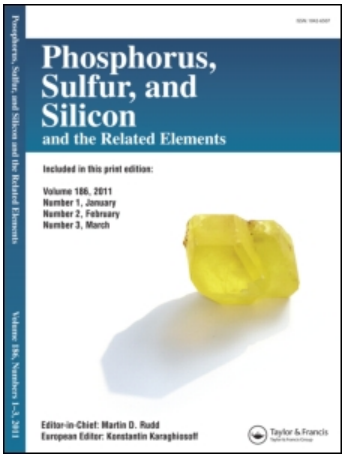

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A FLUORO α,β- AND α,ε-DIKETONE. SYNTHONS FOR PHOSPHORUS AND TIN CONTAINING RING SYSTEMS

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Selected phosphorus(III) compounds, $PR^1R^2R^3$ was added to the 1,1,1,4,5,5,5-heptafluoro-4-(trifluoro-methyl)-2,3-pen-tanedione oxidatively to give new 1,3,2$\lambda^5\sigma^5$-dioxaphospholenes, including the first $\lambda^5\sigma^5$-phosphorane with an OCN group bonded to phosphorus. In the case of $SnCl_2$ or $Sn[N(SiMe_3)_2]_2$ the respective $\lambda^4\sigma^4$-dioxastannolenes were found. Allowing the 2,6-bis(trifluoroacetyl)-4-methyl-phenol to react with $PR^1R^2R^3$ bicyclic $\lambda^5\sigma^5$P species and cyclic phosphonates were obtained.

Keywords: 1,1,1,4,5,5,5-Heptafluoro-4-(trifluoromethyl)-2,3-pentanedione; 2,6-bis(trifluoroacetyl)-4-methylphenol; 1,3,2$\lambda^5\sigma^5$-dioxaphospholenes; $\lambda^4\sigma^4$-dioxastannolenes; phosphorus(III) compounds;

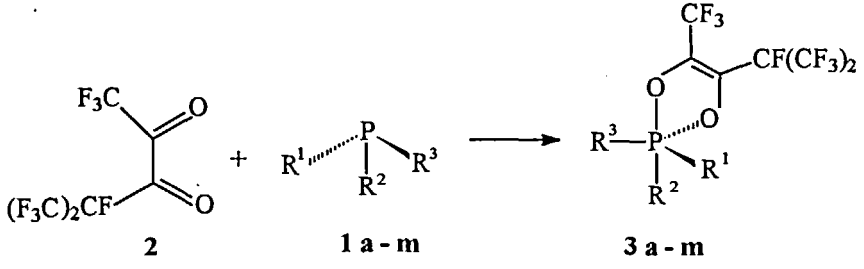
INTRODUCTION

Several examples for the oxidative addition of 1,1,1,4,4,4-hexafluoro-2,3-butanedione to phosphorus(III) derivatives[1 - 4], are known to furnish 1,3,2$\lambda^5\sigma^5$-dioxaphospholenes. Less information is available for

1,1,1,4,5,5,5-heptafluoro-4-(trifluoromethyl)-2,3-pentanedione[5 - 7]. Bis(trifluoromethyl) α,β-unsaturated ketones and $SnCl_2 2H_2O$ yielded 1,2-oxastannolenes in a [4+1] cycloaddition reaction[8]. Dibutyl stannylene, photolytically generated could be trapped using benzil or biacetyl to form the corresponding 1,3,2-dioxastannolenes[9]. The new α,ε-diketone, 2,6-bis(trifluoro-acetyl)-4-methylphenol, was expected to form ring sytems with selected phosphites.

RESULTS AND DISCUSSION

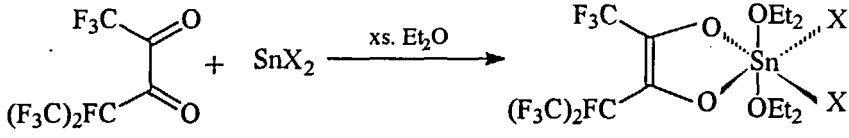
The phosphorus(III) compounds, $PR^1R^2R^3$, **1** [$R^1 = CF_3$, $R^2 = R^3 =$ Me (**1a**), *i*Pr (**1b**), NEt_2 (**1c**); $R^1 = NCO$, $R^2 = R^3 =$ OMe (**1d**), OEt (**1e**), R^2–$R^3 = OCH_2CH_2O$ (**1f**), $OCMe_2CMe_2O$ (**1g**); $R^1 = OSiMe_3$, $R^2 = R^3 =$ OEt (**1h**); $R^1 = NEt_2$, $R^2 = R^3 = OCH_2CF_3$ (**1i**); $R^1 = R^2 = Et_2N$, $R^3 = OCH_2CF_3$ (**1j**), $OCH(CF_3)_2$ (**1k**), OCH_2Ph (**1l**), OC_6F_5 (**1m**)] were reacted with 1,1,1,4,5,5,5-heptafluoro-4-(trifluoro-methyl)-2,3-pentane-dione (**2**) to yield 1,3,2$\lambda^5\sigma^5$-dioxaphospholenes **3a - m**. (SCHEME 1). There was no further interaction of the isocyanato group in **1d - g** with the α,β-diketone.



