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# Fluorinated 1,3-diketones, 2-trifluoroacetyl phenols and their derivatives: versatile reactants in phosphorus chemistry

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**Abstract**

The role of fluorinated β-diketones, their tautomers (keto–enols) and their derivatives as reagents towards $\lambda^3$P compounds is reviewed, including 2-trifluoroacetyl phenols, possessing formally a keto–enol system, and their derivatives. In an 'insertion' reaction phosphine and the keto–enol tautomers of 1,1,1,5,5,5-hexafluoro- and 1,1,1-trifluoropentan-2,4-dione furnished primary (*S*) or (*R*) α-hydroxy phosphines, whose enol functions probably isomerized the corresponding keto compounds. Further addition and isomerisation furnished 1,3α,5,7β-tetrakis(trifluoromethyl)-2-phospha-6-oxa-9-oxabicyclo[3.3.1]-nonan-3β,7α-diol and 1,7-trifluoromethyl-3,5-methyl-2,4,8-trioxa-6-phophaadamantane, exclusively one diastereomer in each case. The main mechanistic feature of these reactions is a consecutive diastereoselective hemiketal cyclization. 1,1,1,5,5,5-Hexafluoro- and 1,1,1-trifluoropentan-2,4-dione, as well as 2-trifluoroacetyl phenol and its imino derivatives reacted diastereospecifically with phosphonous acid dichlorides, $RPCl_2$ to give in a concerted mechanism thermally stable tricyclic $\lambda^5\sigma^5$P phosphoranes containing two five-membered rings and one six-membered ring. Surprisingly, the two $CF_3$ groups bonded to an $sp^3$-hybridized carbon were in a *cisoid* arrangement having closest non-bonding F···F distances of 301.4 or 273.5 pm. These findings reflect the 'through space' F–F coupling constants of the tricyclic phosphoranes ($J_{FF} = 4.0$–7.0 Hz), in solution. 4,4,4-Trifluoro-3-hydroxy-1-phenyl-butan-1-one and methyl or phenyl phosphonous acid dichlorides gave similar tricyclic phosphoranes decomposing at ambient temperature to furnish 1,2$\lambda^5\sigma^4$-oxaphospholanes and (*E*)-1,1,1-trifluoro-4-phenyl-but-2-en-4-one. Dialkylphosphites and 1,1,1,5,5,5-hexafluoropentan-2,4-dione reacted to give either the (*Z*)-enol phosphonates or the respective γ-ketophosphonates from which in two cases four diastereomeric 2-oxo-2,5-dialkoxy-3,5-bis(trifluoromethyl)-3-hydroxy-1,2$\lambda^5\sigma^4$-oxa-phospholanes were obtained. 2-Trifluoroacetyl cyclohexanone, 4,4,4-trifluoro-3-trimethylsiloxy-1-phenylbutan-1-one, 1-benzoyl-2-trifluormethyloxirane, 1-benzoyl-2-trifluoro-methylaziridine, 2-trifluoroacetyl-1-trimethylsiloxybenzene and (trifluoroacetyl-1-phenyl) diethyl phosphate reacted with tris(trimethylsilyl) phosphite to give functionalized α-trimethylsiloxy phosphonates, which could easily be transferred into the respective phosphonic acids. In the case of an oxirane and an aziridine ketone no ring cleavage was observed. For 1,1′-(2-hy-

droxy-5-methyl-*m*-phenylene)-bis-ethanone and 1,1′-(2-trimethylsiloxy-5-methyl-*m*-phenylene)-bis-ethanone benzoxaphospholanes were obtained. Trialkyl phosphites and 1,1,1,5,5,5-hexafluoropentan-2,4-dione furnished cyclic phosphoranes containing the 3-hydroxy-3,5-bis(trifluoromethyl)-1,2$\lambda^5\sigma^5$-oxaphospholene structural element, stable at ambient temperature only in the case of one cyclic phosphite precursor. (*E*)-1,1,1-Trifluoro-4-phenyl-but-2-en-4-one and trimethylphosphite reacted to form 1,2$\lambda^5\sigma^5$-oxaphosphol-4-ene as the sole product. Results similar to the reaction of 1,1′-(2-hydroxy-5-methyl-*m*-phenylene)-bis-ethanone with diethyltrimethylsilylphosphite were obtained for trimethylphosphite and 2-trifluoroacetyl phenol where a deoxygenated phosphorane was found, easily hydrolyzed to give the respective phosphonic acid. With dialkylisocyanato phosphites and the keto components, 1,1,1,5,5,5-hexafluoro- and 1,1,1-trifluoropentan-2,4-dione, 4,4,4-trifluoro-1-phenyl-1,3-butandione, 2-trifluoroacetyl cyclohexanone, 2-trifluoroacetyl phenol and 1,1′-(2-hydroxy-5-methyl-*m*-phenylene)-bis-ethanone reacted in a 'double' cycloaddition to form bicyclic phosphoranes containing the 4,8-dioxa-2-aza-1$\lambda^5\sigma^5$-phosphabicyclo[3.3.0]-oct-6-en-3-one ring system; for the imino derivatives of 2-trifluoroacetyl phenol a corresponding 8-oxa-2,4-diaza- system was generated. For (*E*)-1,1,1,5,5,5-hexafluoro-4-trimethylsiloxy-3-penten-2-one however, a cyclic spiroimino phosphorane was obtained which underwent a [2 + 2] cyclodimerization to form a diazadiphosphetidine. Dimethylpropynyl phosphonite and 1,1,1,5,5,5-hexafluoropentan-2,4-dione yielded diastereoselectively a bisphosphorane, namely 1,4 - bis(trifluoromethyl) - 3,6 - dioxa - 2,2,7,7 - tetramethoxy - 2,7 - di(1 - propynyl) - 2,7-diphosphabicyclo[2.2.1] heptane. When trimethylsilanyl–phosphenimidous acid bis-trimethylsilanyl–amide, $Me_3SiN{=}PN(SiMe_3)_2$, was allowed to react with 1,1,1,5,5,5-hexafluoro- and 1,1,1-trifluoropentan-2,4-dione, (*E*)-1,1,1,5,5,5-hexafluoro-4-trimethylsiloxy-3-penten-2-one, 2-trifluoroacetyl cyclopentanone, 2-trifluoroacetyl phenol and its imino derivatives, 2-imino-1,2$\lambda^5\sigma^4$-oxaphospholenes were found containing two diastereomers in each case, which added hexafluoroacetone across the P=N bond to give 1,3,2$\lambda^5\sigma^5$-oxazaphosphetanes. 

*Keywords:* Fluorinated 1,3-diketones; 2-Trifluoracetyl phenol; Phosphorous chemistry

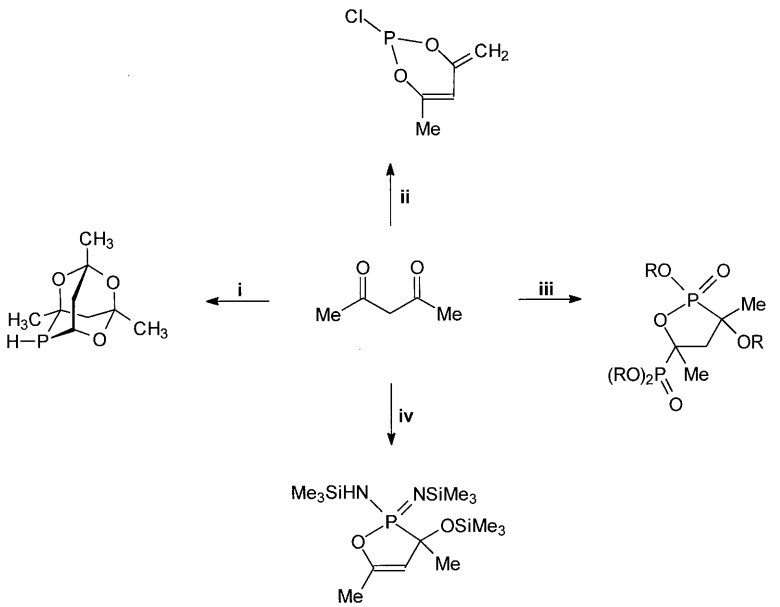
## 1. Introduction

1,3-Diketones are multifunctional molecules, which offer a variety of pathways in their reactions with phosphorus compounds, like phosphines, phosphorus(III) chlorides, phosphites, isocyanatophosphites and $Me_3SiN{=}PN(SiMe_3)_2$. Since 2-acetyl phenols contain formally the same structural unit as found in the tautomers of 1,3-diketones, their phosphorus chemistry will be discussed, too. In the case of pentan-2,4-dione and phosphine, $PH_3$, a phosphaadamantane [1a] was obtained; if the diprimary phosphines $H_2P(CH_2)_nPH_2$ ($n = 2$, 3) was taken, a separable mixture of *rac* and *meso* diastereomeric phospha-adamantane diphosphines were found; [1b] $PCl_3$, diethylchloro phosphite, and ethyl phosphonous dichloride gave 1,3,2-dioxaphosphorinenes [3a,b], diethylphosphinous chloride furnished a 1,2-oxaphospholenium chloride [3], diethylchloro phosphite *syn*- and *anti*-1-methyl-3-oxo-1-butenyl-phosphites [4], dialkylphosphites [5a] and trimethylsilyl phosphites produced 5-phosphono-1,2-oxaphospholanes [5b] and α-trimethylsiloxy-

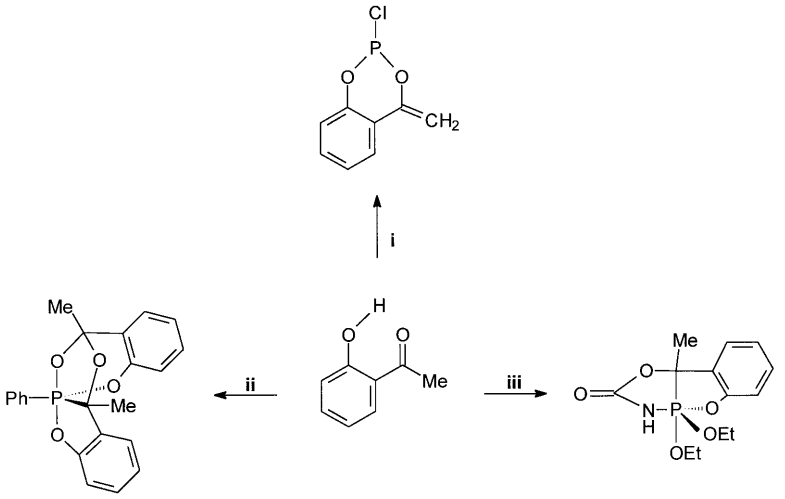
phosphonates [5b,6], which can be converted into vinylphosphonates [6]. $Me_3SiN{=}PN(SiMe_3)_2$ and pentan-1,3-dione furnished an 1,2-oxaphospholene [7] (Scheme 1).

2-Acetyl phenol and $PCl_3$ gave a similar compound like pentan-2,4-dione [2], whereas phenylphosphonous dichloride surprisingly reacted to form diastereoselectively a tricyclic phosphorane in a concerted head-to-tail cyclization. The possible intermediate was proposed to be the respective phosphonite, which in this case could not be isolated [8]. A similar phosphorane was observed when the methyl imine of salicylaldehyde was allowed to react with phenylphosphonous dichloride. Applying diethylisocyanatophosphite a bicyclic ring system was synthesized [9] (Scheme 2). 2-Acetyl-4-methyl-1-trimethylsiloxybenzene or 2,5-diacetyl-4-methylphenol and trimethysilyl phosphites gave 4,5-benzo-1,2-oxaphospholanes [10a,b] (Scheme 3).

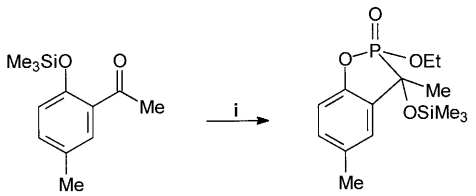
Pentan-2,4-diones and 2-acetyl phenols containing $CF_3$ groups should influence the pathway in their reactions with selected phosphorus compounds, the properties of the respective products and potential application in organic, bioorganic, and medicinal chemistry [11a–c]. Due to the lipophilic and electron-withdrawing effects the trifluoromethyl functionality is already generally accepted as an important pool of valuable buildings blocks. If fluorinated phosphines with chiral centres were formed, they could be considered effective ligands for transitions metals of low valence state and possible catalysts for enantioselective synthesis. Fluoralkylated phosphonates and phosphoranes are possible transition state mimics and of biolog-




Scheme 1. Reactions of pentan-2,4-dione [i: $PH_3$; ii: $PCl_3/Et_3N$; iii: $(RO)_2P(O)H$; $(RO)_2POSiMe_3$; iv: $Me_3SiN = PN(SiMe_3)_2$].




Scheme 2. Reactions of 2-acetylphenol [i: $PCl_3$; ii: $PhPCl_2/Et_3N$; iii: $(EtO)_2PNCO$)].



