-C_3F_7	n-C_5F_{11}	CF_3	C_2F_5

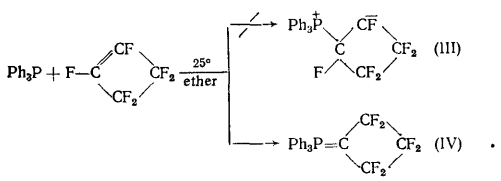
On treatment with tributylphosphine, perfluorobut-2-ene readily gives rise to the fluorine-containing phosphorus ylid (II):[11]



(II)

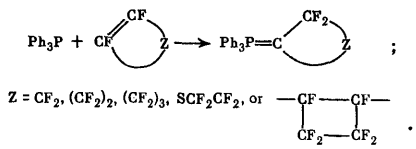
The structure of the ylid was demonstrated by NMR.

An anomalous reaction takes place when perfluorocyclobutene reacts with triphenylphosphine. Initially the betaine structure (III) was attributed to the reaction product[14], but later it was shown by X-ray diffraction[15] that perfluorocyclobutylidenetriphenylphosphorane (IV) is in fact formed¶:



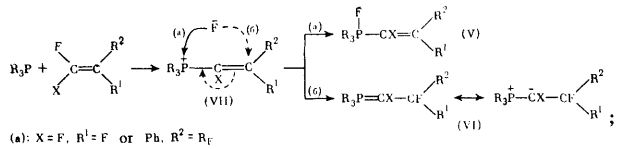
(III) (IV)

Other perfluorocycloalkylidenetriphenylphosphoranes have also been obtained by a similar procedure[16,19]:



Perfluorocyclohexene does not react with triphenylphosphine[16].

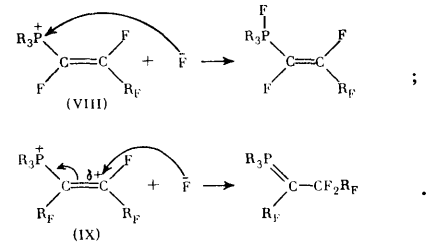
Thus, depending on the structure of the fluoro-olefin, either an alkenylfluorophosphorane (V) or a phosphorus ylid (VI) is formed on treatment with a tertiary phosphine. Evidently, the initial product must be an alkenylphosphonium fluoride (VII) in all cases. From the examples investigated (still very few), it has been suggested[11] that alkenylfluorophosphoranes are obtained only under conditions where the intermediate phosphonium cation contains a fluorine atom in the α-position†, while phosphorus ylids are produced when there is no α-fluorine atom:



(a): X = F, R^1 = F or Ph, R^2 = R_F

(b): X = CF_3, R^1 = F, R^2 = CF_3; XR^1 = $(CF_2)_2$, R^2 = F.

Probably in the latter case the crucial factor is not only the absence of a fluorine atom, but also the presence of the perfluoroalkyl group in the α-position. Perfluoroalkyl groups linked to the carbanionic centre impart stability to the phosphorus ylids (VI) (cf. Chambers[21]), while α-fluorine atoms destabilise the carbon ion (the Hine effect[22]). Another approach to the explanation of the results, associated with the consideration of the competitive influence of substituents on the polarisation of the C=C bond in the alkenylphosphonium cation, is also possible. In the cation (VIII) the partial positive charge on the β-carbon atom is insufficient to allow the attack on the latter by the F^- ion; therefore the positively charged phosphorus atom is attacked. In the cation (IX) the electron-accepting ability of both the perfluoroalkyl and the phosphonium group leads to an appreciable electrophilicity of the β-carbon atom, which promotes the formation of the phosphorus ylid:



(VIII) (IX)

It must be emphasised that the results obtained in the reaction of perfluorocyclobutene with trialkyl phosphite are apparently inconsistent with the proposed schemes. Under

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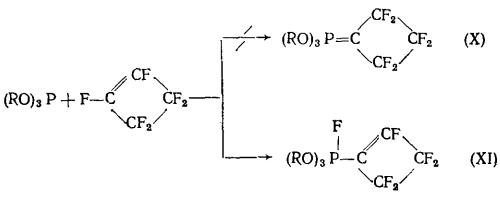
See Johnson[3] about the synthesis of phosphorus ylids by the interaction of tertiary phosphines with α,β-unsaturated carbonyl compounds.

§ The hydrolysis of these phosphoranes leads to α-hydroperfluoro-olefins[12]; thus a convenient method has been found for replacing the "vinyl" fluorine atom by a hydrogen atom. When perfluorobutadiene is treated with tertiary phosphines, relatively unstable cyclic phosphoranes are produced[13].

¶ Analogous ammonium[16-18] and arsonium[16] ylids have also been obtained. When perfluorocyclobutene reacts with tris-(dimethylamino)phosphine, only the products of the substitution of the fluorine atom by the dimethylamino-group are formed[16].

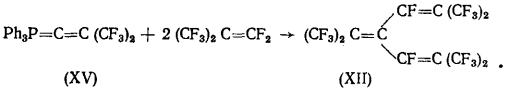
† There is evidence[20] that the phosphorus ylid $Ph_3P=CFCF_2CF_3$ rapidly isomerises to the fluorophosphorane $Ph_3PFCF=CFCF_3$.

these conditions, the product is the substituted vinylfluorophosphorane (XI) and not the phosphorus ylid (X):[23,24]#



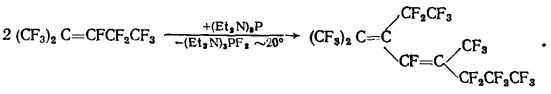
A particularly electrophilic fluoro-olefin—perfluoroisobutene—reacts with tertiary phosphines in an unusual manner. The reaction with triphenylphosphine[25] or with tributylphosphine[26] in acetonitrile§ led to the formation of a cross-conjugated perfluorotriene (XII). The diene (XIII) is formed together with this compound[26]. It has been suggested[25] that the reaction proceeds via a mechanism involving the intermediate formation of perfluoroisobutenylfluorophosphorane (XIV) and its defluorination product—the fluorine-containing cumulene ylid (XV). The addition of a second perfluoroisobutene molecule to the ylid (XV) led to the dienylfluorophosphorane (XVI), which split off triphenylphosphine and gave rise to the diene (XIII). On the other hand, the defluorination of the phosphorane (XVI) and subsequent addition of a third perfluoroisobutene molecule resulted in the formation of the trienylfluorophosphorane (XVII); the perfluorotriene (XII) was produced as a result of the elimination of triphenylphosphine.

The proposed mechanism of the defluorodimerisation and defluorotrimerisation of perfluoroisobutene has found some confirmation by the fact that the reaction of the known ylid (XV) with perfluoroisobutene also yielded the triene (XII):[26]

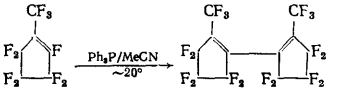


In contrast to perfluoroisobutene, perfluoropropene[25] and the ester of perfluoromethacrylic acid[28] merely dimerise on treatment with triphenylphosphine; analogous reactions on treatment with other bases had been described earlier[27,29,30]¶.

