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Phosphorus, Sulfur, and Silicon and the Related Elements

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Mono, Spiro and Tricyclic Ring Systems Containing Phosphorus

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MONO, SPIRO AND TRICYCLIC RING SYSTEMS CONTAINING PHOSPHORUS

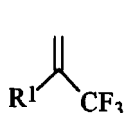
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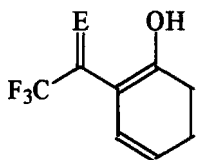
Abstract Activated ketoenols $\text{CF}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{OH})\text{R}^2$ ($\text{R}^2 = \text{CF}_3, \text{CH}_3$) and appropriate phosphorus derivatives ($\text{Me}_3\text{SiN}=\text{PN}(\text{SiMe}_3)_2$, $(\text{R}^5\text{O})_2\text{PNCO}$, PH_3 , R^4PCl_2 , EtOPCl_2 , Et_2NPCl_2) reacted to give $\lambda^5\sigma^4$ -oxaphospholenes, a $\lambda^5\sigma^4\text{P}$ spiro system, a phosphaadamantane and tricyclic $\lambda^5\sigma^5$ -phosphoranes. Reaction mechanisms, ^{19}F NMR spectra were discussed. Several single crystal X-ray structure analyses were conducted.

INTRODUCTION

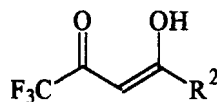
The amino-iminophosphine $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$ (1) and activated ketones 2 ($\text{R}^1=\text{CF}_2\text{H}$, $\text{C}(\text{O})\text{OMe}$) reacted to form $\lambda^5\sigma^4$ -oxaphosphiranes and $\lambda^5\sigma^4$ -dioxaphospholenes;¹ in the case of 2-imino-2-trifluoroacetylphenol 3 ($\text{E} = \text{O}$) only a 4,5,1,2 $\lambda^5\sigma^4$ -benzooxaphospholane was found which added 2 ($\text{R}^1=\text{CF}_3$) to give a $\lambda^5\sigma^4$ -oxazaphosphetane¹. The appropriate substituent at phosphorus gave rise to the formation of mono and bicyclic phosphoranes² whereas tricyclic phosphoranes were synthesized from 3 ($\text{E} = \text{O}$) and several $\lambda^3\text{P}$ derivatives^{3,4}. Phosphonous dichlorides R^4PCl_2 (6) ($\text{R}^4 = \text{Ph}$, CH_2Ph) and the ketoenol 4 ($\text{R}^2=\text{CF}_3$) furnished a tricyclic system, too.⁵



2 ($\text{R}^1 = \text{CHF}_2$,
 $\text{C}(\text{O})\text{OMe}$, CF_3)



3 ($\text{E} = \text{O}$, NR^3)