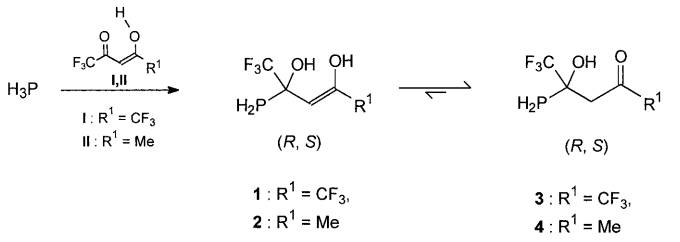

Scheme 3. Reaction of 2-acetyl-4-methyl-1-trimethylsiloxybenzene [i: $(EtO)_2POSiMe_3$].

ical activity. Here we review the reactions of the fluorinated β-diketones and of their derivatives, of trifluoroacetyl phenols, their trimethylsilyl and imino derivatives with numerous phosphorus (III) derivatives.

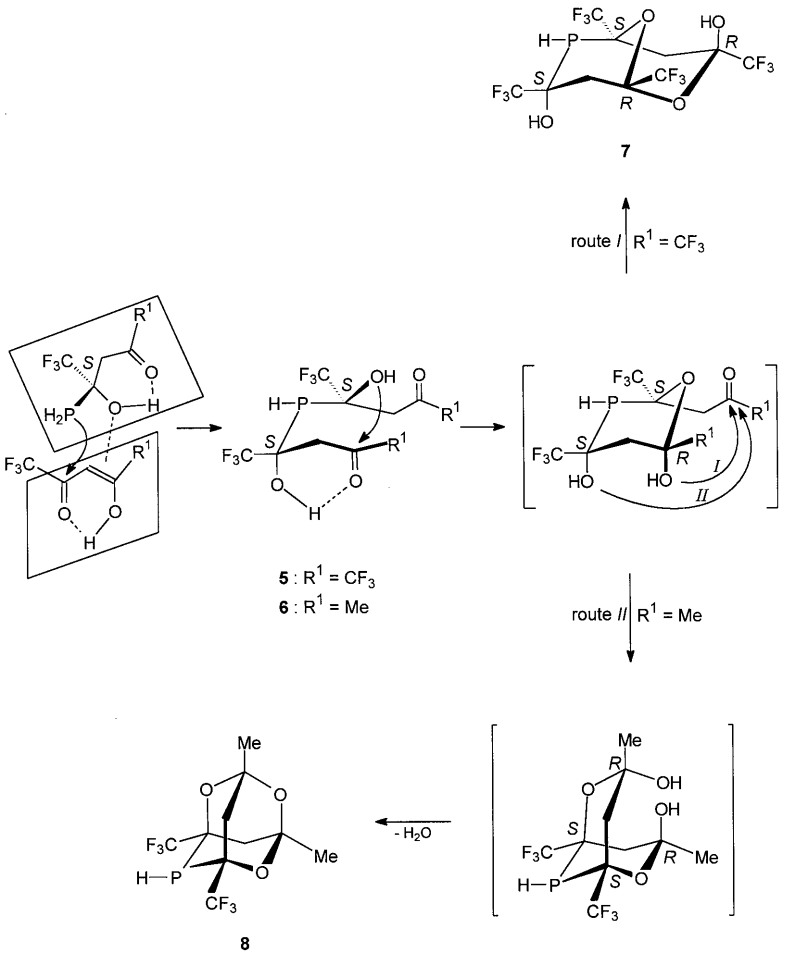
## 2. Reactions of phosphine with 1,1,1,5,5,5-hexafluoro- and 1,1,1-trifluoropentan-2,4-dione

In an 'insertion' reaction phosphine, $PH_3$ and the keto–enol tautomers of 1,1,1,5,5,5-hexafluoro-**I** and 1,1,1-trifluoropentane-2,4-dion **II** furnished the primary (*S*) or (*R*) α-hydroxy phosphines **1** and **2** [12], whose enol functions probably isomerized with formation of the corresponding keto compounds **3** and **4** (Scheme 4).

Further addition and isomerisation afforded secondary bis(α-hydroxy-γ-keto) phosphines **5** and **6**, which produced colorless crystalline solids, surprisingly 1,3α,5,7β-tetrakis(trifluoromethyl)-2-phospha-6-oxa-9-oxabicyclo[3.3.1]-nonan-3β,7α-diol **7** and 1,7-trifluoromethyl-3,5-methyl-2,4,8-trioxa-6-phophaadamantane




Scheme 4.




Scheme 5.

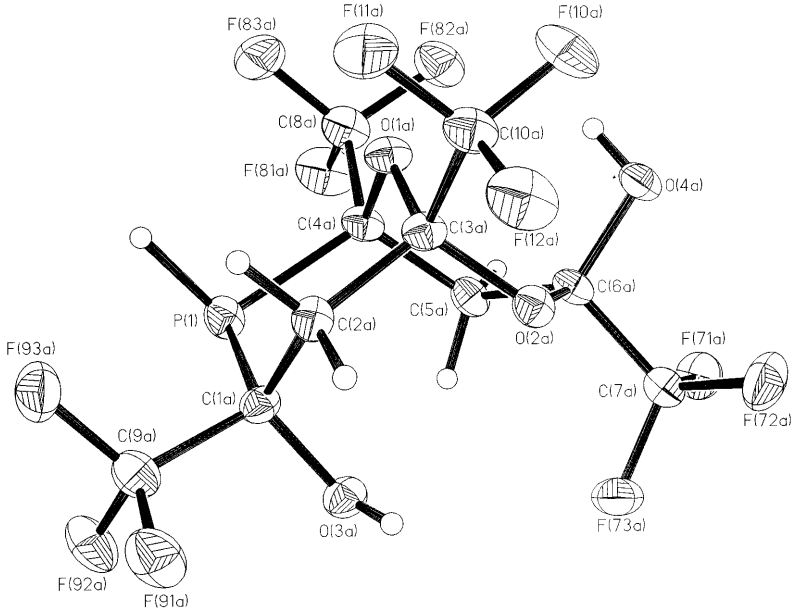



Fig. 1. Molecular structure of 1,3α,5,7β-tetrakis(trifluoromethyl)-2-phospha-6-oxa-9-oxabicyclo[3.3.1]-nonane-3β,7α-diol (**7**) [12]; reprinted by permission of Wiley-VCH Publishers.

**8** (Scheme 5), in good yields, exclusively one diastereomer in each case. The main mechanistic feature of these reactions is a consecutive diastereoselective hemiketal cyclization. The $PH_2$ group probably added to the keto functions, assuming an orientation of the internal chelates [13] by an additional attractive OH···π interaction [14] (see Scheme 5); the pathway is depicted for the (*S*) primary phosphine, exemplarily to give the (*RR*) and (*SS*) secondary phosphines exclusively. Via a cyclic chair-configurated hemiketal (intermediate, $R^1 = CF_3$, route *I*, Scheme 8) and by virtue of the anomeric effect a new (*R*)-carbon center is created starting from the (*SS*)-precursor and a new (*S*)-carbon center from the (*RR*) precursor. A further anomeric effect controlled hemiketal cyclisation with the remaining keto function furnishing the bicyclic secondary phosphine **7** in the (1*S*,3*S*,5*R*,7*R*) or the mirror image (1*R*,3*R*,5*S*,7*S*) configuration, which was found in the X-ray diffraction investigation, too (Fig. 1). Clearly, the two hydroxy groups are in an *endo*/*exo* position, unavailable for intra-molecular water abstraction to give a heteroadamantane system. The intermediate (R = Me, route *II*, Scheme 5) led to a bicyclic phosphine having (*RRSS*) or (*SSRR*) configuration. The double chair conformation of the two rings in close vicinity to one another, enable a condensation reaction to give the phosphaadamantane **8** and water like in the case of pentane-2,4-dione and phosphine. For the solid state molecular structure of **8** see Fig. 2. The primary phosphine precursors were not separated successfully because of their thermal instability.

With the diprimary phosphines $H_2P(CH_2)_nPH_2$ ($n = 2$, 3) and the diketone **II** bis(phosphaadamantyl)alkanes and the respective $PdCl_2$ coordination compounds were synthesized [1b].

## 3. Reactions of phosphonous acid chlorides and their derivatives

### *3.1. 1,1,1,5,5,5-Hexafluoro- and 1,1,1-trifluoropentan-2,4-dione*

1,1,1,5,5,5-Hexafluoropentan-2,4-dione **I** reacted diastereospecifically with phosphonous acid dichlorides **III**, $R^2PCl_2$ [$R^2$ = Me (**a**), Et (**b**), *i*-Pr (**c**), *t*-Bu (**d**), $Me_3SiCH_2$ (**e**), $PhCH_2$ (**f**), Ph (**g**)] to give in a concerted mechanism thermally stable moisture sensitive tricyclic $\lambda^5\sigma^5$P phosphoranes **9a–g** containing two, five- and one, six-membered ring (Scheme 6). Nevertheless, the very fast formation of compounds **9** might have prevented from obtaining NMR spectroscopic evidence for the intermediate phosphonite, proposed as precursor for the concerted diastereospecific reaction. Trapping experiments using hexafluoroacetone failed. Due to bulkier substituents, the reactions of the dichlorides **IIIc–e** require higher temperatures and longer reaction times than the other ones. Hydrolysis experiments were carried out in one case, namely with compound **IIIg** ($R^2$ = Ph) resulting in the degradation of

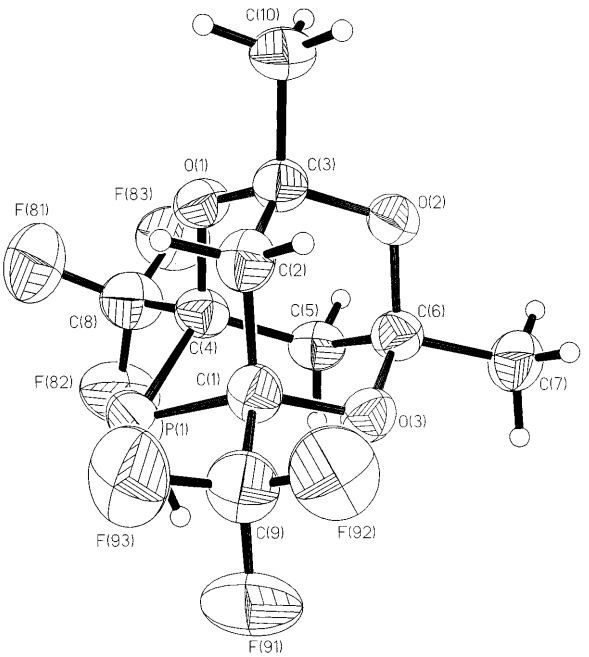
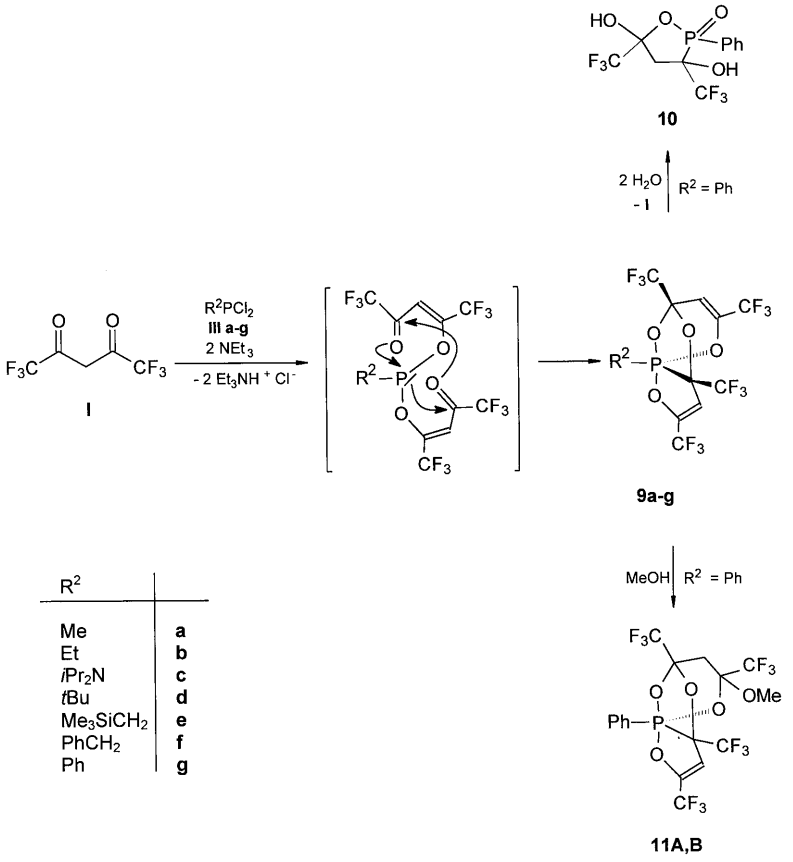



Fig. 2. Molecular structure of 1,7-trifluoromethyl-3,5-methyl-2,4,8-trioxa-6-phophaadamantane (**8**) [12]; reprinted by permission of Wiley-VCH Publishers.