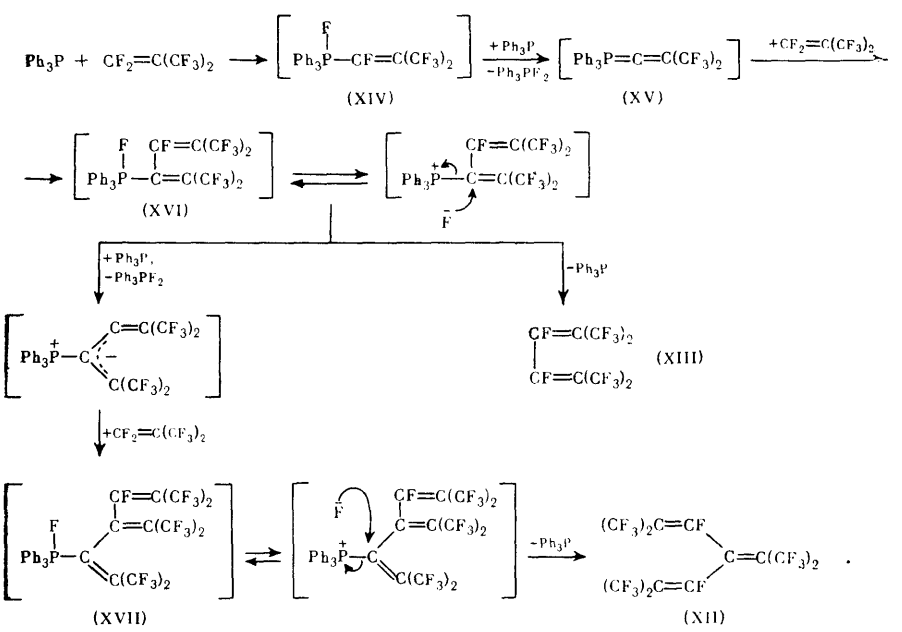
Perfluoropropene reacts vigorously with tris(dimethylamino)phosphine (the relevant paper gives no information about the products)[11]. The perfluoropropene dimer—perfluoro-2-methylpent-2-ene—undergoes defluorodimerisation on treatment with tris(diethylamino)phosphine[32]:



Perfluoro-1-methylcyclopentene reacts similarly with triphenylphosphine[32]:



Scheme



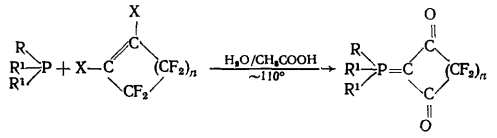
The decomposition of the adduct (XI) on heating leads to products of the substitution of the β-fluorine atom by an alkoxy-group[24] in addition to the products of the Arbuzov rearrangement[23].

§ The reaction in ether yielded the phosphoranes $(CF_3)_2C{=}CFPF_2Bu_2$ and $(CF_3)_2C{=}CBuPF_2Bu_2$, probably via the intermediate formation of the phosphorane $(CF_3)_2C{=}CFPFBu_3$.[26] When perfluoroisobutene was treated with trialkyl phosphites, the stable phosphoranes $(RO)_3PFCF{=}C(CF_3)_2$ were obtained; on heating they give rise to products of the Arbuzov rearrangement[23,27].

¶ Trialkyl phosphites react with perfluoropropene to give the products of the Arbuzov rearrangement[31], while the reactions with perfluoromethacrylic acid esters give rise to the fluorophosphoranes $(RO)_3PFCF{=}C(CF_3)COOR^1$, which decompose on heating into $ROPF_2$ and $(RO)_2C{=}C(CF_3)COOR^1$.[27]

The mechanism of these reactions is probably analogous to that of the conversion of perfluorisobutene into the diene (XIII).

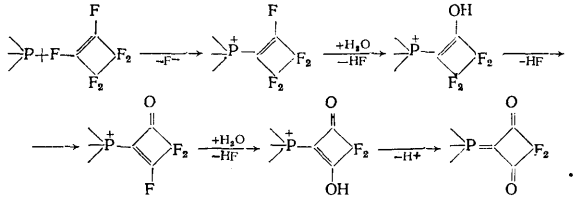
On treatment with tertiary phosphines in the presence of acetic acid and water, the cyclic diketo-ylids (XVIII) are formed from 1,2-dichloroperfluorocycloalkenes or perfluorocycloalkenes (C_4 and C_5):[14,33,34]



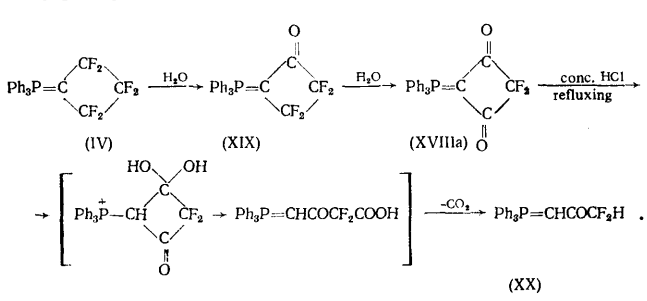
n	1	1	2	2	2	2
R	Ph	Ph	Ph	Ph	Bu	Bu
R^1	Ph	Ph	Ph	Ph	Ph	Bu
X	Cl	F	Cl	F	Cl	Cl

(XVIII): a—R=R^1=Ph, n=1; b—R=R^1=Ph, n=2; c—R=R^1=n-Bu, n=2; d—R=n-Bu, R^1=Ph, n=2.

A mechanism involving vinyl substitution on treatment with phosphine followed by the hydrolysis of the fluorine atoms has been proposed for this reaction[14], for example:



The hydrolysis of perfluorocyclobutylidenetriphenylphosphorane (IV) leads to the monoketo-ylid (XIX) [16] or the diketo-ylid (XVIIIa).[14,15]. Under more severe conditions, the diketo-ylid decomposes, forming difluoroacetylmethylenetriphenylphosphorane (XX):[34]

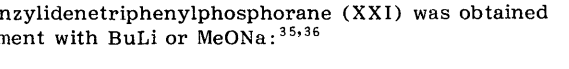


(IV) (XIX) (XVIIIa) (XX)

On refluxing with a tertiary phosphine in aqueous acetic acid solution, perhalogenocyclohexenes do not give rise to the corresponding diketo-ylids[14]. Triphenylphosphine oxide and 2-chloro-1-hydroperfluorocyclohexene are formed from 1,2-dichloroperfluorocyclohexene and Ph_3P under these conditions[34].

2. Interaction of Tertiary Phosphines with Other Organofluorine Compounds

Certain fluorine-containing phosphorus ylids can be obtained by the method most widely used for the synthesis of phosphorus ylids in general—by the dehydrohalogenation of phosphonium salts (the "salt method").[3] Thus alkylation of triphenylphosphine with pentafluorobenzyl bromide led to the corresponding phosphonium salt, from which pentafluorobenzylidenetriphenylphosphorane (XXI) was obtained on treatment with BuLi or MeONa:[35,36]



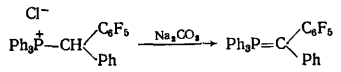
(XXI)

Triphenylphosphine was used as the dehydrobrominating agent in the reaction with α-bromopentafluoroacetophenone[37]:



(XXII); m.p. 134—137°.

