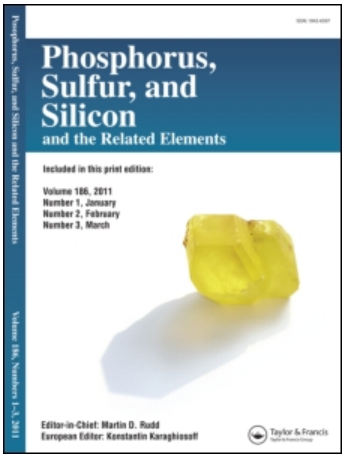

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PHOSPHITES AND HEXAFLUOROACETONE-HEXAFLUOROACETYLACETONES: A COMPARISON

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Abstract Selected acyclic and cyclic phosphites $(RO)_2PX$ (1-5) were reacted with activated ketones $(CF_3)_2CO$ (6) and $Z\text{-}CF_3C(O)CH{=}C(OH)CF_3$ (7a) / $E\text{-}CF_3C(O)CH{=}C(OSiMe_3)CF_3$ (7b) in order to study the influence of R and X on the product formation. A new type of insertion, a 1,4 group shift and cycloaddition reactions yielding five membered rings and bicyclic fused systems were observed. In most cases phosphonates and their $\lambda^5\sigma^5$ P derivatives were obtained. The ketones in question can be considered versatile reactants in phosphorus chemistry.

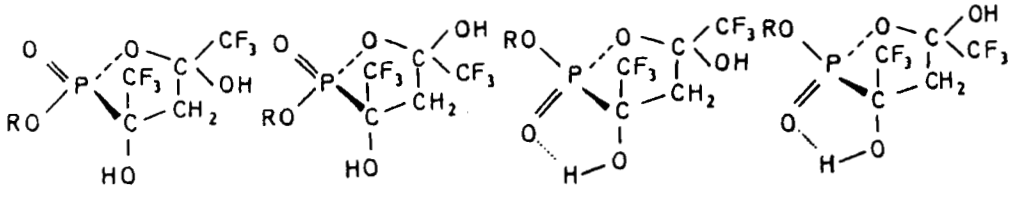
INTRODUCTION

The alkylphosphites $(RO)_2PX$ [X = Cl (1), OH (2)[1], OMe (3), $OSiMe_3$ (4), NCO (5); R = Me (a), Et (b), R-R = CH_2-CH_2 (c), CMe_2CMe_2 (d)] were allowed to interact with hexafluoroacetone (6) (1,1,1,3,3,3-hexafluoropropane-2-one) and the enol 7a (Z-1,1,1,5,5,5-hexafluoro-4-hydroxy-3-pentene-2-one) or its O-silylated derivative 7b (E-1,1,1,5,5,5-hexafluoro-4-(trimethylsiloxy)-3-pentene-2-one) to investigate their electrophilic or nucleophilic capacity. In some cases reactions had to be reinvestigated.

It is known that chlorophosphite **1b** and ketone **6** yielded a chlorophosphorane in an oxidative addition reaction followed by a loss of ethylchloride and formation of a cyclic phosphate.[2] An important side reaction had been overlooked. Compounds **1a** and **1b** formed the insertion products $(RO)_2POC(CF_3)_2Cl$ (**8a, b**) in high yield at -40 °C besides the expected chlorophosphoranes probably via a radical mechanism. The cyclic phosphites **1c** and **1b** did not furnish cycloaddition products but only compounds **8c** and **8d** which were much more stable than **8a** and **8b**. In an Arbuzov reaction compounds **8** were converted by **3a** to give either

phosphates $(MeO)_2P(O)OC(CF_3)_2P(OR)_2$ (R = Me, Et) or phosphonates $(MeO)_2P(O)C(CF_3)_2OP(OR)_2$ (R-R = CH_2CH_2, CMe_2CMe_2). Similar experiments were carried out with 1 and **7a/7b** where the enol functions $CH=C(OH)CF_3/CH=C(OSiMe_3)CF_3$ were involved.[3]