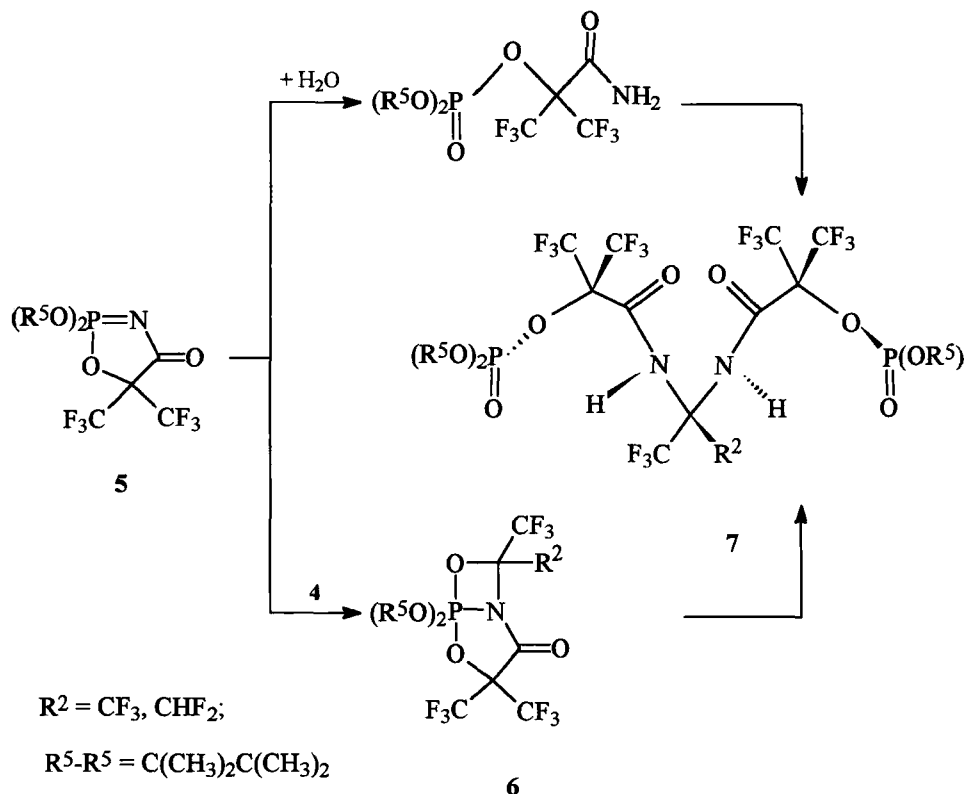


4 ($\text{R}^2 = \text{CF}_3, \text{CH}_3$)

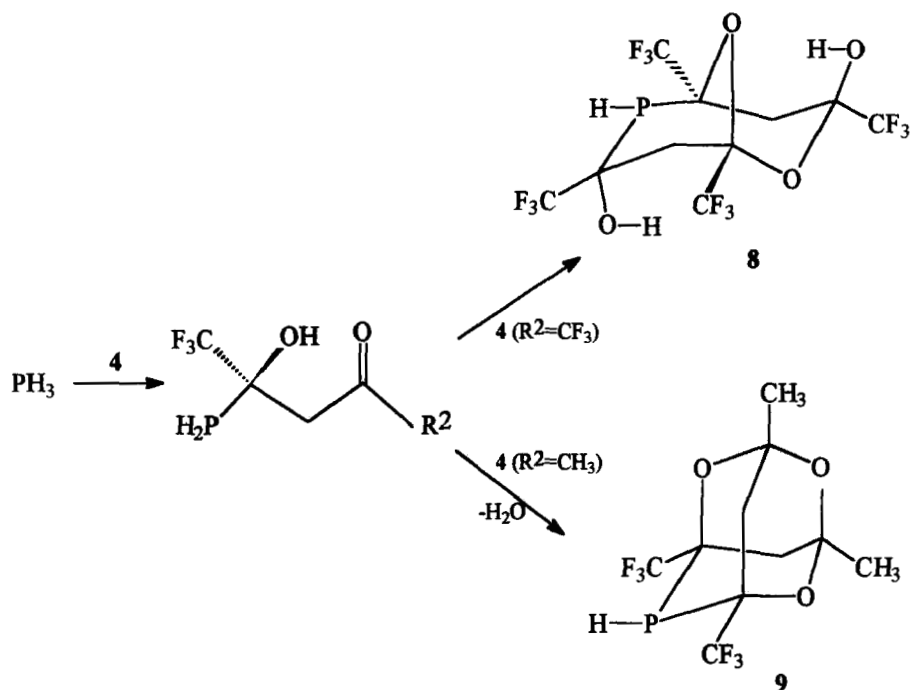
RESULT AND DISCUSSION

The ketoenols **4** ($R^2 = \text{CF}_3, \text{CH}_3$) added to compound **1** yielding in each case diastereomeric mixtures (5:1) of 2-imino-1,2 $\lambda^5\sigma^4$ -oxaphospholenes, which reacted with **2** ($R^1 = \text{CF}_3$) to form only *one* 1,3,2 $\lambda^5\sigma^5$ -oxazaphosphetane. A different mechanism is proposed for **1** and the trimethylsilyl derivative of **4**.

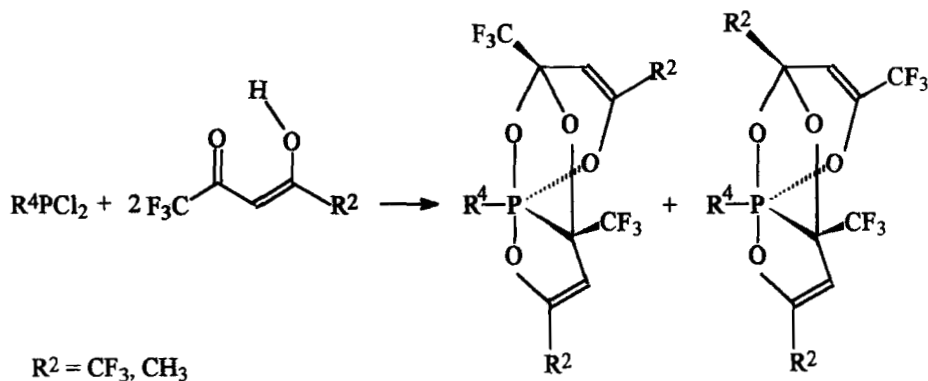
The isocyanatophosphite $\text{OCNP}(\text{OR}^5)_2$ ($R^5\text{-}R^5 = \text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2$) and **2** ($R^1 = \text{CF}_3$) built up a spirocyclic $\lambda^5\sigma^4\text{P}$ ringsystem **5** which did not dimerize but underwent a [2+2] cycloaddition across the $\text{P}=\text{N}$ double bond with **1** ($R^1 = \text{CF}_3, \text{CHF}_2$) to give 1,3,2 $\lambda^5\sigma^5$ -oxazaphosphetanes **6**, which reacted with the hydrolysis product of **5** to form the bis-phosphate **7**. The molecular structure was confirmed by x-ray diffraction.