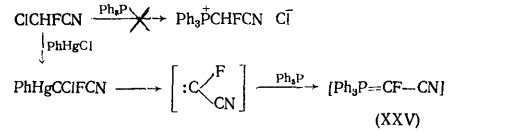
Pentafluorodiphenylmethyltriphenylphosponium chloride (XXIII) is converted into pentafluorodiphenylmethylenetriphenylphosphorane (XXIV) even on treatment with sodium carbonate[38]:



(XXIII) (XXIV); m.p. 206—209°.

According to patent data[39-42], the ylid $Ph_3P{=}CH(CH_2)_2CF_2$. .COOH has been obtained by treating the corresponding phosphonium salt with sodium hydride.

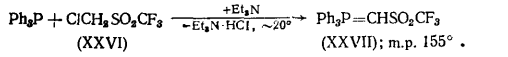
The "salt" method is frequently unsuitable for the synthesis of fluorine-containing phosphorus ylids. Thus, in contrast to pentafluorobenzyl bromide, decafluorodiphenylmethyl bromide[43] and the compounds $(CF_3)_2CHX$ [20,44] are incapable of alkylating triphenylphosphine. 2,2,2-Trifluoroethyl iodide reacts slowly with Ph_3P on irradiation, but trifluoroethyl idenetriphenylphosphorane $Ph_3P{=}CHCF_3$ cannot be obtained from the phosphonium salt formed[45]. The ester of chlorofluoroacetic acid[46] and its nitrile[47] also failed to give rise to quaternary salts on reaction with triphenylphosphine. However, the corresponding phosphorus ylid (XXV) can be obtained from the nitrile by a different method—via chlorocyanofluoromethyl(phenyl)mercury:[47,48]



(XXV)

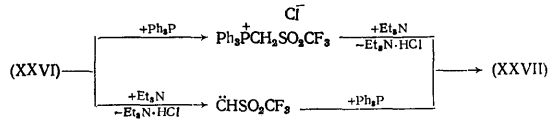
A carbene (cyanofluoromethylene) may be formed as an intermediate in this process†.

The stable trifluoromethanesulphonylmethylenetriphenylphosphorane (XXVII) has been obtained from chloromethyl trifluoromethyl sulphone (XXVI) and triphenylphosphine in the presence of triethylamine[50]:



(XXVI) (XXVII); m.p. 155°.

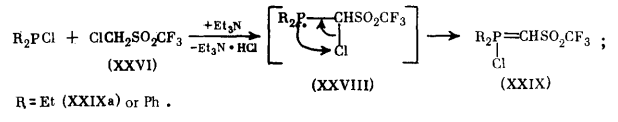
A phosphonium salt is probably formed initially and is then dehydrohalogenated by triethylamine, although the "carbene" mechanism is not ruled out:



Another mechanism has been proposed for the reaction of the sulphone (XXVI) with the chlorides of diphenyl- and diethyl-phosphinous acids. It has been suggested that this involves the initial substitution of the chlorine atom attached to the phosphorus atom with formation of tertiary phosphines (XXVIII), which rearrange to the more stable *P*-chlorosubstituted phosphorus ylids (XXIX),[50] probably as a result of

† The phosphorus ylid $(CF_3)_3F{=}CFCHF_2$ is formed when tris(trifluoromethyl)phosphine interacts with trifluoroethylidene generated from the silane $HCF_2CF_2SiF_3$ or from difluoromethylperfluorocyclopropane[49].

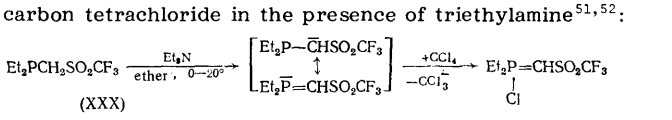
the nucleophilic attack by the phosphorus atom on the halogen, which has been rendered positive:



(XXVI) (XXVIII) (XXIX)

R = Et (XXIXa) or Ph.

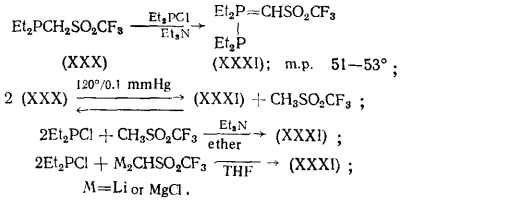
The ylid (XXIXa) has also been obtained by the reaction of trifluoromethanesulphonylmethyldiethylphosphine (XXX) with carbon tetrachloride in the presence of triethylamine[51,52]:



(XXX)

The chlorine atom in the phosphorus ylids (XXIX) is readily substituted by the diethylamino-group on treatment with Et_2NH.[50,51,53]

Sulphonylmethylphosphine (XXX) reacts with chlorodiethylphosphine in the presence of triethylamine to form an unusual phosphorus ylid (XXXI) containing the P–P bond[51,53]. The same phosphinophosphorus ylid is formed on heating sulphonylmethylphosphine in the absence of other reactants[51] and also from chlorodiethylphosphine and methyl trifluoromethyl sulphone[53]:



(XXX) (XXXI); m.p. 51–53°;

2 (XXX) ⇄ (XXXI) + $CH_3SO_2CF_3$;

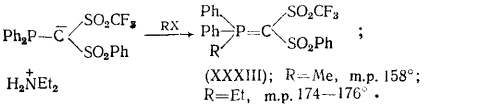
$2Et_2PCl + CH_3SO_2CF_3 \xrightarrow{Et_3N,\ ether}$ (XXXI);

$2Et_2PCl + M_2CHSO_2CF_3 \xrightarrow{THF}$ (XXXI);

M = Li or MgCl.

The structure of the *P*-substituted ylids (XXIX) and (XXXI) as well as related compounds has been confirmed by spectroscopic data. Thus the infrared spectra exhibit a characteristic bathochromic shift of the SO_2 absorption frequencies under the influence of the electron-donating "ylid" carbon atom[50,51]. The non-equivalence of the two dialkylphosphinyl groups is clearly manifested in the ^1H and ^{31}P NMR spectra of ylids of type (XXXI).[51]

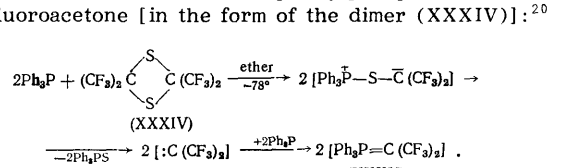
The salts of phosphinodisulphone (XXXII) are alkylated with transfer of the reaction centre and the formation of the phosphorus ylids (XXXIII):



(XXXII) (XXXIII); R = Me, m.p. 158°; R = Et, m.p. 174–176°.

The structure of ylids of type (XXXIII) has been inferred from their infrared spectra[51,54].