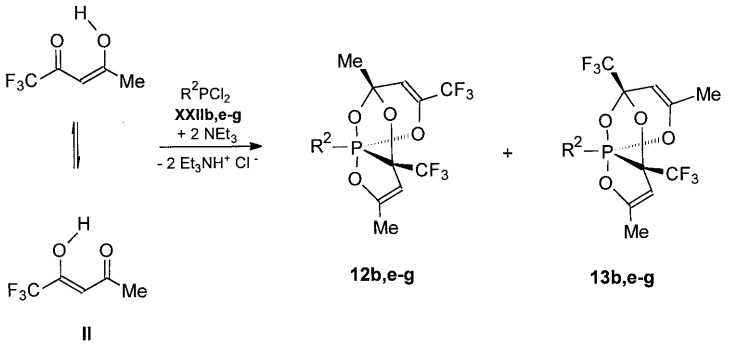

Scheme 6.

the tricyclic system with formation of **I** and the solid, non-hygroscopic 3,5-dihydroxy-2-oxo-1,2$\lambda^5\sigma^4$-oxaphospholane **10**, which could be isolated after fractional crystallization. Surprisingly, with methanol the tricyclic system was preserved. A Markovnikov addition across the double bond in the six-membered ring from both possible sides took place, creating one more chiral center to yield the two isomeric phosphoranes, **11A** and **11B**. The other double bond in the five-membered ring was not attacked (see Scheme 6) [15].

The reactions of the phosphonous acid dichlorides, $R^2PCl_2$ **III** [$R^3 = Et$ (**b**), $Me_3SiCH_2$ (**e**), $PhCH_2$ (**f**), Ph (**g**)] with the tautomer of 1,1,1-trifluoropentan-2,4-dione **II** were conducted at 0°C and ambient temperature, respectively, due to the lower reactivity of **II**. Since two different HO functions are present in the two tautomeric (*Z*) forms of **II** three different intermediate phosphonites might have been expected, but only two were found (see Scheme 7), to give diastereoselectively two regioisomeric phosphoranes **12** and **13** in the ratio 4.2:1 (**12b**: **13b**), 6.7:1 (**12e**: **13e**), 7.2:1 (**12f**: **13f**) and 10.1:1 (**12g**: **13g**) with $CF_3$ in the bridge-head position in

both cases (see Scheme 7). These findings account for a slight preference for the tautomer having the hydroxyl group at C(4) and a considerable influence of the substituent at phosphorus. Isomers **12** and **13** could be separated by fractional crystallization [15].

The solid state molecular structures of **9e**, **11A** and **12g** (e.g. see Fig. 3) exhibited two oxygen atoms in the axial position of a slightly distorted trigonal-bipyramidal geometry at phosphorus. Surprisingly, the two $CF_3$ groups bonded to an $sp^3$-hybridized carbon were in a *cisoid* arrangement having closest non-bonding F···F distances [F(133)···F(142)] of 301.4 (**9e**) (Fig. 3) or 273.5 pm (**11A**). These findings reflect the 'through space' F–F coupling constants of the tricyclic phosphoranes ($J_{FF} = 4.0–7.0$ Hz), in solution. Only one set of signals was observed for compounds **9**, **12** and **13** proving their diastereospecific formation. The $^{19}$F-NMR spectra for compounds **9**, and **11A** exhibited four signals due to four magnetically inequivalent $CF_3$ groups. The coupling constants $J_{FF}$ [4.2–4.9 Hz (**9**) and 7.0 Hz (**11A** and **11B**)] are obviously due to a 'through-space' interaction, since a through-




Scheme 7.

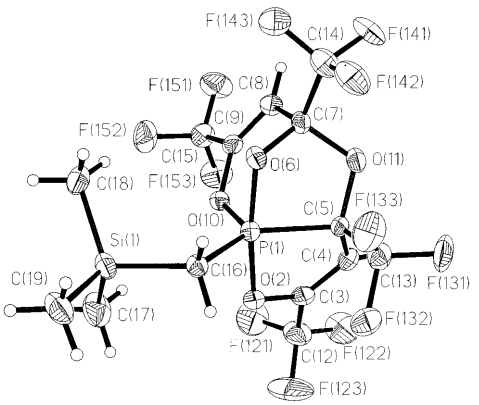
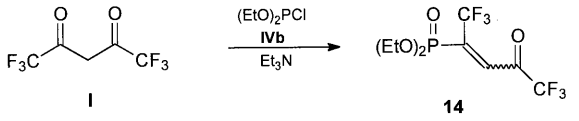



Fig. 3. Molecular structure of 3,5,7,9-tetrakis(trifluoromethyl)-1-trimethylsilylmethyl-2,6,10,11-tetraoxa-1-phospha-(V)tri-cyclo-[5.3.1.$0^{1,5}$]-undeca-3,8-diene (**9e**) [15]; reprinted by permission of Wiley.




Scheme 8.

bond mechanism would involve six or seven single bonds indicating a *cisoid* arrangement of the $CF_3$ groups at C(5) and C(7). No $J_{FF}$ coupling was observed, as expected in phosphoranes **12**, the molecule having no $CF_3$ pairs in the necessary vicinity. Similar non-bond coupling phenomena of $CF_3$ groups facing each other were found in another tricyclic system (see Section 3.2) and in a spirophosphorane where the $^{19}F-^{19}F$ homocorrelated $^{2}D$-NMR spectrum served to prove this assumption [16].

When chlorodiethylphosphite **IVb** reacted with **I** in the presence of an auxiliary base phosphonate **14** was obtained (Scheme 8) [17].

### *3.2. 4,4,4-Trifluoro-3-hydroxy-1-phenylbutan-1-one*

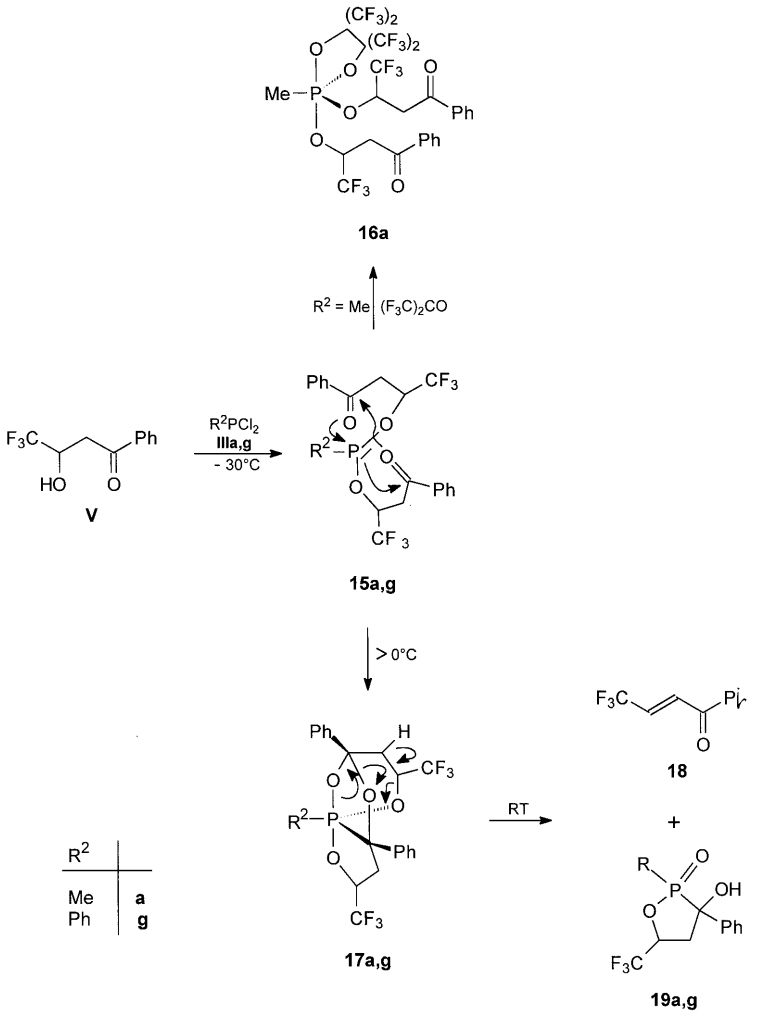
The reaction of 4,4,4-trifluoro-3-hydroxy-1-phenyl-butan-1-one (**V**) [18] with the phosphonous dichlorides $R^2PCl_2$ **III** [$R^2$ = Me (**a**), $R^2$ = Ph (**g**)] afforded unequivocally the phosphonites **15a** and **15g** at temperatures below 0°C, which were characterized by their typical $\delta_P$ shift values, but not isolated. Compound **15a** could be trapped using hexafluoroacetone which added oxidatively at phosphorus to form the 1,3,2$\lambda^5\sigma^5$-dioxaphospholane **16a** when the temperature was above 0°C. Compounds **15a** and **15g** rearranged in a concerted mechanism (cf. chapter 3.1) to probably give the unstable diastereomeric tricyclic phosphoranes **17a** and **17g,** which decomposed shortly after their formation to give the unsaturated ketone **18** [18] and the corresponding stereoisomeric oxaphospholanes **19a** and **19g**. The latter could have been formed by a rearrangement process found for the tricyclic system obtained from dibenzoylmethane and phenyl phosphonous dichloride [19]. These observations are in contrast to the properties of the tricyclic phosphoranes obtained from fluorinated 2-hydroxy-2-penten-4-ones **I** and **II**. It is thermodynamically favorable to cleave a strained $\lambda^5\sigma^5$P tricyclic system into a monocyclic five-membered ring with a $\lambda^5\sigma^4$ phosphorus and an α,β-unsaturated carbonyl compound where the conjugation between C=C and C=O bonds decreases significantly the energy of the whole system [20].

Despite C-2 in β-hydroxyketone **V** being a chiral centre only one sharp $^{31}$P-NMR signal was found in the expected region for phosphonites **15a** ($\delta_P = 206$) and **15g** ($\delta_P = 181$) with (*RR*/*SS*) and *RS* configuration. The same is true for the monocyclic phosphorane **16a**, where in addition one $^{19}$F-NMR signal ($\delta_F = -68.4$) at ambient temperature for the four dioxaphospholane $CF_3$ groups is indicating rapid pseudorotation on the NMR time scale. When the tricyclic ring is formed the configuration differences become evident. Obviously during the diastereospecific phosphorane formation the two phenyl groups will occupy strictly a *cisoid* position

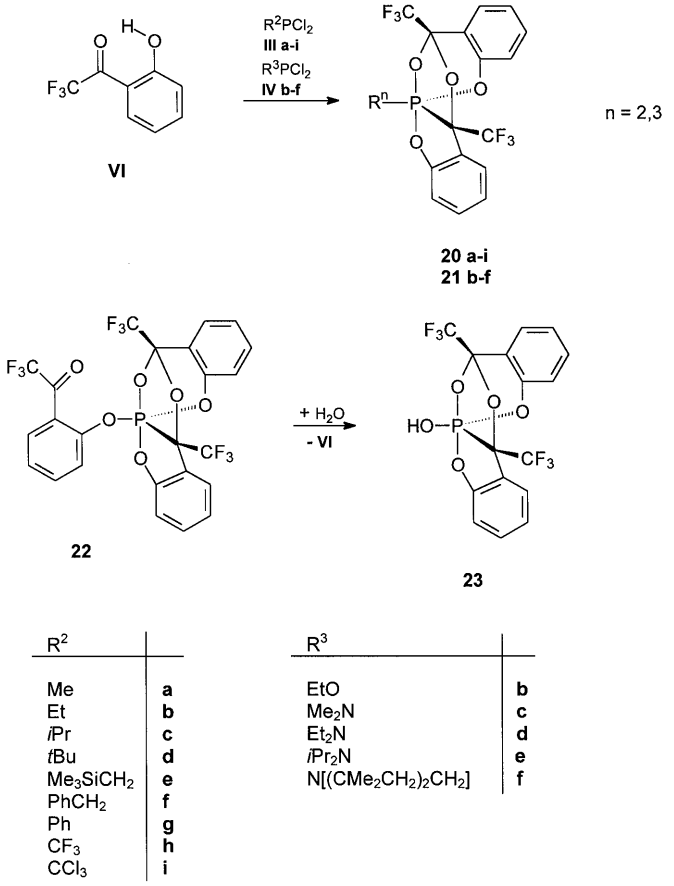
comparable to what was found for the interaction of phosphonous dichlorides and **I** (see Scheme 9). The X-ray structure investigation of **16a** revealed a slightly distorted trigonal bipyramid at phosphorus with 11.1% deviation along the Berry pseudorotation coordinate [21]. The bond lengths for equatorially located endo and exocyclic oxygen differ markedly.