2 **1 a - m** **3 a - m**

SCHEME 1

Diketone **2** oxydized anhydrous tin(II) chloride to give the yellow 2,2-dichloro-4-trifluoromethyl-5-hepta-fluoroisopropyl-1,3,2-dioxa-stannolene (82 % yield) which is acidic enough to add two molecules of diethyl ether (SCHEME 2). Like other tin(IV) etherates, it decomposed under loss of the coordinated diethyl ether at 62°C. The corresponding dioxastannolene was found in the case of $Sn[N(SiMe_3)_2]_2$ (92% yield).

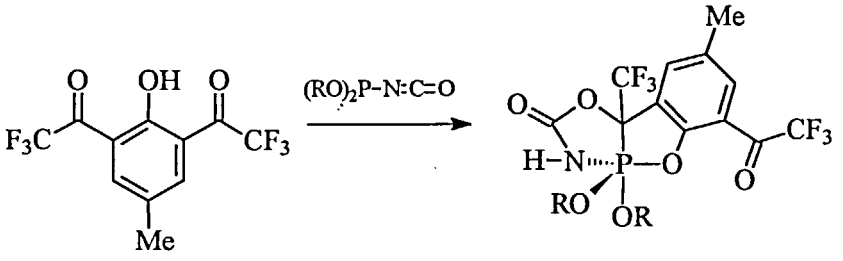


2

4: X = Cl , **5:** X = $N(SiMe_3)$

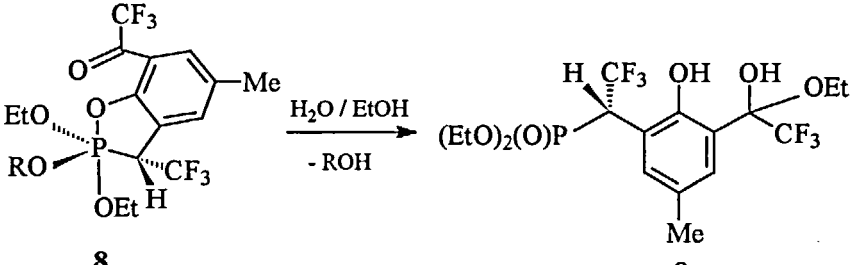
SCHEME 2

2,6-Bis(trifluoroacetyl)-4-methylphenol (**6a**) and phosphites **1e** and **1g** reacted to furnish bicyclic $\lambda^5\sigma^5$ phosphoranes **7e** and **7g** (SCHEME 3); using phosphite **1h** the α-C deoxygenated 1,2-oxaphosphole **8** was obtained which was hydrolyzed to furnish the γ,ε-dihydroxy phosphonate **9** (SCHEME 4). However, the O-trimethylsilylated diketone **6b** and phosphite **1h** yielded to give 1,2-oxaphosphole **10** (SCHEME 5). From diketone **6a** and ethanolamine the corresponding diimine was obtained furnishing the bicyclic phosphite **11** (SCHEME 6).



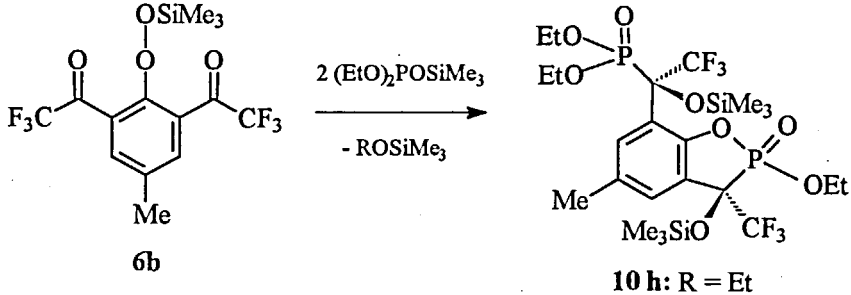
6a **7e:** R = Et, **7g:** R-R = CMe_2CMe_2

SCHEME 3



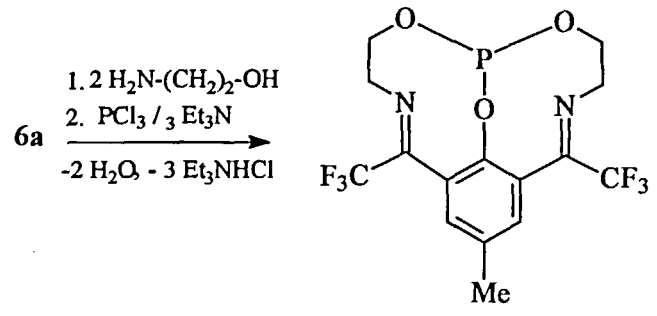
8 **9**

SCHEME 4



6b **10 h:** R = Et

SCHEME 5



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SCHEME 6

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