A promising method of synthesising fluorine-containing ylids apparently involves the interaction of tertiary phosphines with fluorine-containing thioketones#. Thus the unstable hexafluoroisopropylidenetriphenylphosphorane (XXXV) has been obtained from triphenylphosphine and thiohexafluoroacetone [in the form of the dimer (XXXIV)][20]:

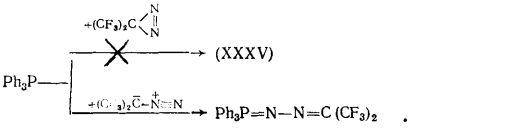


(XXXIV) (XXXV)

The reaction mechanism has not been demonstrated. It may be that bis(trifluoromethyl)carbene is formed as an intermediate.

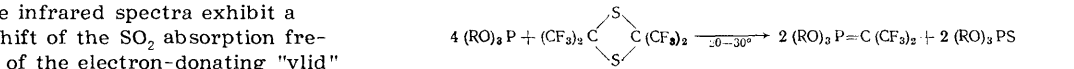
The phosphorus ylid (XXXV) has been used successfully *in situ* in the Wittig reaction (see below). The use of tributylphosphine or tris(dimethylamino)phosphine instead of triphenylphosphine in an analogous reaction leads to a decrease of the yield of olefins[20]. In an earlier study[60] of the interaction of the dimer (XXXIV) with tributylphosphine only Bu_3PF_2 was isolated.

It was not possible to obtain the ylid (XXXV) from triphenylphosphine and other sources of bis(trifluoromethyl)carbene. Triphenylphosphine does not react with bis(trifluoromethyl)diazirine even under severe conditions[61], while the reaction with bis(trifluoromethyl)diazomethane yields the iminophosphorane (XXXVI):[62]



(XXXVI)

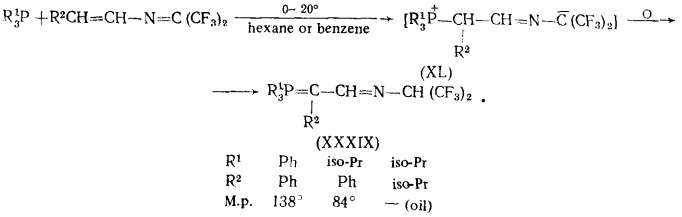
The stable hexafluoroisopropylidenetrialkoxyphosphoranes have been obtained from the dimer (XXXIV) and trialkyl phosphites (XXXVII):[60,63]



(XXXIV) (XXXVII)

R	Me (a)	Et	iso-Pr	n-$C_{12}H_{25}$
b.p.	61–62°/0.35 mmHg	74–75°/0.25 mmHg	75–76°/0.05 mmHg	– (decomp.)

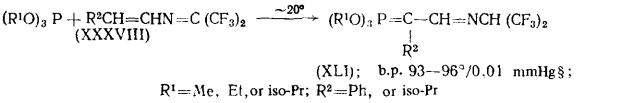
The interaction of tertiary phosphines with hexafluoroacetone *N*-alkenylimines (XXXVIII) led to the formation of substituted phosphorus ylids (XXXIX), probably as a consequence of the prototropic rearrangement of the intermediate betaines (XL):[64,65]



(XL) (XXXIX)

R^1	Ph	iso-Pr	iso-Pr
R^2	Ph	Ph	iso-Pr
M.p.	138°	84°	– (oil)

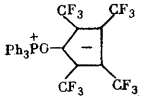
When trialkyl phosphites are used instead of phosphines, the relatively unstable ylids (XLI) are formed and readily rearrange (see below):[64,65]



(XXXVIII) (XLI); b.p. 93–96°/0.01 mmHg§;

R^1 = Me, Et, or iso-Pr; R^2 = Ph, or iso-Pr

The interaction of tertiary phosphines with perfluoroketones and perfluoroaldehydes has been described[55–58]. The betaine



has been obtained from perfluorotetramethylcyclopentadienone and triphenylphosphine[59].

§ The boiling point of compound (XLI) with $R^1 = R^2$ = iso-Pr is indicated.

3. Interaction of Phosphorus Ylids with Fluorine-containing Compounds

Phosphorus ylids are very readily acylated[3], such reactions including also those occurring on treatment with derivatives of fluorine-containing carboxylic acids. Thus the stable trifluoroacetylmethylenetriphenylphosphorane (XLII) has been obtained from methylenetriphenylphosphorane and ethyl trifluoroacetate[66]. When the initial ylid is generated with the aid of butyl-lithium, butyldiphenylphosphorane (XLIII) is formed in addition to triphenylphosphorane (XLII); it has been shown that the phenyl group in the ylid (XLII) is substituted by the butyl group on treatment with n-BuLi:[66]

$$Ph_3P{=}CH_2 \xrightarrow[-70\to+25^\circ]{CF_3COOEt} \underset{\text{(XLII) m.p. 233°}}{Ph_3P{=}CHCOCF_3} \xrightarrow[25^\circ]{n\text{-BuLi}} \underset{\text{n-Bu}}{Ph_2P{=}CHCOCF_3}$$
(XLIII); m.p. 138°.

The chlorides of perfluorocarboxylic acids can acylate also inactive phosphorus ylids. Thus perfluoroacylphosphorus ylids have been obtained from methoxycarbonylmethylenetriphenylphosphorane and the chloride of trifluoroacetic or perfluorobutyric acid (XLIV):[67]

$$Ph_3P{=}CHCOOMe \xrightarrow{R_FCOCl} \underset{\text{(XLIV)}}{Ph_3P{=}C(COR_F)COOMe};$$
$R_F = CF_3$, or $n\text{-}C_3F_7$.

Cyanomethylene- and ethoxycarbonylmethylene-triphenylphosphoranes react with the dichloride of perfluoroglutaric acid to give stable bisylids (XLV):[45]¶

$$4Ph_3P{=}CHR + ClCO(CF_2)_3COCl \xrightarrow[\text{benzene}]{25^\circ} \underset{\text{(XLV)}}{\rightarrow Ph_3P{=}CRCO(CF_2)_3COCR{=}PPh_3} + 2Ph_3\overset{+}{P}CH_2R\ Cl^-;$$
m.p. 248–260° (R=CN), 194–195° (R=COOEt).

The initial phosphorus ylid is taken in excess in order to bind the HCl evolved.

The acylation of benzylidene- and pentafluorobenzylidene-triphenylphosphoranes by pentafluorobenzoyl chloride led to stable fluorine-containing phosphorus ylids (XLVI)[35]:

$$Ph_3P{=}CHR + C_6F_5COCl \xrightarrow[\text{benzene}]{15^\circ} \underset{\text{(XLVI)}}{Ph_3P{=}CRCOC_6F_5};$$
m.p. 244–247° (R=Ph), 245–246° ($R=C_6F_5$).