### 3.3. 2-Trifluoroacetyl phenol and its imino derivatives

Reacting 2-trifluoroacetyl phenol **VI** [22] with the phosphonous acid dichlorides **III**, $R^2PCl_2$ [$R^2$ = Me (**a**), Et (**b**), *i*-Pr (**c**), *t*-Bu (**d**), $Me_3SiCH_2$ (**e**), $PhCH_2$ (**f**), Ph (**g**),




Scheme 9.

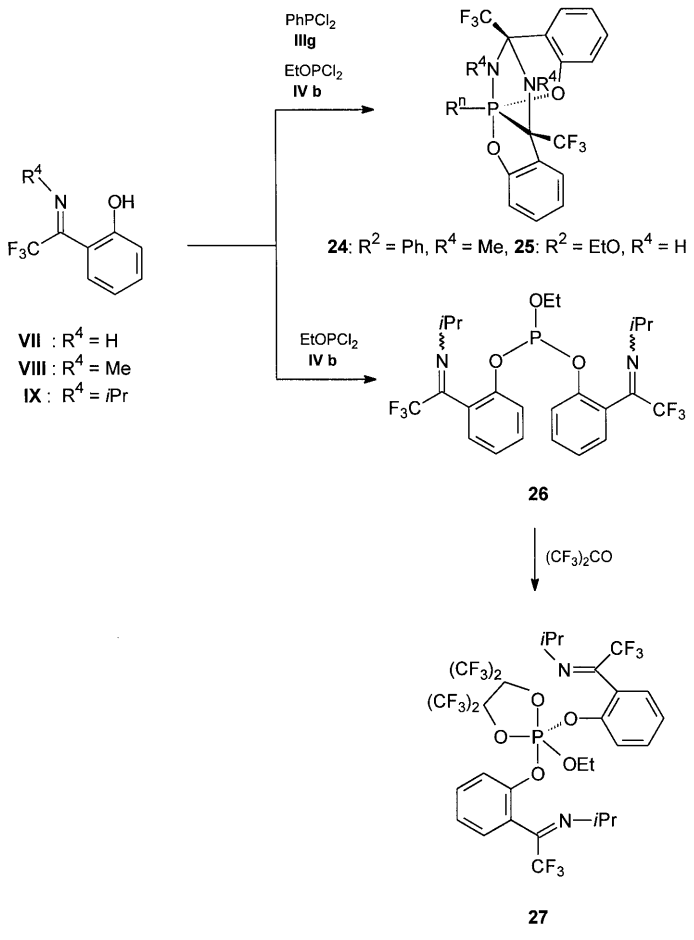



Scheme 10.

$CF_3$ (**h**), $CCl_3$ (**i**)] or with the phosphorus(III) derivatives $R^3PCl_2$ **IV** [$R^3$ = EtO (**b**), $NMe_2$ (**c**), $NEt_2$ (**d**), N*i*$Pr_2$ (**e**), N[$(CMe_2CH_2)_2CH_2$] (**f**)] in the presence of an auxiliary base diastereospecifically tricyclic phosphoranes **20a**–**i** and **21b**–**f** moisture sensitive solids, were obtained like in the case of **I** or **II** (Scheme 10) [8,23,24]. The two $CF_3$ groups are in a *cisoid* arrangement, derived from the $^{19}$F-NMR spectra in line with a shortest non-bonding F···F distance of the two $CF_3$ groups (282.2 pm) in the solid state structure of **20a** [23].

Surprisingly, if phosphorus trichloride, **IVa** was applied, again diastereospecifically the solid, moisture-sensitive tricyclic tetraoxaphosphorane **22** was obtained. Obviously, an intermediate, namely tris(2-trifluoroacetyl phenyl) phosphite was formed, which underwent the the before mentioned diastereospecific cyclization (Scheme 10). Hydrolysis of **22** resulted in the formation of hydroxyphosphorane **23** [25].

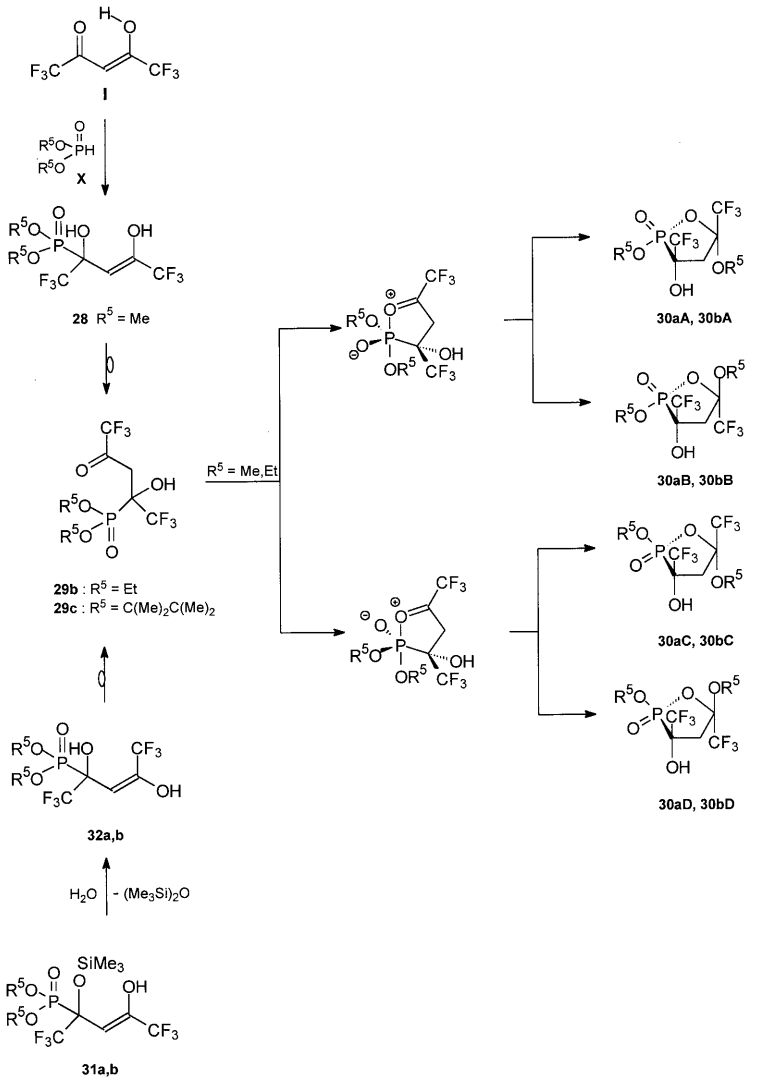
The (*N*-alkyl)imino derivatives of **VI**, **VII** and **VIII** (**VII**: $R^4 = H$, **VIII**: $R^4 = Me$) [26] furnished the moisture-sensitive, solid tricyclic phosphoranes **24** and **25** with the phosphorus chlorides **IIIg** and **IVb**, respectively. In the case of **IX** ($R^4 = i$-Pr) [26], the bulkier substituent at nitrogen directs the reaction to give the stable phosphite **26**, which did not rearrange to yield the expected tricyclic system but added hexafluoroacetone oxidatively to form phosphorane **27** (Scheme 11) [27]. The $^{31}P$- and $^{19}F$-NMR spectrum of phosphite **26** showed at ambient several overlapping signals due to a *syn-anti*-isomerization of the imino fragment slow on the NMR time scale [27]. Upon raising the temperature up to 77°C only one resonance was observed in each case.



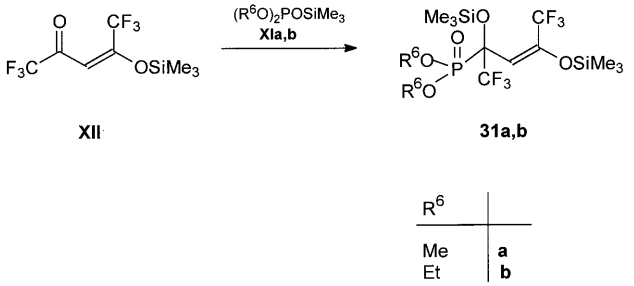

Scheme 11.

## 4. Reactions of dialkylphosphites with 1,1,1,5,5,5-hexafluoropentane-2,4-dione

The dialkylphosphites $(R^5O)_2P(O)H$, **X** [$R^5$ = Me (**a**), Et (**b**); $R^5$–$R^5$ = $CMe_2CMe_2$ (**c**)] and diketone **I** in its tautomeric form reacted to give either the (*Z*)-enol phosphonate **28a** $(R^5O)_2P(O)C(CF_3)(OH)CH{=}C(OH)CF_3$ ($R^5$ = Me) or, after fast rearrangement, the respective α-ketophosphonates $(R^5O)_2P(O)C(CF_3)(OH)CH_2C(O)CF_3$, **29b** and **29c** ($R^5$ = Et; $R^5$–$R^5$ = $CMe_2CMe_2$). From **28a** (via rearrangement) and **29b** through two possible trigonal-bipyramidal transition states and subsequent migration of the respective alkoxy group $R^5O$ four diastereomeric 2-oxo-3-hydroxy-1,2$\lambda^5\sigma^4$-oxaphospholanes **30a** and **30b** were obtained (Scheme 12) [28].




Scheme 12.




Scheme 13.

Hydrolysis of the (*E*)-phosphonate $(R^5O)_2P(O)C(CF_3)(OSiMe_3)CH{=}C(OSiMe_3)$-$CF_3$, **31a** and **31b** [28], synthesized from $(R^6O)_2POSiMe_3$ **XI** ($R^6$ = Me (**a**), Et (**b**)) and (*E*)-$CF_3C(O)CH{=}C(OSiMe_3)CF_3$ **XII** [29] (Scheme 13), gave the corresponding (*E*)-enol phosphonates **32a** and **32b** which rearranged in turn to form the α-ketophosphonates **29** mentioned above.

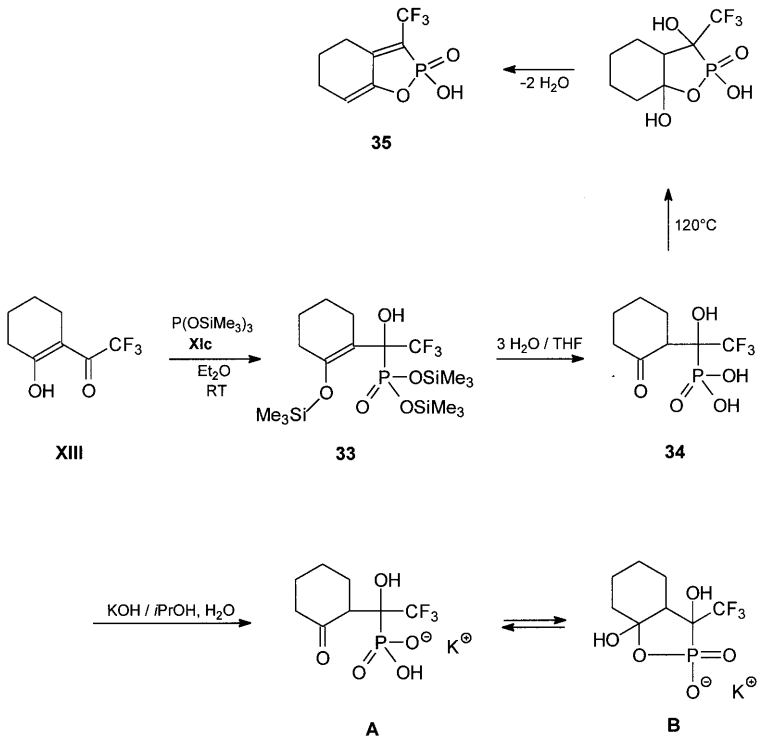
## 5. Reactions of trimethylsilyl phosphites

### *5.1. 2-Trifluoroacetyl cyclohexanone*

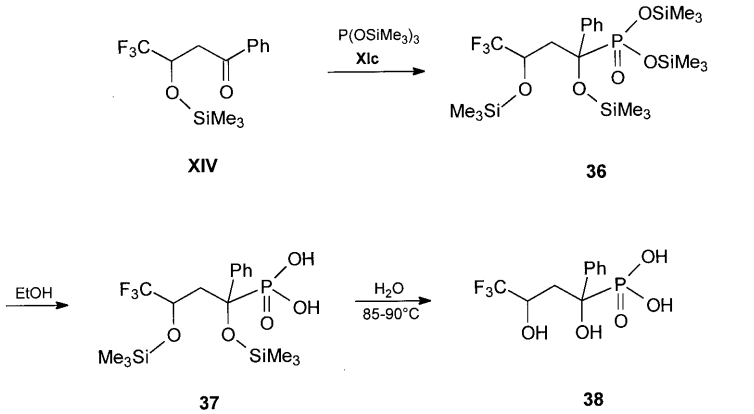
2-Trifluoroacetyl cyclohexanone (**XIII**) [48] and tris(trimethylsilyl) phosphite (**XIc**) reacted to give phosphonate (**33**), a colorless solid at ambient temperature in 46% yield (Scheme 14). The nucleophilic phosphorus added to the $CF_3CO$ keto carbon followed by trimethylsilyl group migration. Hydrolysis of **33** results in the formation of the β-keto phosphonic acid **34**, isolated and characterized as the potassium salt, whose $^{31}P$- and $^{19}F$-NMR spectra showed two sets only, probably due to the presence of two tautomers **A** and **B** (**A**:**B** = 83:17) in DMSO-$d_6$ solution (Scheme 14). An attempt to distill **34** led to its further heterocyclization to give phosphonate **35** characterized as its morpholinium salt [30].

