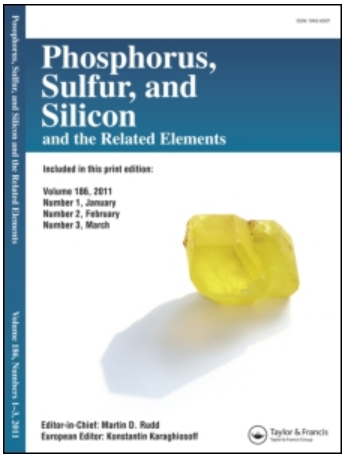


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Mono, Spiro and Tricyclic Ring Systems Containing Phosphorus

Georgios Bekiaris[a]; Rolf-Dieter Hund[a]; Frank Uwe Seifert[a]; Gerd-Volker Röschenthaler[a]
[a] Institute of Inorganic and Physical Chemistry, University of Bremen, Leobener Straße, Bremen, Germany

To cite this Article Bekiaris, Georgios , Hund, Rolf-Dieter , Seifert, Frank Uwe and Röschenthaler, Gerd-Volker(1994) 'Mono, Spiro and Tricyclic Ring Systems Containing Phosphorus', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 289 — 292
To link to this Article: DOI: 10.1080/10426509408021837
URL: http://dx.doi.org/10.1080/10426509408021837

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 289-292
Reprints available directly from the publisher
Photocopying permitted by license only

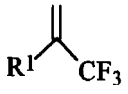
MONO, SPIRO AND TRICYCLIC RING SYSTEMS CONTAINING PHOSPHORUS

GEORGIOS BEKIARIS, ROLF-DIETER HUND, FRANK UWE SEIFERT AND GERD-VOLKER RÖSCHENTHALER
Institute of Inorganic and Physical Chemistry, University of Bremen,
Leobener Straße, Postfach 330440, D-28334 Bremen, Germany

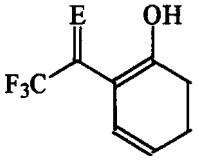
Abstract Activated ketoenols $CF_3C(O)CH=C(OH)R^2$ (R^2 = CF_3, CH_3) and appropriate phosphorus derivatives ($Me_3SiN=PN(SiMe_3)_2$, $(R^5O)_2PNCO$, PH_3, R^4PCl_2, $EtOPCl_2$, Et_2NPCl_2) reacted to give $\lambda^5\sigma^4$-oxaphospholenes, a $\lambda^5\sigma^4$P spirosystem, a phosphaadamantane and tricyclic $\lambda^5\sigma^5$-phosphoranes. Reaction mechanisms, ^{19}F NMR spectra were discussed. Several single crystal X-ray structure analyses were conducted.

INTRODUCTION

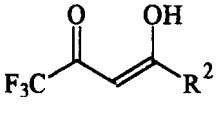
The amino-iminophosphine $(Me_3Si)_2NP=NSiMe_3$ (1) and activated ketones 2 ($R^1=CF_2H$, C(O)OMe) reacted to form $\lambda^5\sigma^4$-oxaphosphiranes and $\lambda^5\sigma^4$-dioxaphospholenes;[1] in the case of 2-imino-2-trifluoroacetylphenol 3 (E = O) only a 4,5,1,2$\lambda^5\sigma^4$-benzooxaphospholane was found which added 2 ($R^1=CF_3$) to give a $\lambda^5\sigma^4$-oxazaphosphetane[1]. The appropriate substituent at phosphorus gave rise to the formation of mono and bicyclic phosphoranes[2] whereas tricyclic phosphoranes were synthesized from 3 (E = O) and several λ^3P derivatives[3,4]. Phosphonous dichlorides R^4PCl_2 (6) (R^4 = Ph, CH_2Ph) and the ketoenol 4 ($R^2=CF_3$) furnished a tricyclic system, too. [5]



2 (R^1 = CHF_2, C(O)OMe, CF_3)



3 (E = O, NR^3)