Active phosphorus ylids are capable of reacting with hexafluorobenzene[38] and with 2-phenylperfluoropropene[68] to form pentafluorophenylylids [(XXI) or (XXIV)] and the phenylperfluoropropenylylid (XLVII):

$$Ph_3P{=}CHR + C_6F_6 \xrightarrow[\text{ether}]{\sim 20^\circ} [Ph_3\overset{+}{P}CHRC_6F_5\ \bar{F}] \xrightarrow[-Ph_3\overset{+}{P}CH_2R\ \bar{F}]{+Ph_3P{=}CHR} Ph_3P{=}CRC_6F_5;$$
R=H (XXI), or Ph (XXIV);

$$2Ph_3P{=}CHMe + CF_2{=}CPhCF_3 \xrightarrow{\sim 20^\circ} \left[Ph_3P{=}C(Me){-}CF{=}C(Ph)CF_3\right] + Ph_3\overset{+}{P}CH_2Me\ \bar{F}.$$
(XLVII)

Under the reaction conditions, the ylid (XLVII) splits off an F^- anion and is converted into the allenylphosphonium salt (XLVIII), whose hydrolysis gives rise to the allene (XLIX) as well as its isomerisation [compound (L)] and dehydrofluorination [compound (LI)] products[68]:

$$(XLVII) \rightarrow \left[Ph_3\overset{+}{P}{-}C(Me){=}C{=}C(Ph)CF_3\ F^-\right] \xrightarrow{H_2O} \underset{\text{(XLVIII)}}{} MeCH{=}C{=}C(Ph)CF_3 \ (XLIX) +$$
$$+ MeC{\equiv}C{-}CH(Ph){-}CF_3 + MeC{\equiv}C{-}C(Ph){=}CF_2.$$
(L) (LI)

The chemistry of cumulene phosphorus ylids has appreciably developed recently[5]. In particular, hexaphenylcarbodiphosphorane (LII) and the "ylidoketen" (LIII) are of interest.

The ylid (LII) reacts with hexafluoroacetone to form the extremely stable "ylido-oxaphosphetan" (LIV);[69–73] an analogous result was obtained using dodecafluorotetramethylethylenedioxytriphenylphosphorane (LV) instead of hexafluoroacetone[72]:

$$Ph_3P{=}C{=}PPh_3 + (CF_3)_2CO \xrightarrow[\text{diglyme}]{40\text{–}50^\circ} \underset{\text{(LII)}}{} \xrightarrow{} Ph_3P{=}C(CF_3)_2{-}O{-}PPh_3$$
(LII) + Ph_3P (LV) $\xrightarrow[\text{diglyme}]{65\text{–}75^\circ}$
(LIV), m.p. 157–158°

Thus a stable cyclic adduct of a phosphorus ylid with a ketone—the intermediate of the Wittig reaction—was in this instance isolated and characterised for the first time. The structure of the adduct (LIV) was demonstrated by X-ray diffraction[74]. Its stability can be accounted for by the strengthening of the C–O bond by the influence of the trifluoromethyl groups and the high electron density at the carbon atom linked to the phosphorus atom, which apparently prevents the dissociation of the C–P bond[72].

However, when the adduct (LIV) is heated above 110 °C, the second stage of the Wittig reaction nevertheless takes place—the adduct splits into the phosphine oxide and hexafluoroisobutenylidenetriphenylphosphorane (XV):[69–73]

$$(LIV) \xrightarrow[5\text{–}10\ min]{120\text{–}125^\circ} Ph_3P{=}C{=}C(CF_3)_2 + Ph_3PO.$$

The cumulene ylid (XV) cannot be fully separated from triphenylphosphine oxide.

When the adduct (LIV) reacts with various acids, phosphonium salts are formed and these can also be regarded as substituted phosphorus ylids[70–73] (see Section III, 3 below).

The "ylidoketen" (LIII) reacts with hexafluoroacetone and p-chloro-α,α,α-trifluoroacetophenone to form diketo-ylids (LVI), probably as a result of the cycloaddition of the initial ylid to the alkylideneketen (LVII), formed by the Wittig reaction[75]:

$$Ph_3P{=}C{=}C{=}O + C(CF_3)(R){=}O \xrightarrow{-Ph_3PO} \underset{\text{(LVII)}}{[C(CF_3)(R){=}C{=}C{=}O]} \xrightarrow{+(LIII)}$$
(LIII)

$$\rightarrow Ph_3P{=}C\left(\begin{array}{c}C(=O)\\ \\ C(=O)\end{array}\right)C(CF_3){=}C(R);$$
(LVI)

R=*n*-ClC_6H_4 (m.p. 246–247°), or CF_3.

¶ The ylid $Ph_3P{=}CFCN$ (XXV) cannot be obtained from cyanomethylenetriphenylphosphorane by fluorination with $FClO_3$.[43]

4. The Preparation of Wittig–Horner Reagents

The α-phosphonate carbanions, formed when the esters of alkylphosphinic acids are treated with bases, are analogues of phosphorus ylids:

$$(RO)_2PCHXY \xrightarrow[-BH]{+B^-} (RO)_2\bar{P}-CXY \leftrightarrow (RO)_2P=CXY \ .$$

These carbanions are widely used for the "olefination" of carbonyl compounds (the Wittig–Horner reaction).

The diethyl ester of α-fluoroethoxycarbonylmethylphosphonic acid was obtained by the Arbuzov reaction from the ester of bromofluoroacetic acid and triethyl phosphite and was converted on treatment with sodium or sodium hydride into the stable fluorine-containing anion (LVIII):[76–78]

$$(EtO)_3P + BrCHFCOOEt \xrightarrow[-EtBr]{145^\circ} (EtO)_2PCHFCOOEt$$

$$\xrightarrow[ether,\ \sim 0^\circ]{Na \text{ or } NaH} (EtO)_2\bar{P}CFCOOEt \ .$$

(LVIII)

The phosphonate carbanion obtained was used to synthesise the esters of unsaturated α-fluorine-substituted carboxylic acids (see Section III, 2 below).

The phenyl-substituted phosphonate carbanion (LIX), obtained from the ester of α-hydroxybenzylphosphonic acid, has been used to synthesise α-fluorostilbene (see Section III, 2 below):[79]

$$(EtO)_2PCHPh \xrightarrow{Et_2NCF_2CHFCl} (EtO)_2PCHPh \xrightarrow{-H^+} (EtO)_2\bar{P}CFPh \ .$$

(LIX)

III. PROPERTIES

The properties of fluorine-containing phosphorus ylids depend to a large extent on the nature of the substituents at the phosphorus atom and at the carbanionic centre.

1. Stability. Physical and Physicochemical Properties

The phosphorus ylids containing acyl or sulphonyl groups capable of delocalising the negative charge are distinguished by a special stability[4,7]†. Polyfluoroacyl- and polyfluoroalkanesulphonyl-methylenephosphoranes should be still more stable owing to the electron-withdrawing effect of the polyfluoroalkyl groups. Special studies in this field have not been made. However, there are data indicating a special stability of fluorine-containing phosphorus ylids such as trifluoroacetylmethylenetriphenylphosphorane (XLII),[66] pentafluorobenzoylmethylenetriphenylphosphorane (XXII),[37] and trifluoromethanesulphonylmethylenediethylchlorophosphorane (XXIXa).[51] Pentafluorodiphenylmethylenetriphenylphosphorane (XXIV) is still more stable than its non-fluorinated analogue[38].