### *5.2. 4,4,4-Trifluoro-3-trimethylsiloxy-1-phenylbutan-1-one, 1-benzoyl-2-trifluoro-methyl-oxirane and 1-benzoyl-2-trifluoro-methylaziridine*

When 4,4,4-trifluoro-3-trimethylsiloxy-1-phenylbutan-1-one (**XIV**) [31] reacted with tris(trimethylsilyl) phosphite (**XIc**) the phosphonate **36** was formed (Scheme 15), possessing two chiral centres. Two singlet signals in the $^{31}P$-NMR spectrum are observed in the expected region ($\delta = 5.19$ and 6.10) with the respective diastereomeric pairs in a 70:30 ratio, which reflects the directing influence of the preferred conformations at the chiral carbon in **XIV** in the course of the nucleophilic attack of phosphorus at the keto carbon. Obviously a two step hydrolysis takes place; the first involving phosphorus yielding two diastereomers of the phosphonic acids **37** ($\delta_P = 12.3$ and 12.7), the second, slower process at the silyl ether leading finally to the extremely hygroscopic solid α,γ-hydroxy phosphonic acid **38**, $\delta_P = 20.1$ (**38A**) and 19.3 (**38B**) (**A**:**B** = 70:30) (Scheme 15).




Scheme 14.




Scheme 15.

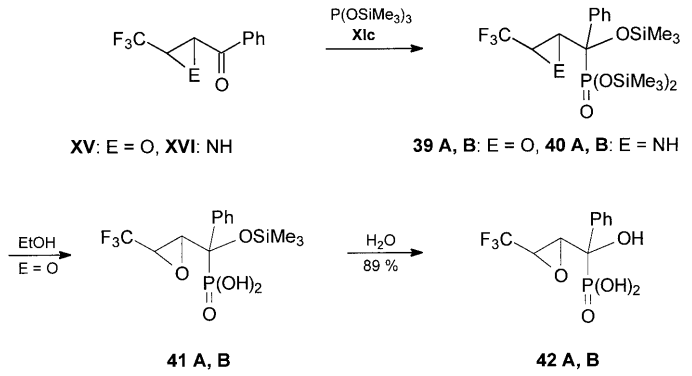
When the epoxy ketone **XV** [32] or 1-benzoyl-2-trifluoromethylaziridine (**XVI**) and tris(trimethylsilyl) phosphite (**XIc**) reacted, the epoxy or aziridinyl phosphonate **39** or **40** [33] consisting of two diastereomers **A** and **B** (**A**:**B** = 3:2) have been formed. The stepwise hydrolysis of **39** led to the phosphonic acids **41A** and **41B**

and, finally, **42A** and **42B**; the diastereomeric ratio did not change. During the hydrolysis the oxirane ring stayed intact, which was confirmed by the X-ray single-crystal structure analysis of **42A**. Two independent molecules, having slightly different bond length and angles with an (*RRR*) configuration (three chiral centers) have been found in the unit cell showing *intra*- and *inter*molecular hydrogen bonding [31] (Scheme 16).

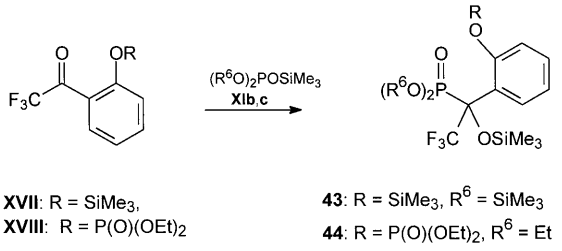
### *5.3. 2-Trifluoroacetyl-1-trimethylsiloxybenzene, (2-trifluoroacetyl-1-phenyl) diethyl-phosphate, 1,1′-(2-hydroxy-5-methyl-m-phenylene)-bis-ethanone, 1,1′-(2-trimethylsiloxy-5-methyl-m-phenylene)-bis-ethanone*

Phosphite **XIb**, **c** and 2-trifluoroacetyl-1-trimethylsiloxybenzene (**XVII**) furnished α-trimethylsiloxy phosphonate (**43**) (Scheme 17) [34]; when (2-trifluoroacetyl-1-phenyl) diethyl-phosphate (**XVIII**) was allowed to react with diethyl-bis(trimethylsilyl) phosphite (**XIb**) [25], the phosphono–phosphate **44** was produced with $\delta_P = 13.1$ ($^3J_{PF} = 6.5$ Hz) and $\delta_P = -8.5$) (Scheme 17) [25].

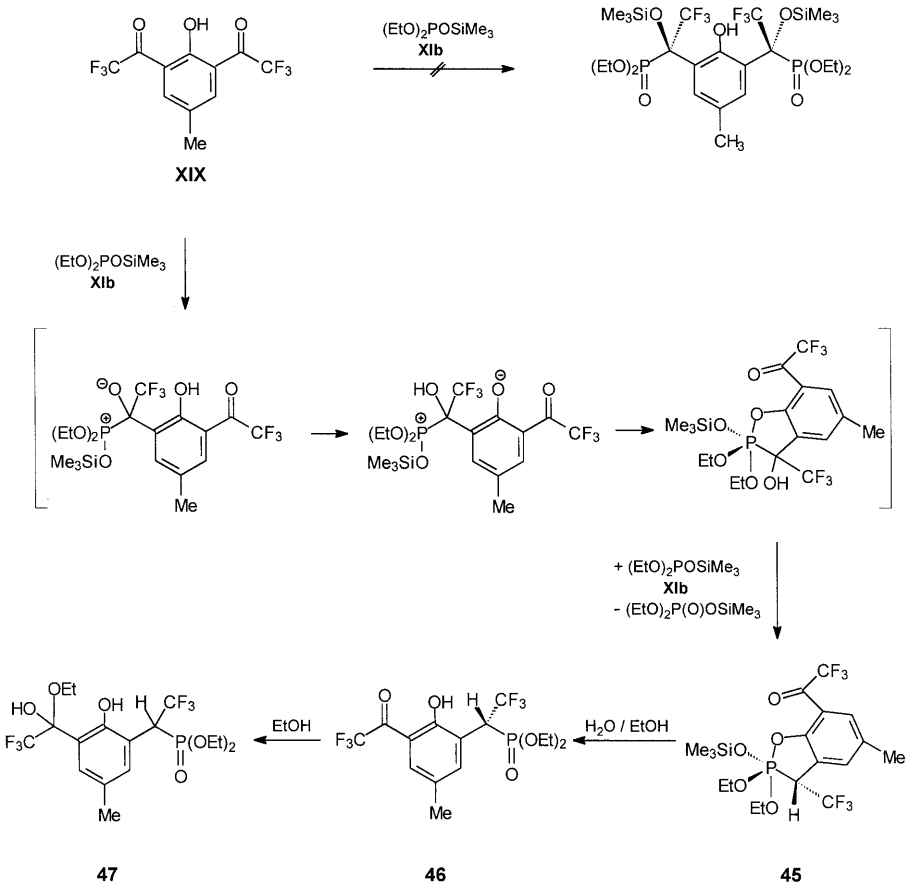
The reaction of 1,1′-(2-hydroxy-5-methyl-*m*-phenylene)-bis-ethanone (**XIX**) with diethyltrimethylsilyl phosphite (**XIb**) in a 1:2 ratio did not afford the expected bisphosphonate (Scheme 18), but the solid 1,2$\lambda^5\sigma^5$-oxaphosphole **45**, via a 1,3 and




Scheme 16.




Scheme 17.




Scheme 18.

a 1,5-dipolar intermediate, which underwent ring closure to give an α-hydroxy phosphorane not observed in the reaction mixture, however obviously, deoxygenated rapidly by an excess of **XIb** to form compound **45**. Hydrolysis ($H_2O$–EtOH) cleaved the phosphole ring furnishing the γ-hydroxy phosphonate **46** (Scheme 18) [35]. A similar pathway was found when 2-trifluoroacetyl phenol was allowed to react with trimethyl phosphite [34]. If compound **46** was recrystallized from ethanol, the solvent added to the ε-keto function yielding phosphonate **47** whose molecular structure was established (Fig. 4) [35].

1,1′-(2-Trimethylsiloxy-5-methyl-*m*-phenylene)-bis-ethanone **XX** [35] and the phosphites **XIb** and **XIc** surprisingly produced the liquid phosphono phospholes **48b** and **48c**. No deoxygenation was observed [35]. The precursor intermediate for **48** could be a bisphosphonate (Scheme 19).

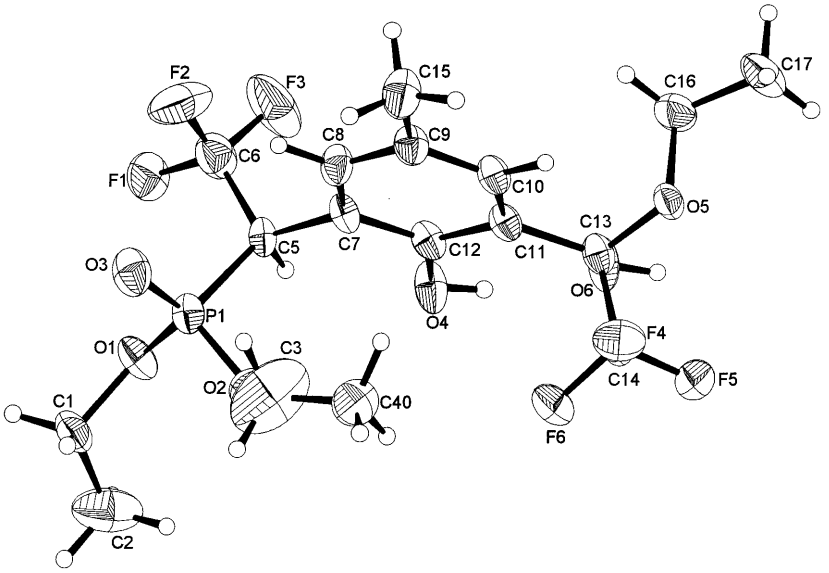
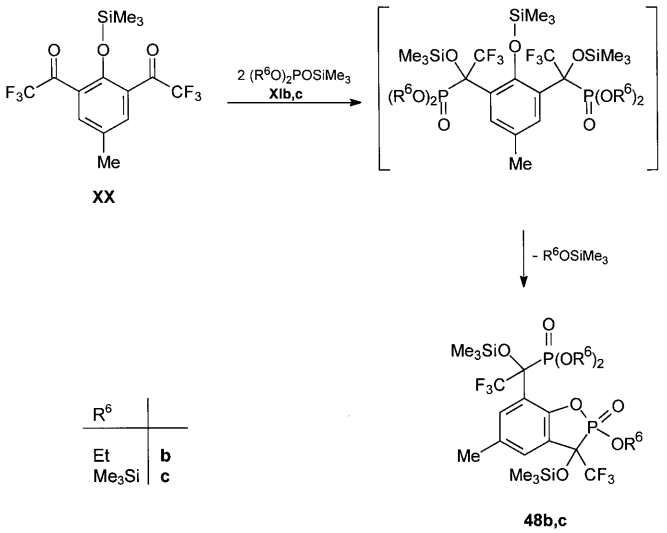



Fig. 4. Molecular structure of 1-[2′-hydroxy-3′-(2″, 2″, 2″-trifluoroethanone)-5′-methylphenyl]-2,2,2-trifluoroethyldiethylphosphonate (**47**) [35]; by permission of Dr E. Lork.