The dialkylphosphites **2a** and **2b** producing **6** to furnish the phosphonates $(RO)_2P(O)C(CF_3)_2OH$ which rearranged in the presence of base yielding the phosphates $(RO)_2P(O)OCH(CF_3)_2$.[4,5] The respective phosphonates could be converted into the corresponding phosphate thermally, too. Ketone **7a** also gave phosphonates, chiral compounds $(Z)-(RO)_2P(O)C(CF_3)(OH)CH=C(OH)CF_3$ (**9a,b,d**). Slowly **9a**, but rapidly **9b** and **9d** rearranged to yield the keto tautomers $(RO)_2P(O)C(CF_3)(OH)CH_2-C(O)CF_3$ (**10a, b, d**) which underwent ring closure reaction via nucleophilic attack of the keto-oxygen at phosphorus and alkoxide migration to give rise of four diasteromeric oxaphospholanes **11a** and **11b**:



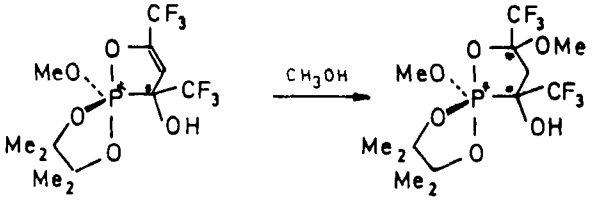
11a and 11b

Using long-range F-F coupling information and retention time measurements from column chromatography a nmr signal-molecular structure assignment could be achieved.

Ketone **6** converted phosphites **3a - d** into the $1,3,2\lambda^5\sigma^5$-dioxaphospholanes $(RO)_2(MeO)P[OC(CF_3)_2C(CF_3)_2O]$ (**12a**[6], **12b**[7], **12c, 12d**). In the case of **3c** two isomers were obtained, **12c** and the $1,3,4\ ^5\sigma^5$ species which has a rigid geometry around phosphorus at room temperature and showed extensive F-F "through space" coupling.

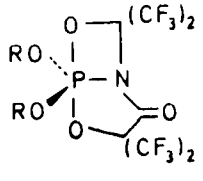
The same trialkylphosphites reacted with **7a** yielded $\lambda^5\sigma^5$-oxaphospholenes **13a - d**. Compounds **13a** and **13b** were stable only below -80 °C, but could be characterized spectroscopically. No product was found due oxygen abstraction from **7a**.[8] The spirocyclic phospholenes **13c** and

13d were reasonable stable at room temperature. Methanol was added to **13d** giving the oxaphospholane **14d** representing four diastereomers, because of three chiral centres in the molecule:



13d **14d**

A 1,4-trimethylsilyl group shift[9] was observed in the reaction of **4a-d** with **6** and **7b** giving the phosphonates $(RO)_2P(O)C(CF_3)_2OSiMe_3$ and E-$(RO)_2P(O)C(CF_3)(OSiMe_3)CH=C(OSiMe_3)CF_3$ respectively which hydrolyzed to form the Z-phosphonates **9a - d**. In the case of **6** also cyclo addition took place resulting in the formation of trimethylsiloxy-phosphoranes which were thermally stable in the case of **4c** and **d**. The isocyanato derivatives **5a** and **5b** added **6** in a (3+2) and (2+2) cyclo-addition furnishing the bicyclic system **15**.[10,11]



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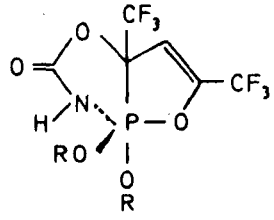
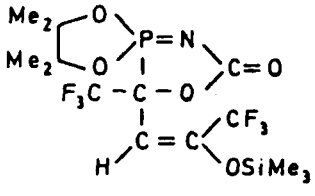
However, **7a** reacted with **5a - d** to yield the bicyclic ringsystems **16a - d** with a direct P-C bond. Here also a (3+2) process gave rise to form an intermediate containing a P=N double bond across which the Z-orientated HO-group added in a (2+2) fashion.[12] The molecular structure of **16a - d** was determined by x-ray analysis and nmr spectroscopy. Carbon is unequivocally in apical position in a slightly distorted trigonal bipyramide:



16

Starting from the E-isomer **7b** and phosphite **5d** the (3+2) addition product **17d** could be observed at high temperature, whereas at ambient temperature (2+2) dimerization occurred to give a diazadiphosphetidine.



17d

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