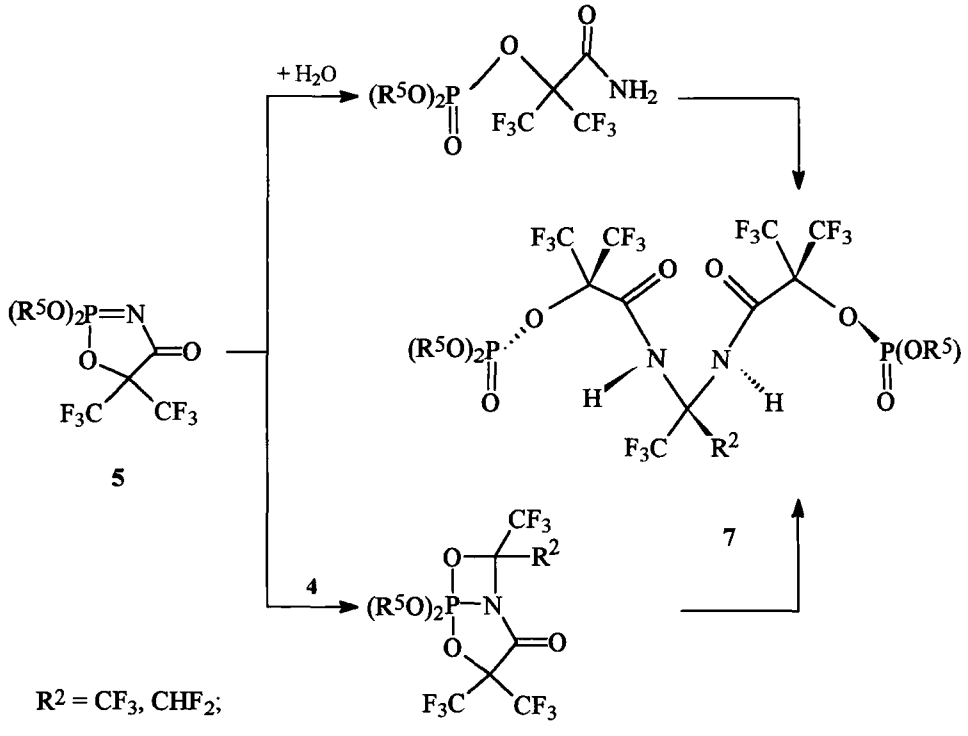


4 (R^2 = CF_3,CH_3)

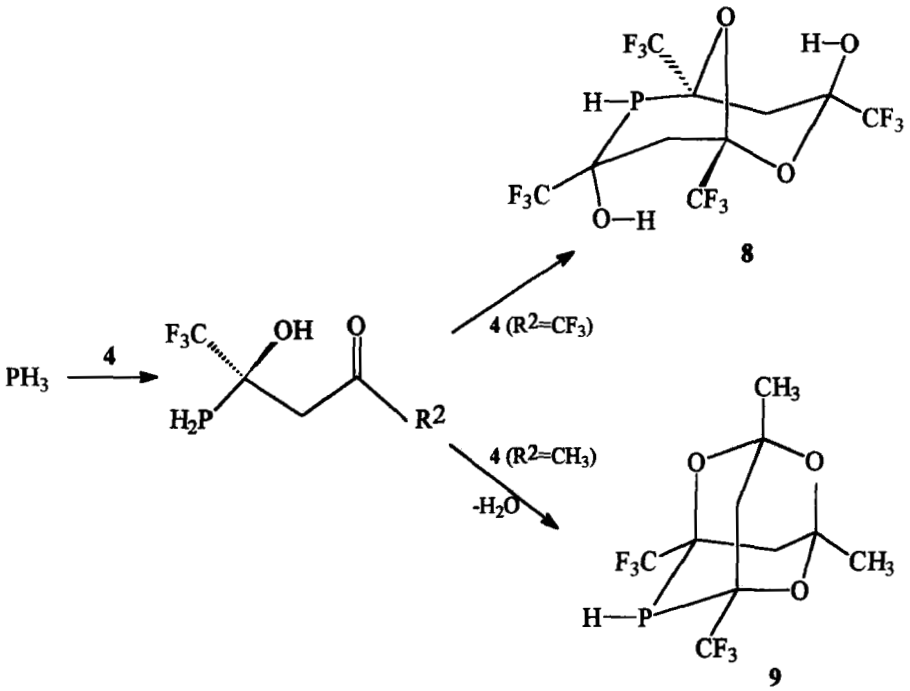
RESULT AND DISCUSSION

The ketoenols **4** (R^2 = CF_3, 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=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**.