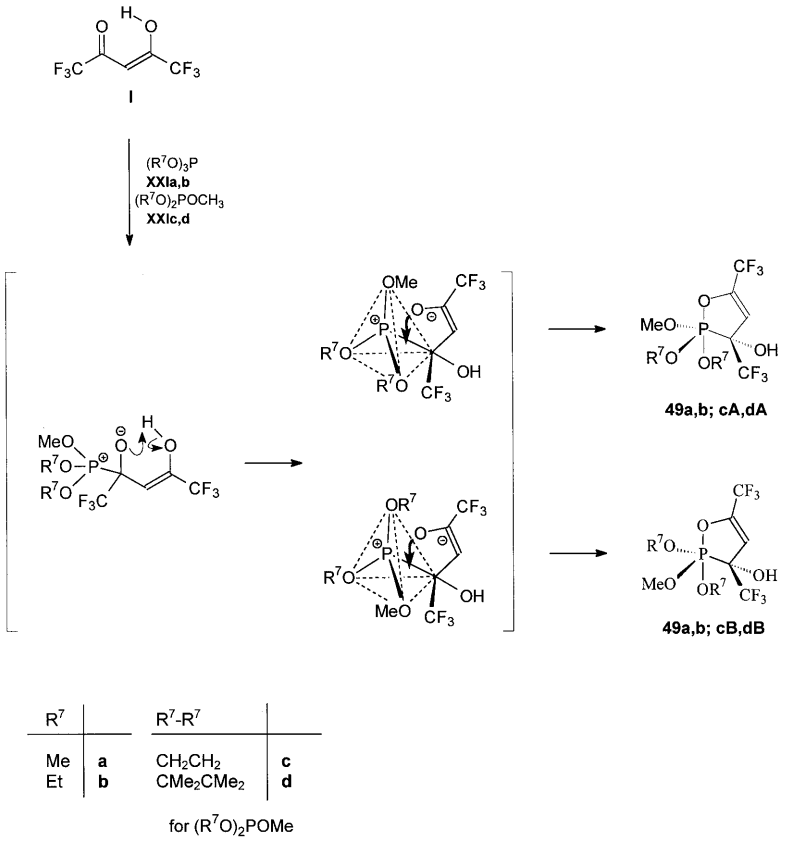



Scheme 19.

## 6. Reactions of trialkylphosphites

### 6.1. 1,1,1,5,5,5-Hexafluoropentan-2,4-dione

The triethylphosphite $(R^7O)_2POEt$ **XXIb** ($R^7 = Et$), and (*Z*)-1,1,1,5,5,5-hexafluoro-2-hydroxy-2-penten-4-one, the tautomer of **I**, were found to furnish triethylphosphate and 2,4-bis(trifluoromethyl)-3-oxetanol via a phosphorane containing a six-membered ring system, stable only at low temperature [36]. However, for $(R^7O)_2POEt$ **XXIe** ($R^7$–$R^7 = CMe_2CMe_2$) a spirocyclic system, 5-ethoxy-2,2,3,3-tetramethyl-7,9-bis(trifluoromethyl)-1,4,6-trioxa-5$\lambda^5\sigma^5$-phosphaspiro-[4.4]non-7-en-9-ol (**49g**) was obtained featuring the 3-hydroxy-3,5-bis(trifluoromethyl)-1,2$\lambda^5\sigma^5$oxaphospholene structural element and moreover, consisting of two diastereomers **A** ($\delta_P = -22$) and **B** ($\delta_P = -25$) (**A**:**B** = 1:1) (also see Scheme 20) [36]. Upon reinvestigation of the reaction [37] with the trialkylphosphites $(R^7O)_3P$ **XXI** ($R^7 = Me$ (**a**), $R^7 = Et$ (**b**)) and $(R^7O)_2POMe$ **XXI** ($R^7$–$R^7 = CH_2CH_2$ (**c**), $R^7$–$R^7 = CMe_2CMe_2$ (**d**)) in all cases the 3-hydroxy-3,5-bis(trifluoromethyl)-1,2$\lambda^5\sigma^5$-




Scheme 20.

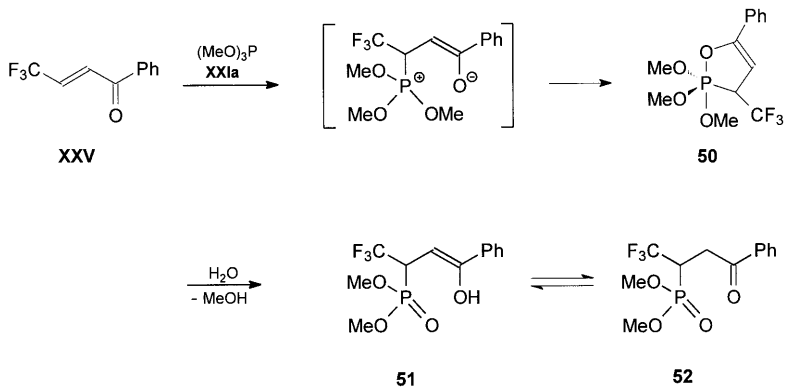
oxaphospholenes (**49a**–**d**) were obtained (Scheme 20), but 2,2,2-trimethoxy- (**49a**) and 3,3,3-triethoxy-3-hydroxy-3,5-bis(trifluoromethyl)-1,2$\lambda^5\sigma^5$-oxaphospholene (**49b**) decomposed above −80°C (**49a**) and −90°C (**49b**), respectively, without formation of 2,4-bis(trifluoromethyl)-3-oxetanol, mentioned above. Phosphorane **49c** was stable up to −10°C, two diastereomers **A** und **B** (**A**:**B** = 3:1) were observed. The same isomeric ratio was found for **49dA** and **49dB**, a solid stable at ambient temperature (Scheme 20).

The formation of the phospholenes could be rationalized by assuming a nucleophilic attack of phosphorus at the keto carbon of **I**. After a 1,5 proton shift the enolate oxygen in its turn attacked phosphorus nucleophilically, probably through one tetrahedral face (Scheme 21). Two diastereomers were observed due to hindered pseudo-rotation of the substituents in the trigonal-pyramidal geometry [12].

### *6.2. (E)-1,1,1-Trifluoro-4-phenyl-but-2-en-4-one*

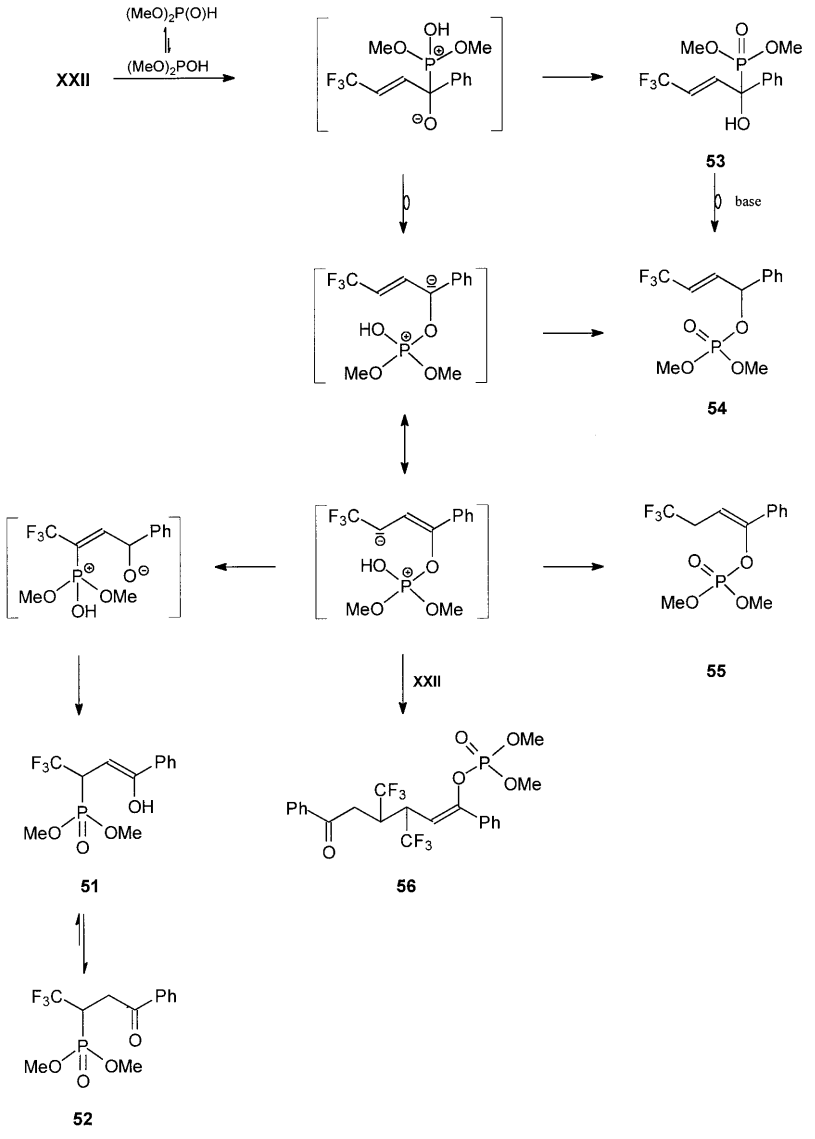
(*E*)-1,1,1-Trifluoro-4-phenyl-but-2-en-4-one (**XXII**) [38] and trimethylphosphite **XXIa** reacted to form the moisture-sensitive liquid 1,2$\lambda^5\sigma^5$-oxaphosphol-4-ene **50** as sole product in near quantitative yield (Scheme 21). Since compound **XXII** exists as a pure *trans*-isomer ($^3J_{HH} = 15.57$ Hz) only *one* isomer of compound **50**, was obtained stereoselectively in a [4 + 1] addition, and the initial attack of phosphorus is at the β-carbon atom with subsequent ring closure. When water was added the enolic form **51** of the resulting ketophosphonate **52** was produced [39].

If the reaction of ketone **XXII** and **XXIa** was carried out in a small amount of wet benzene, dimethylphosphite **Xa** was apparently formed by hydrolysis and additional products were observed. The reaction afforded, along with **50** and **52**, probably phosphonate **53** ($\delta_P = 33.3$), as a result of a 1,2-addition of $(MeO)_2P(O)H$. Phosphates **54**, **55**, **56A** and **56B** (two diastereomers of the derivative of an unknown 1,6-diketone) surprisingly obtained as solids, were probably the products of a phosphite mediated reductive C–C bond formation (head-to-head attack)

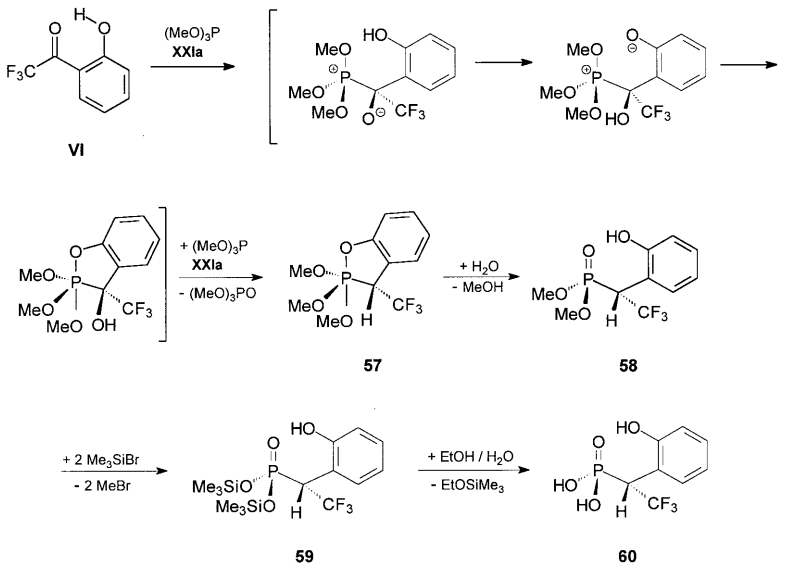



Scheme 21.

(Scheme 22) [39]. A comparable pathway was observed upon reaction of dialkyl phosphites with non-fluorinated α,β-unsaturated ketones where a head-to-tail attack occurs [40]. The possible mechanism (see Scheme 22) for the reaction of dimethyl phosphite and the unsaturated ketone implied a nucleophilic attack of $(MeO)_2POH$, tautomer of $(MeO)_2P(O)H$ (**Xa**), to give an intermediate, followed by 1,4-prototropy producing phosphonate **53**. Rearrangement of this intermediate




Scheme 22.




Scheme 23.

resulted in a 1,3-dipolar system undergoing a 1,4-proton shift to produce the allyl phosphate **54**. The same compound can be obtained by a base-catalyzed rearrangement from **53**. The 1,3-dipolar system, after rearranging to a 1,5-dipolar intermediate gave rise to the formation of phosphate **56** when additional **XXII** was involved.

### *6.3. 2-Trifluoroacetyl phenol*

Results similar to the reaction of 1,1′-(2-hydroxy-5-methyl-*m*-phenylene)-bis-ethanone (**XIX**) with diethyltrimethylsilyl phosphite (**XIb**) described in 4.3 were obtained in the case of trimethylphosphite (**XXIa**) and 2-trifluoroacetyl phenol (**VI**) [34], where not the expected α-hydroxyphosphorane was found but its deoxygenated analogue, namely phosphorane **57**, a colourless liquid, easily hydrolyzed to yield phosphonate **58**, which, in turn, could be converted into the trimethylsilylated derivative **59**, precursor of the final phosphonic acid **60** (Scheme 23).