† In general the phosphorus ylids $R_3^1P=CR^1R^2$ can be divided into three groups: the reactive ylids (R^1, R^2 = H or alkyl), the "moderate" ylids (R^1 = 1-alkenyl, 1-alkynyl, aryl, or halogeno-group; R^2 = ditto, H, or alkyl), and the stable ylids (R^1 = COR, COOR, CN, or SO_2R; R^2 = any group)[7].

Like the alkoxycarbonyl groups, the trifluoromethyl groups can stabilise carbanions[21]. It was therefore to be expected that ylids of the type $R_3P=C(CF_3)_2$ are extremely stable. However, it was found that hexafluoroisopropylidenetriphenylphosphorane (XXXV) is unstable and can be used in the Wittig reaction *in situ*[20]. It may be that the instability of such compounds can be accounted for by their stability to eliminate fluoride ion from the β-position. Analogous β-elimination in the case of the alkenylylid (XLVII) leads to the allenylphosphonium salt (XLVIII)[68] (see Section II, 3 above). However, ylids such as hexafluoroisopropylidenetrialkoxyphosphoranes (XXXVII)[60] and perfluorocyclobutylidenetriphenylphosphorane (IV)[17] proved to be extremely stable.

The stable fluorine-containing phosphorus ylids isolated are usually high melting crystalline substances. However, under the usual conditions some of them are liquids [for example, $Et_2PCl=CHSO_2CF_3$ (XXXIXa)[50,52] or $(R^1O)_3P=CR^2CH=NCH(CF_3)_2$ (XLI)[64,65]].

Table 1. The chemical shifts in the ^{31}P NMR spectra of fluorine-containing phosphorus ylids.

Ylid	Chemical shift, p.p.m.	References	Ylid	Chemical shift, p.p.m.	References
(II)	−23.7*	[11]	(XVIIIc)	−21.7**	[14]
(IV)	−5.6**	[14]	(XVIIId)	−12.8**	[14]
(XV)	−4.1*	[72]	(LIV)	−7.3 and +54.0*	[71, 72]
(XVIIIa)	−3.0*, −4.1**	[75, 14]	(LVI)	−1.9*	[75]
(XVIIIb)	−10.2**	[14]	(LXII)	−21 ÷ −22*	[72]

*Relative to the external standard—85% H_3PO_4.
**Relative to the internal standard—$(EtO)_3PO$.

The spectra of certain fluorine-containing phosphorus ylids have been investigated: infrared[14,34,45,50–52,54,64–66,75], ^1H NMR,[14,34,51,52,65,66,70–72] ^{19}F NMR,[11,14,17,34,38,50,60,70–73,75] ^{31}P NMR,[11,14,51,65,70–72,75] and mass spectra[75]. The structure of the ylids (IV) and (LIV) was confirmed by X-ray diffraction[15,72,74].

Table 2. The spin–spin coupling constants between ^{19}F and ^{31}P nuclei in fluorine-containing phosphorus ylids.

Ylid	*m**	*J*, Hz	Refs.	Ylid	*m**	*J*, Hz	Refs.
(XV)	4	3.5	[72]	(XXXVIIa)	3	13	[60]
(XVIIIa)	4	20.5	[34]	(LIV)	4	0.8	[72]
(XVIIIb)	4	1.1	[34]	(LVI)**	6	1.1	[75]

*Here *m* is the number of bonds separating the ^{19}F and ^{31}P nuclei.
**R = CF_3.

In the ^{31}P NMR spectra of fluorine-containing phosphorus ylids with three phenyl groups at the phosphorus atom the chemical shift due to the "ylid" phosphorus nucleus is in the range from −2 to −10 p.p.m. (Table 1). The replacement of the phenyl group by the n-butyl group leads to a downfield displacement of the ^{31}P NMR signal. Spin–spin interaction between the ^{19}F and ^{31}P nuclei, even those fairly remote from one another, is frequently observed in the ^{19}F NMR spectra (Table 2).

2. The Wittig Reaction

In contrast to halogenomethylenephosphoranes[1], the behaviour of other fluorine-containing phosphorus ylids in the Wittig reaction has still been inadequately investigated. As a rule these ylids exhibit a moderate or even a low reactivity in relation to carbonyl compounds. However, in certain cases it is possible to obtain fluorine-containing unsaturated compounds.

Hexafluoroisopropylidenetriphenylphosphorane (XXXV) reacts *in situ* under mild conditions with various aliphatic, aromatic, and heterocyclic aldehydes to form the corresponding olefins[20]#:

$$[Ph_3P{=}C(CF_3)_2] + RCHO \xrightarrow[ether]{-78\div+20^\circ} RCH{=}C(CF_3)_2 + Ph_3PO\ ;$$
(XXXV) (yield = 26–62%)

R=Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, $O_2NC_6H_4$, C_6F_5, PhMeCH, n-C_6H_{13}, PhCH=CH, 2-furfuryl, 2-pyridyl, or *m*-$CF_3C_6H_4$.

The reaction of the ylid (XXXV) with ketones cannot be achieved—owing to its low reactivity, there is sufficient time for its decomposition[20].

The cumulene ylid (XV) readily reacts with both aldehydes and ketones, but this leads to the formation of complex mixtures of unidentified substances[73]. The cumulated triene (LX) was isolated in the reaction with diphenylketen[72]:

$$Ph_3P{=}C{=}C(CF_3)_2 + Ph_2C{=}C{=}O \rightarrow Ph_2C{=}C{=}C{=}C(CF_3)_2 + Ph_3PO\ .$$
(XV) (LX)

Pentafluorobenzylidenetriphenylphosphorane (XXI) reacts with pentafluorobenzaldehyde[36], *p*-chloro and *p*-nitro-benzaldehydes[38], and *t*-butyl- and trimethylsilyl-propiolaldehydes[80] to form the corresponding olefins:

$$Ph_3P{=}CHC_6F_5 + RCHO \rightarrow RCH{=}CHC_6F_5\ ;$$
(XXI)

R=C_6F_5, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$, $Me_3CC{\equiv}C$, or $Me_3SiC{\equiv}C$.

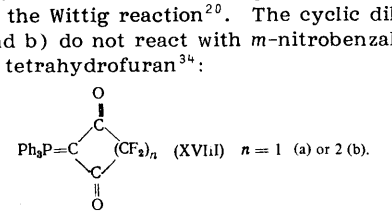
The *trans*-olefins are then usually formed preferentially.

trans-Decafluorochalcone (LXI) has been obtained by the reaction of pentafluorobenzoylmethylenetriphenylphosphorane (XXII) with pentafluorobenzaldehyde[37]:

$$Ph_3P{=}CHCOC_6F_5 + C_6F_5CHO \rightarrow C_6F_5CH{=}CHCOC_6F_5\ .$$
(XXII) (LXI)

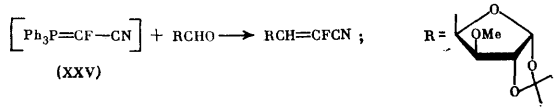
According to patent data[39–42], the phosphorus ylid $Ph_3P{=}CH(CH_2)_2CF_2COOH$ is used to synthesise fluorine-containing analogues of prostaglandin.