Phosphine, PH_3 , and the ketoenols **4** yielded the bicyclic compound **8** and the phosphadamantane **9**. Both secondary phosphines possess five chiral centers, but only *one* diastereoisomer was formed. The molecular structures of **11** and **12** were determined by X-ray diffraction.

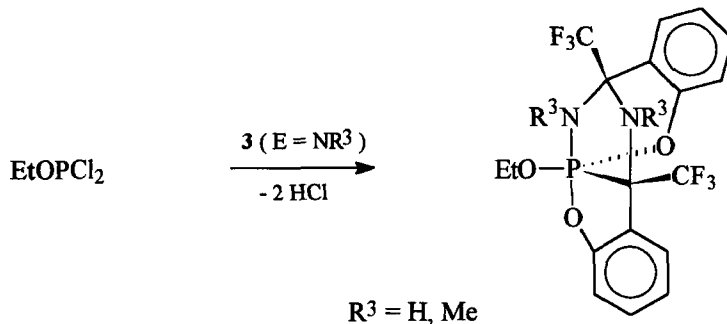


Tricyclic phosphoranes were obtained stereospecifically reacting phosphonous dichlorides R^4PCl_2 and compounds **4** ($\text{R}^2 = \text{CF}_3$; $\text{R}^4 = \text{Alk}$; $\text{R}^2 = \text{CH}_3$; $\text{R}^4 = \text{Et}$, CH_2Ph , CH_2SiMe_3 , Ph). Products for $\text{R}^2 = \text{CF}_3$ could be hydrolyzed to give 2-oxo-1,2,5-oxaphospholanes, however methanol added across one $\text{C} = \text{C}$ double bond. Two constitutional isomers were found for $\text{R} = \text{CH}_3$ which could be separated using fractional crystallisation. The long range $^{19}\text{F} - ^{19}\text{F}$ coupling is characteristic for one isomer.

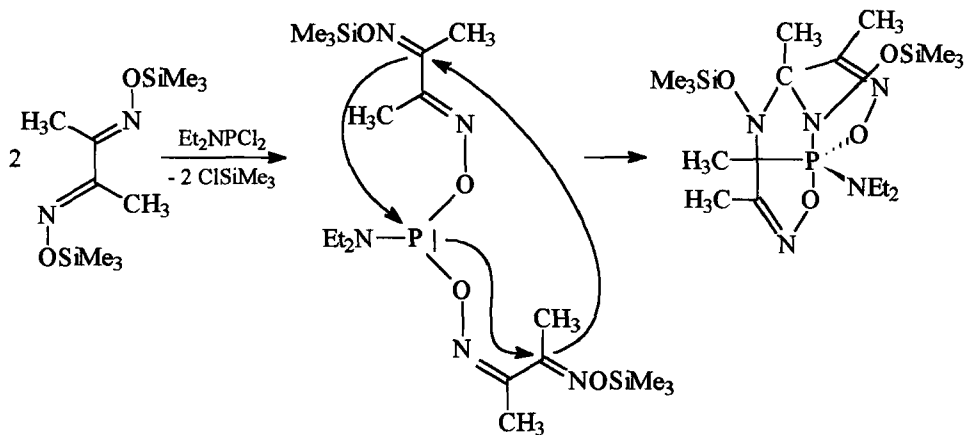


Molecular structures of several phosphoranes and their derivatives were investigated.

Compound **3** ($E = NR^3$, $R^3 = H, Me$) and $EtOPCl_2$ gave tricyclic phosphoranes.



Since disylated diacetyldioxime has the similar structural elements like **3** or **4**, it is not surprising that Et_2NPCl_2 produces a tricyclic system.



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