## 7. Reactions of dialkylisocyanato phosphites

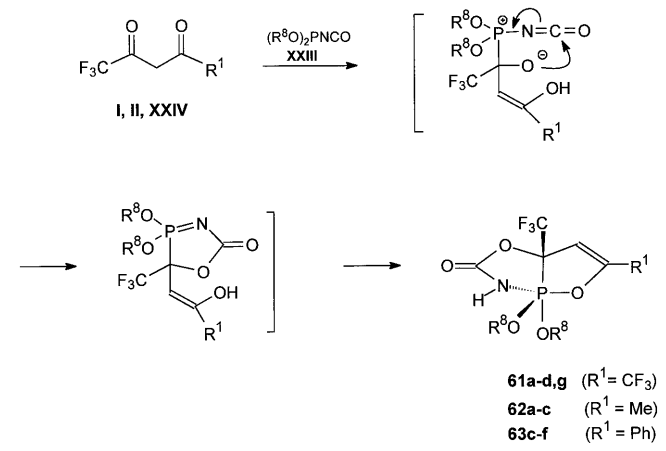
### *7.1. 1,1,1,5,5,5-Hexafluoro- and 1,1,1-trifluoropentan-2,4-dione, 4,4,4-trifluoro-1-phenylbutan-1,3-dione*

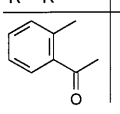
Bicyclic $\lambda^5\sigma^5$-phosphoranes **61a**–**d** [41,42], **61g** ($R^1 = CF_3$) [43], **62a**–**c** ($R^1 = Me$) [41,42], **63c**–**f** ($R^1 = Ph$) [42], colorless moisture sensitive solids, were obtained from

the *iso*cyanatophophites **XXIII** $(R^8O)_2PNCO$ [$R^8$ = Me (**a**), Et (**b**); $R^8$–$R^8$ = $CH_2CH_2$ (**c**), $CMe_2CMe_2$ (**d**), $CH(Me)CH_2CH_2$ (**e**), $CF_2CF_2CF_2H$ (**f**), 1,2-$C_6H_4C(O)$ (**g**)] and the β-diketones **I**, **II** and 4,4,4-trifluoro-1-phenylbutan-1,3-dione (**XXIV**). A double cycloaddition process is in effect, apparently involving in the β-diketones (*Z*)-keto enol tautomeric forms (Scheme 24) [41,42]. The equatorial–axial–equatorial arrangement of the bicyclic system, a 4,8-dioxa-2-aza-1$\lambda^5\sigma^5$-phosphabicyclo[3.3.0]-oct-6-en-3-one, was confirmed by X-ray structure analysis for **61d** and **62a** [42]. The trigonal-bipyramidal structure in solution with carbon in axial position could be derived from the typical $^1J_{PC}$ values [42]. The ambient $^1$H-, $^{13}$C-NMR spectra clearly show that pseudo-rotation processes were slow on the NMR time scale and that, therefore the axial and equatorial substituents $OR^8$ can easily be distinguished. Only one diastereomer is present, confirmed also by $^{19}$F- and $^{31}$P-NMR spectra (Scheme 24) [41,42].

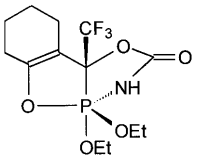
### *7.2. 2-Trifluoroacetyl cyclohexanone*

In the reaction of $(EtO)_2PNCO$ (**XXIIIb**) with 2-trifluoroacetyl cyclohexanone (**XIII**) in a similar pathway (see Section 6.1) gave phosphorane (**64b**) (Scheme 25) [30].



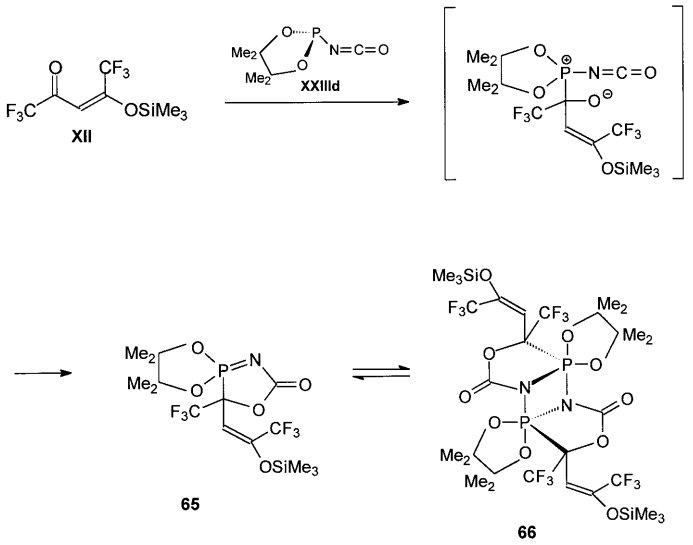

| $R^1$ | | $R^8$ | | $R^8$- $R^8$ | | $R^8$ - $R^8$ | |
|---|---|---|---|---|---|---|---|
| $CF_3$ | **I** | Me | **a** | $CH_2CH_2$ | **c** |  | **g** |
| Me | **II** | Et | **b** | $CMe_2CMe_2$ | **d** | | |
| Ph | **XXVII** | $HCF_2CF_2CH_2$ | **f** | $CHMeCH_2CH_2$ | **e** | | |

Scheme 24.



64b

Scheme 25.



Scheme 26.

### 7.3. (E)-1,1,1,5,5,5-Hexafluoro-4-trimethylsiloxy-3-penten-2-one

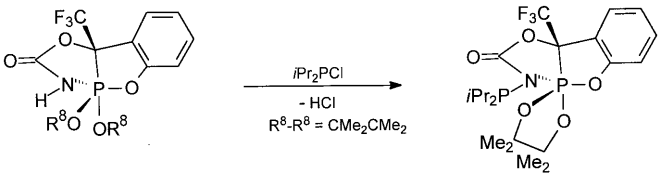
Compound **XXIIId** $(R^8O)_2PNCO$ [$R^8$–$R^8 = CMe_2CMe_2$ (**d**)] reacted with (*E*)-1,1,1,5,5,5-hexafluoro-4-trimethylsiloxy-3-penten-2-one (**XII**), the trimethylsiloxy derivative of **I**, no double cycloaddition was possible due to its (*E*)-configuration. In this case, however, a cyclic spiroiminophosphorane **65** was obtained which underwent a [2 + 2] cyclodimerization to form a diazadiphosphetidine **66** (Scheme 26) [44].

### 7.4. 2-Trifluoroacetyl phenol and its imino derivatives

From 2-trifluoroacetyl phenol **VI** and the *iso*cyanatophophites (**XXIII**) $(R^8O)_2PNCO$ [$R^8$ = Me (**a**), Et (**b**); $R^8$–$R^8 = CH_2CH_2$ (**c**), $CMe_2CMe_2$ (**d**)] phosphoranes **67a**–**d** with similar structural features were analogously obtained (see Sections 6.1 and 6.2) [45] (Scheme 27). In the case of **67d** the NH function showed

reactivity towards di*iso*propyl phosphinous acid chloride *i*-$Pr_2PCl$ to yield the *N*-substituted phosphorane **68** [$\delta_P = -27.9$ ($\lambda^5$P), $\delta = 101.0$ ($\lambda^3$P)] (Scheme 27).

The reaction of the ketimines **VII–IX** and the isocyanato phosphite **XXIIId** analogously also produced phosphoranes **69–71** (Scheme 28) [35], containing the two anellated five-membered rings with a 2,4-diaza-8-oxa instead of a 2-aza-4,8-dioxa system, however if **XXV** ($R^8 = CH_2CH_2NMe_2$) was used as one component, the formation of the bicyclic ring system was prevented and only the addition of the HO group to the OCN moiety was observed, yielding the amido phosphite **72** ($\delta_P = 137.5$) with a urethane grouping (Scheme 28) [35].

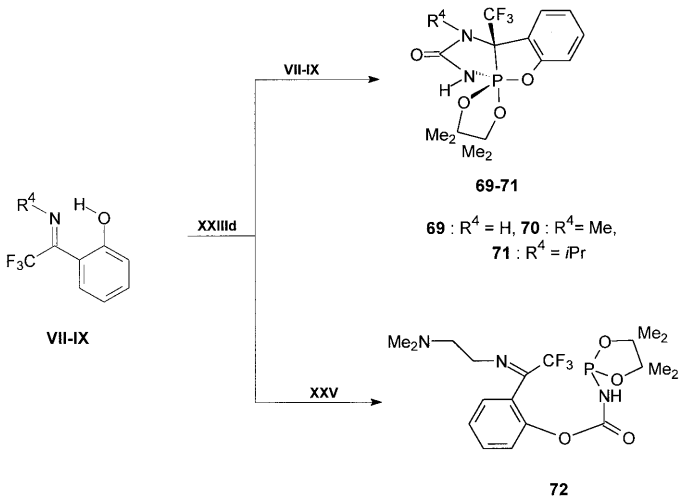



67a-d

68d

| $R^8$ | | $R^8$-$R^8$ | |
|---|---|---|---|
| Me | **a** | $CH_2CH_2$ | **c** |
| Et | **b** | $CMe_2CMe_2$ | **d** |

Scheme 27.

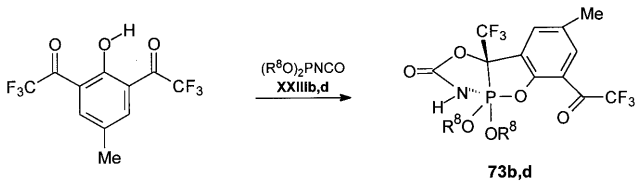



69-71

**69** : $R^4$ = H, **70** : $R^4$ = Me,
**71** : $R^4$ = *i*Pr

72

Scheme 28.




Scheme 29.

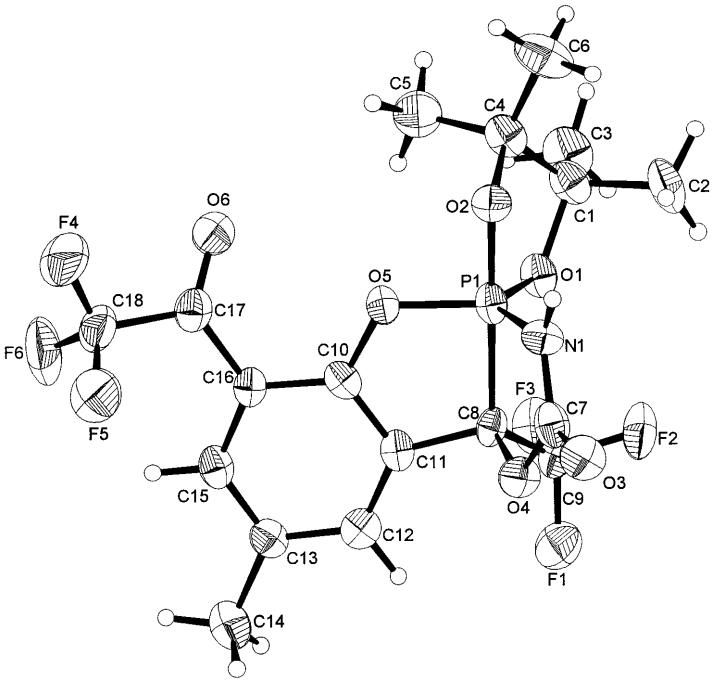



Fig. 5. Molecular structure of 1,1-(3′,3′,4′,4′-tetramethylenedioxy)-5-trifluoromethyl-6,7-benzo-10-methyl-12-(2″,2″,2″-trifluoroethane-1″-one)-4,8-dioxa-2-aza-1-$\lambda^5\sigma^5$-phosphabicyclo[3.3.0]oct-6-en-3-one **73d**; [35] by permission of Dr E. Lork

### *7.5. 1,1′-(2-Hydroxy-5-methyl-m-phenylene)-bis-ethanone*

Reaction of the isocyanato phosphites **XXIIIb,d** with 1,1′-(2-hydroxy-5-methyl-*m*-phenylene)-bis-ethanone **XIX** resulted in the formation of two phosphoranes **73b** and **73d** similar to those described in 6.1–6.4 (Scheme 29, Fig. 5). Surprisingly, at the additional $CF_3CO$ function no further attack of **XXIIIb,d** was observed [35].

## 8. Reactions of dimethyl-propynyl phosphonite with 1,1,1,5,5,5-hexafluoro pentan-2,4-dione

Dimethylpropynyl phosphonite (**XXVI**) and pentandione (**I**) yielded diastereoselectively the crystalline bisphosphorane, 1,4-bis(trifluoromethyl)-3,6-dioxa-2,2,7,7-tetramethoxy-2,7-di(1-propynyl)-2,7-diphosphabicyclo[2.2.1]heptane **74** containing a bicyclic ring system with two five membered rings [46]. The structure was confirmed by $^{1}H\{^{31}P\}$- and $^{13}C$-NMR spectra (Scheme 30).