Perfluorocyclobutylidenetriphenylphosphorane (IV) does not undergo the Wittig reaction[20]. The cyclic diketoylids (XVIII, a and b) do not react with *m*-nitrobenzaldehyde on refluxing in tetrahydrofuran[34]:



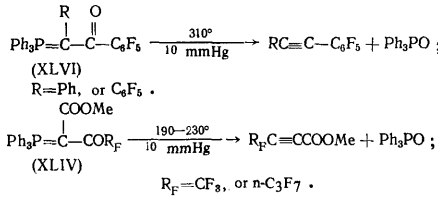
(XVIII) $n = 1$ (a) or 2 (b).

Cyanofluoromethylenetriphenylphosphorane (XXV) reacts with aldehydosugars to form the products of the Wittig reaction[47,48]:



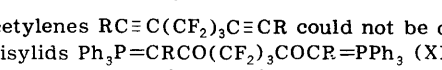
(XXV)

Like the usual acylmethylenephosphoranes, their fluorine-containing analogues—pentafluorobenzoylylids (XLVI) [35] and also trifluoroacetyl- and perfluorobutyryl-ylids (XLIV) [67]—are capable of undergoing the intramolecular Wittig reaction to form the corresponding acetylenes:



(XLVI)

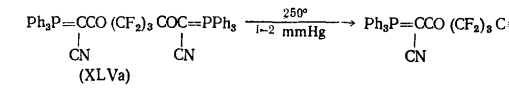
R=Ph, or C_6F_5.



(XLIV)

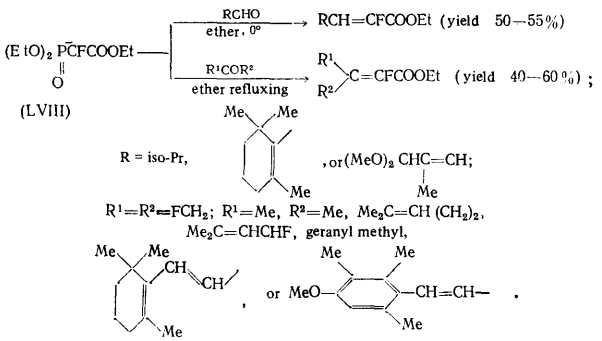
R_F=CF_3, or n-C_3F_7.

The diacetylenes $RC{\equiv}C(CF_2)_3C{\equiv}CR$ could not be obtained from the bisylids $Ph_3P{=}CRCO(CF_2)_3COCR{=}PPh_3$ (XLV, R=CN or COOEt); in the case of the dinitrile (XLVa) an ylid containing the C≡C triple bond was isolated[45]:



(XLVa)

The Wittig–Horner reaction has also been used to synthesise fluorine-containing unsaturated compounds. The reaction of the stable α-phosphonatecarbanion (LVIII) with aldehydes and ketones yielded various unsaturated fluorine-containing esters[76–78]:



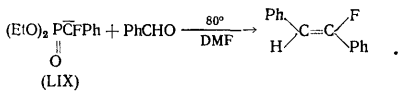
(LVIII)

R = iso-Pr, , or $(MeO)_2CHC{=}CH$;

$R^1{=}R^2{=}FCH_2$; R^1=Me, R^2=Me, $Me_2C{=}CH(CH_2)_2$, $Me_2C{=}CHCHF$, geranyl methyl,

In the reaction of the anion (LVIII) with ketones the yields of unsaturated compounds are lower than in the case of the analogous non-fluorinated anions. The reactions with asymmetric ketones give rise to mixtures of the *cis*- and *trans*-isomers, but the reaction with aldehydes is stereospecific—only the *cis*-isomers are obtained[76].

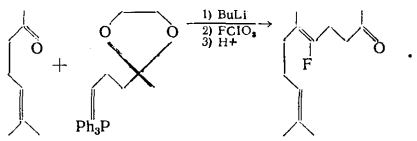
Trans-α-fluorostilbene has been obtained in 40% yield from the phenyl-substituted anion (LIX) and benzaldehyde[79]:



(LIX)

Fluorine-containing analogues of prostaglandin have been obtained with the aid of the Wittig–Horner reaction[81].

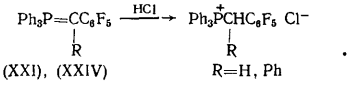
The SCOOPY (α-Substitution plus Carbonyl Olefination via β-Oxido Phosphorus Ylids) reaction is also used to synthesise fluorine-containing unsaturated compounds[7,82–85] (cf. Tyuleneva et al.[1]), for example:



It has been claimed[20] that the trimethoxy-ylid $(MeO)_3P{=}C(CF_3)_2$ (XXXVIIa) does not react either with benzaldehyde or with trifluoroacetophenone.

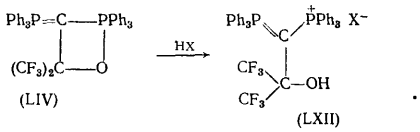
3. Other Reactions

Phosphorus ylids usually combine very readily with acids to form phosphonium salts[3]. Fluorine containing phosphorus ylids behave similarly. Thus the reaction of pentafluorophenylylids (XXI) and (XXIV) with dry HCl yielded phosphonium chlorides[38]:



(XXI), (XXIV) R=H, Ph

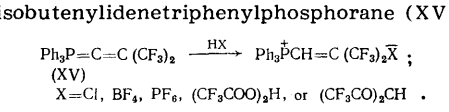
Analogous reactions with the cyclic ylid (LIV) lead to the dissociation of the P–O bond and the formation of the salts (LXII):[73]



(LIV) (LXII)

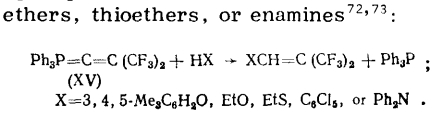
The salts (LXII) with X = Cl,[71] Br,[70] BF_4,[70,72] PF_6,[70–72] BPh_4,[70] or CF_3COO [72] have been obtained in this way.

Alkenylphosphonium salts have been synthesised from hexafluoroisobutenylidenetriphenylphosphorane (XV):[72]



(XV) X=Cl, BF_4, PF_6, $(CF_3COO)_2H$, or $(CF_3CO)_2CH$.

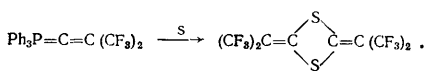
When the ylid (XV) is treated with alcohols, phenols, amines, or mercaptans the C–P bond is split with elimination of a tertiary phosphine and the formation of the corresponding alkenyl ethers, thioethers, or enamines[72,73]:



(XV) X=3, 4, 5-$Me_3C_6H_2O$, EtO, EtS, C_6Cl_5, or Ph_2N .