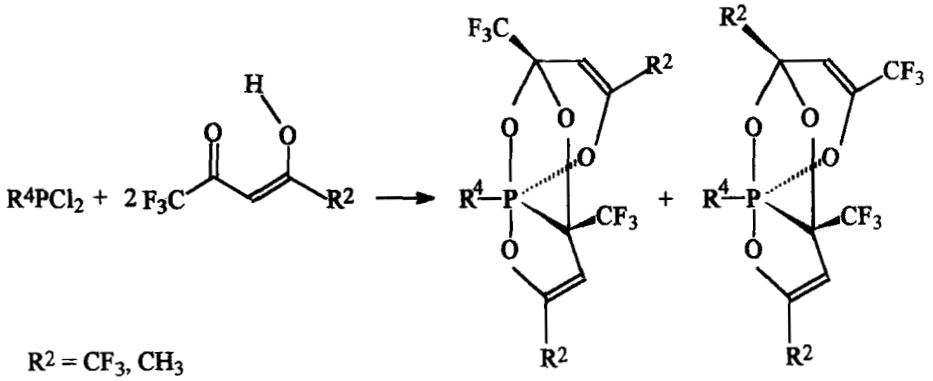
The isocyanatophosphite $OCNP(OR^5)_2$ (R^5-R^5= $C(CH_3)_2C(CH_3)_2$) and **2** (R^1= CF_3) built up a spirocyclic $\lambda^5\sigma^4$P ringsystem **5** which did not dimerize but underwent a [2+2] cycloaddition across the P=N double bond with **1** (R^1= CF_3, CHF_2) to give 1,3,2$\lambda^5\sigma^5$-oxazaphosphetanes **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 phosphaadamantane **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.

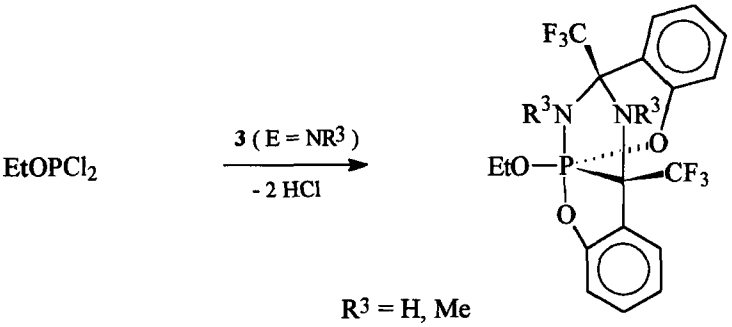


Tricyclic phosphoranes were obtained stereospecifically reacting phosphonous dichlorides R^4PCl_2 and compounds **4** ($R^2 = CF_3$; R^4 = Alk; $R^2 = CH_3$; R^4 = Et, CH_2Ph, CH_2SiMe_3, Ph). Products for $R^2 = CF_3$ could be hydrolyzed to give 2-oxo-1,2$\lambda^5\sigma^4$-oxaphospholanes, however methanol added across one C = C double bond. Two constitutional isomers were found for R = CH_3 which could be seperated using fractional crystallisation. The longe range ^{19}F - ^{19}F coupling is characteristic for one isomer.



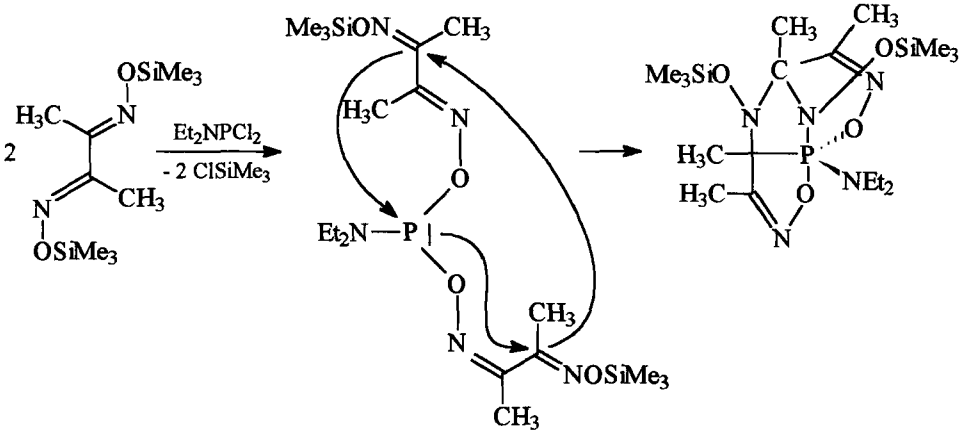
Molecular structures of several phosphoranes and their derivatives were investigated.

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



R^3 = H, Me

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



REFERENCES

1. F.U. Seifert and G.-V. Röschenthaler, Z. Naturforsch. 48b, 1089 (1993).
2. R.-D. Hund and G.V. Röschenthaler, Phosphorus, Sulfur & Silicon, 62, 65 (1991); 73, 99 (1992).
3. R.-D. Hund and G.V. Röschenthaler, Phosphorus, Sulfur & Silicon, 66, 301 (1992).
4. R.-D. Hund, U. Behrens and G.V. Röschenthaler, Phosphorus, Sulfur & Silicon, 69, 119 (1992).
5. G. Bekiaris and G.V. Röschenthaler, Z. Naturforsch. 45b, 1460 (1990).