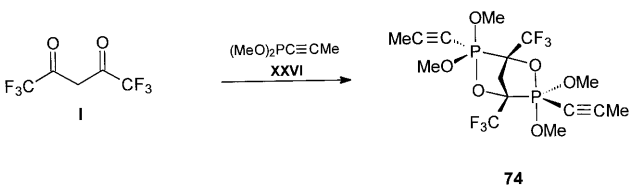
## 9. Reactions of trimethylsilyl-phosphenimidous acid bis-trimethylsilylamide

### *9.1. 1,1,1,5,5,5-Hexafluoro- and 1,1,1-trifluoropentan-2,4-dione, (E)-1,1,1,5,5,5-hexafluoro-4-trimethylsiloxy-3-penten-2-one*

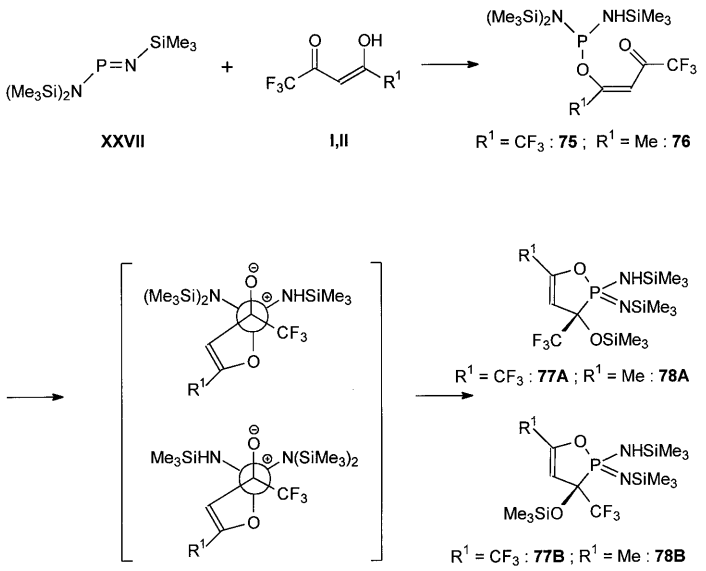
The reaction of the aminoimino phosphine, $Me_3SiN{=}PN(SiMe_3)_2$ (**XXVII**) and 1,1,1,5,5,5-hexafluoro- **I** and 1,1,1-trifluoropentan-2,4-dione (**II**) furnished a diastereomeric mixture of the 2-imino-1,2$\lambda^5\sigma^4$-oxaphospholenes **77A,B** and **78A,B** (**A**:**B** = 5:1). The first step was a 1,2-addition of the enolic HO group to the P=N bond to give the amido phosphites **75** and **76**, where phosphorus attacked the electrophilic keto carbon closing the ring, yielding two possible diastereomeric 1,3-dipolar transition states. After 1,4 trimethylsilyl shifts two diastereomers for each pentandione were formed, the products were characterized by their $^{1}H$-, $^{13}C$-, $^{19}F$- and $^{31}P$-NMR spectra (Scheme 31) [47].

A different pathway, possibly a [1 + 4] cycloaddition was probably in effect when $Me_3SiN{=}PN(SiMe_3)_2$ (**XXVII**) and (*E*)-$CF_3C(O)CH{=}C(OSiMe_3)CF_3$ (**XII**), furnished the two diastereomeric 2-imino-1,2$\lambda^5\sigma^4$-oxaphospholenes **79A,B** (**A**:**B** = 1:1) (Scheme 32) [47].

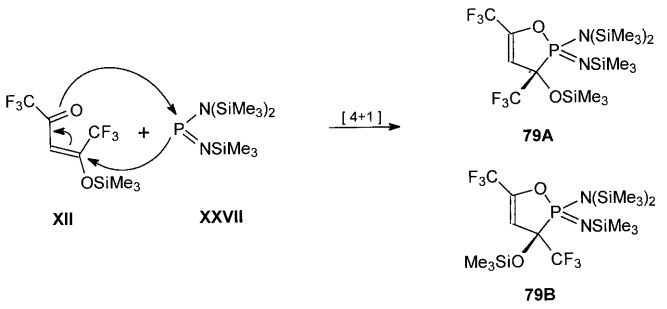
The phospholenes **77A,B**–**79A,B** underwent a non-concerted [2 + 2] cycloaddition reaction at the P=N bond with hexafluoroacetone via a 1,4 dipole to give one stereoisomer only, namely the 1,3,2$\lambda^5\sigma^4$-oxazaphosphetanes **80**–**82**, whose molecular structures in the case of **80** and **81** were determined by X-ray diffraction [47]. Two transition states are possible, in which the hexafluoroacetone oxygen attacked different sites probably for steric reasons (to avoid the contact with the $OSiMe_3$ groups), either the tetrahedral front or back face (Scheme 33).




Scheme 30.




Scheme 31.



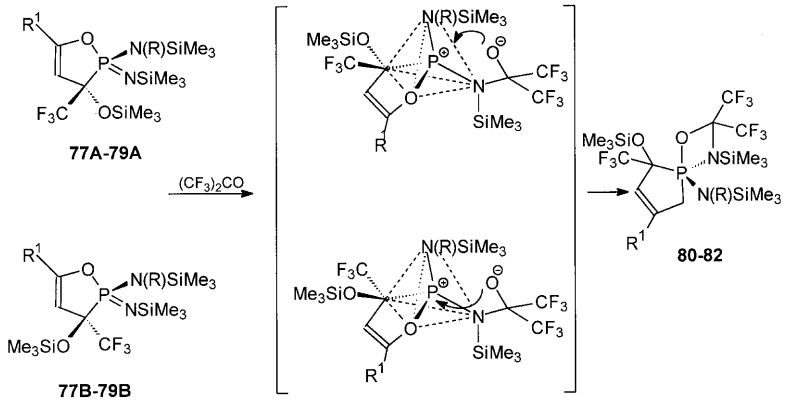

Scheme 32.

### 9.2. 2-Trifluoroacetyl cyclopentanone

For 2-trifluoroacetyl cyclopentanone (**XXVIII**) and compound **XXVII** like for the fluoro 2,4-pentanediones **I** and **II** two diastereomers, **A** and **B** (**A**:**B** = **10:3**), of the 1,2$\lambda^5\sigma^4$-oxaphospholene (**83**) were obtained and isolated yielding the 1,3,2$\lambda^5\sigma^5$-oxazaphosphetane (**84**) upon addition hexafluoroacetone (Scheme 34) [30].

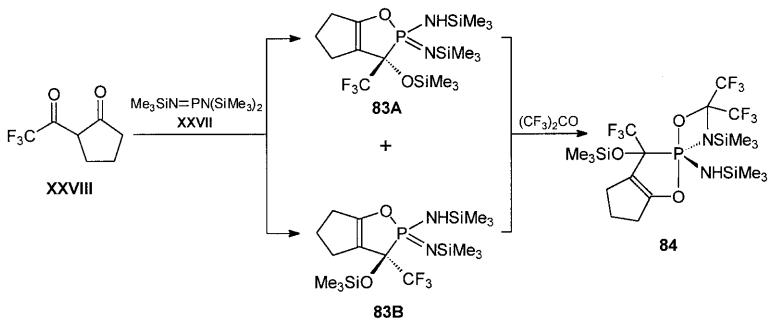
### 9.3. 2-Trifluoroacetyl phenol and its imino derivatives

When 2-trifluoroacetyl phenol (**VI**) was allowed to react with **XXVII** two diastereomers, **A** and **B** (**A**:**B** = 5:1), of the 1,2$\lambda^5\sigma^4$-oxaphospholene (**85**) were found (Scheme 35) [49]. Hexafluoroacetone and **85** gave the 1,3,2$\lambda^5\sigma^5$-oxazaphosphetane (**86**) (Scheme 35).

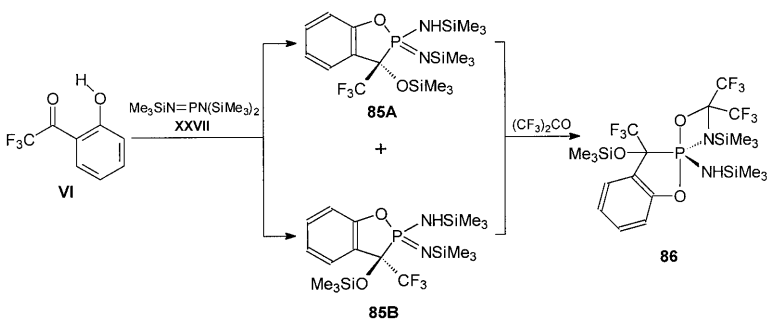



R = H, $R^1$ = $CF_3$ : **77, 80**
R = H, $R^1$ = Me : **78, 81**
R = $SiMe_3$, $R^1$ = $CF_3$ : **79, 82**

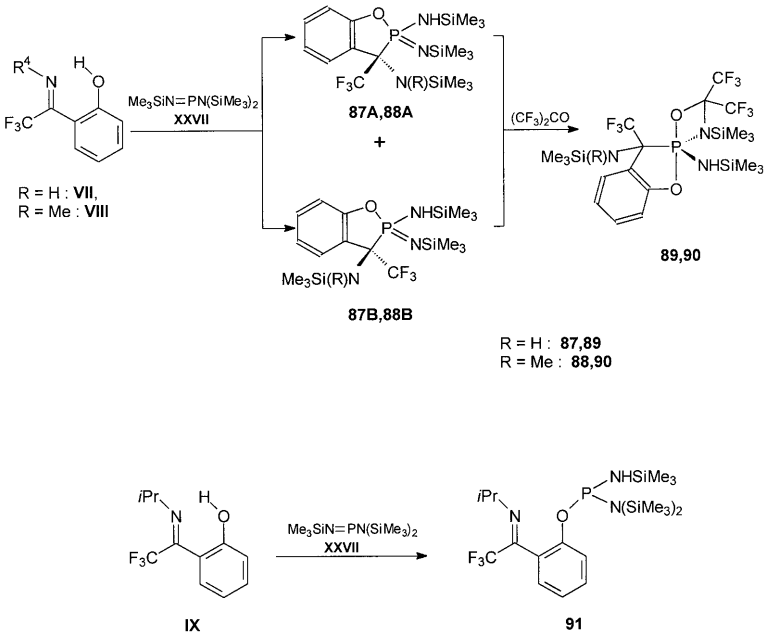
Scheme 33.




Scheme 34.




Scheme 35.




Scheme 36.

The imine derivatives **VII** ($R^4 = H$) and **VIII** ($R^4 = Me$) gave the $1,2\lambda^5\sigma^4$-oxaphospholenes **87A,B** (**A**:**B** = **5**:**1**) and **88A,B** (**A**:**B** = 2:1) in analogy to **VI** (Scheme 36) [35]. Hexafluoroacetone again yielded the $1,3,2\lambda^5\sigma^5$-oxazaphosphetanes **89** and **90**. From **IX** ($R^4 = i$-Pr) the amidophosphite **91** was isolated and characterized being the stable representative of the first step intermediate in the interaction of fluorinated keto enols with **IX**; the ring closure was prevented, probably because of the steric influence of the relatively bulky isopropyl group [35].

## 10. Conclusions

Phosphorus derivatives, $PH_3$, $H_2P(CH_2)_nPH_2$, $RPCl_2$, $(RO)_2P(O)H$, $(RO)_3P$, $(RO)_2POSiMe_3$, $(RO)_2PNCO$ and $Me_3SiN{=}PN(SiMe_3)_2$, reacted with trifluoromethylated 1,3-diketones, ketoenols, 2-trifluoroacetyl phenols and their derivatives to give acyclic, mono-, bi- and tricyclic $\lambda^3\sigma^3P$, $\lambda^5\sigma^4P$, $\lambda^5\sigma^5P$ systems containing HP, HO, C=O, C=C and NH functionalities. The large variety of products show the versatility of the keto reagents in phosphorus organic chemistry where the presence of the $CF_3$ group influences the reaction pathway and offers an additional NMR-spectroscopical probe. In several cases compounds were formed diastereospecifically, e.g. from 1,1,1-trifluoro-2,4-pentanedione phosphine or diprimary phosphines bulky secondary phosphines, phosphaadamantanes were obtained with more than three chiral centers, which can be used as ligands in coordination

chemistry for possible catalysts [1b]. Trifluoromethylated $\lambda^5\sigma^4$P ring systems with additional exocyclic HO and $Me_3SiO$ groups, namely 1,2$\lambda^5\sigma^4$P-oxaphospholanes and -oxaphospholenes are useful buildings blocks in organic chemistry and potentially biological active compounds like the α-hydroxy and α,γ-dihydroxyphosphonates [50]. The latter could be considered transition state mimics for enzymatic ester hydrolysis whereas the tricyclic $\lambda^5\sigma^5$ phosphoranes are either models for phosphoric ester hydrolysis intermediates [51] or precursor for monocyclic 1,2$\lambda^5\sigma^4$P-oxaphospholanes. The investigations reviewed here should be extended to 1,3-diketones and ketoenols with longer poly or perfluorinated chains what would allow more insights into the mechanistic features and offer further products with unusual properties.

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