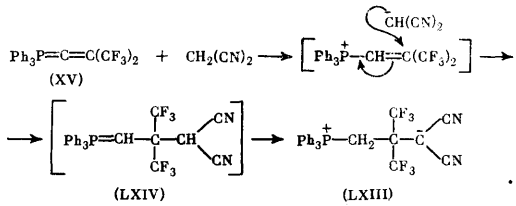
The reaction with *O*-deuteromethanol produced the deuterated ether $MeOCD{=}C(CF_3)_2$.[72]

The dimer of bis(trifluoromethyl)thioketen has been obtained from the ylid (XV) on treatment with sulphur:



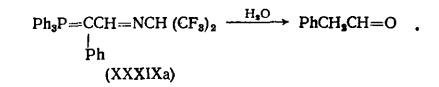
(XV)

Yet another reaction pathway is observed on treatment with malonodinitrile: this results in the formation of the betaine (LXIII), probably as a result of the prototropic isomerisation of the ylid (LXIV):[72]



(XV) (LXIV) (LXIII)

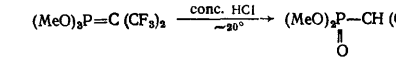
Hydrolysis of the phosphorus ylid (XXXIXa) leads to the splitting of the C=P and C=N bonds[65]:



(XXXIXa)

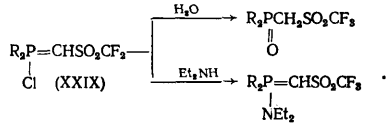
When perfluorocyclobutylidenetriphenylphosphorane (IV) is hydrolysed under mild conditions, the β-fluorine atoms are hydrolysed[14–16], whereas under severe conditions the ring is ruptured[34] (see Section II, 1 above). The diketo-ylid (XVIIIb) does not change on being refluxed with 50% sulphuric acid[34].

Hydrolysis of the trimethoxyphosphorus ylid (XXXVIIa) leads to a phosphonate ester[60]:



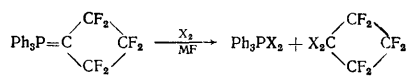
(XXXVIIa)

P-Chloro-ylids (XXIX) are converted on hydrolysis into phosphine oxides[50], while on treatment with diethylamine they give rise to phosphorus ylids containing the diethylamino-group at the phosphorus atom[50,51,53]:

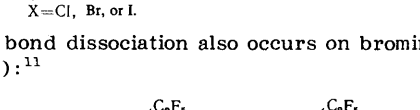


(XXIX)

The ylid (XXXVIIa) is readily brominated[60]:

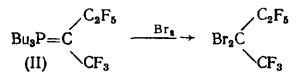


The diketo-ylids (XVIII, a and b) are not brominated and are not oxidised by permanganate[34]§. In the presence of metal fluorides, the more reactive ylid (IV) is halogenated with dissociation of the C=P bond[16]:



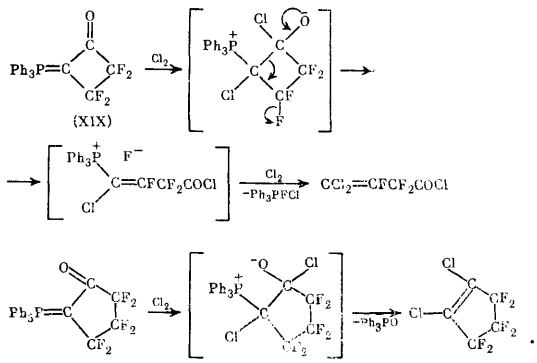
(IV) X=Cl, Br, or I.

A similar bond dissociation also occurs on bromination of the ylid (II):[11]



(II)

When the four-membered cyclic monoketo-ylid (XIX) is chlorinated, the ring is ruptured with formation of perhalogenovinylacetyl chloride; the five-membered analogue gives rise to dichloropentafluorocyclopentene[16]:



(XIX)

Stable cyclic diketoylids (XVIII, a and b) cannot be alkylated with methyl iodide on refluxing in acetone[34]. The ylid (LIV), containing the oxaphosphetan ring, also does not react with methyl iodide[71,72].

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§ On oxidation with CrO_3 in acetic acid, the ylid (XVIIIb) gives rise to perfluorosuccinic acid[34].

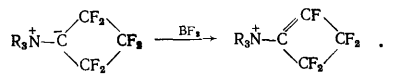
Pentafluorobenzylidenetriphenylphosphorane (XXI) is acylated at the "ylid" carbon atom[35] (see Section II, 3 above).

On treatment with metal salts, perfluorocyclobutylidenetriphenylphosphorane (IV) is converted into polyfluorocyclobutenylphosphonium salts[16]:

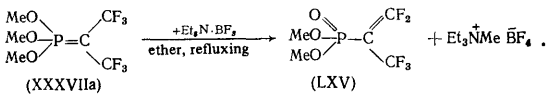


(IV)

The ylid structure is similarly converted into the cycloalkenylammonium structure on treatment of trialkylammonium perfluorocyclobutylids with boron trifluoride etherate[17]:

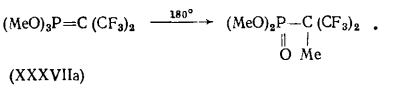


An analogous reaction is apparently possible also for the corresponding phosphorus ylids and the reverse reaction, involving the conversion of cycloalkenylphosphonium tetrafluoroborate into a phosphorus ylid—takes place on treatment with KF (cf. Burton and Shinya[11]). Treatment of the trimethoxyphosphorane (XXXVIIa) with the adduct of triethylamine and boron trifluoride leads to the simultaneous elimination of the alkyl group and the fluorine atom with formation of the phosphorus analogue of perfluoromethacrylic acid ester (LXV):[86]



(XXXVIIa) (LXV)

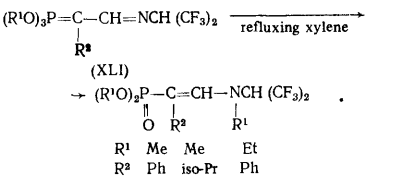
Certain phosphorus ylids containing alkoxy-groups at the phosphorus atom are capable of rearranging with transfer of the alkyl group from the oxygen atom to a carbon or nitrogen atom. Thus hexafluoroisopropylidenetrimethoxyphosphorane (XXXVIIa) is converted into the ester of hexafluoro-t-butylphosphonic acid on heating to 180 °C:[60]



(XXXVIIa)

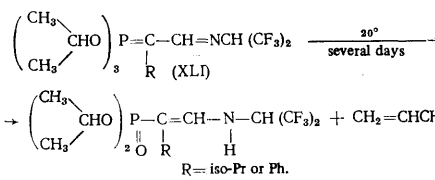
In the presence of SbF_5, the reaction temperature is reduced to 140 °C.[87]

The phosphorus ylids (XLI) are converted slowly at room temperature and rapidly on heating into substituted phosphonate esters containing an alkyl group at the nitrogen atom[64,65]:



R^1	Me	Me	Et
R^2	Ph	iso-Pr	Ph

Apart from a rearrangement, when the ylids (XLI) are heated, the elimination of the alkyl group R^1 in the form of an olefin is observed. Such a reaction takes place particularly readily for tri-isopropoxyphosphoranes[64,65]:



R= iso-Pr or Ph.

Thus fluorine-containing phosphorus ylids exhibit a varied reactivity. Further investigation of the chemistry of these interesting compounds is necessary.

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