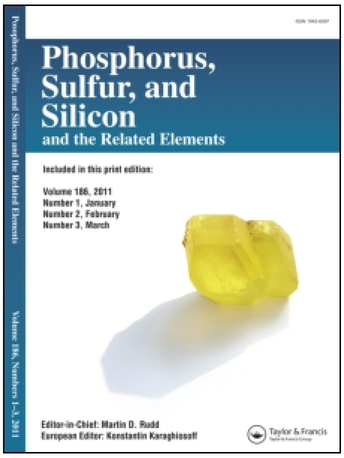

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NEW SYNTHETIC ROUTE TO PHOSPHAZENES FROM TRIAZAPHOSPHOLES

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NEW SYNTHETIC ROUTE TO PHOSPHAZENES FROM TRIAZAPHOSPHOLES

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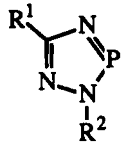
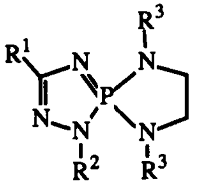
One saturated ring spirophosphazene **2** and cyclic phosphazenes **3** were prepared by reaction of triazaphospholes **1** with amines and diamines and iodine or enamine.



1



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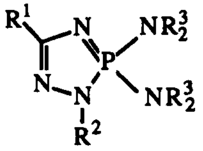
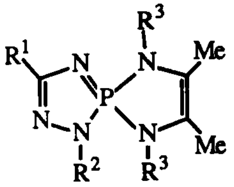


3

Key words: Dicoordinated phosphorus compounds; oxydative reaction; spirophosphazene; cyclic phosphazene.

As far as spirophosphazenes are concerned, we reported[1] the synthesis of **4** and **5** by reaction of diazadienes with the corresponding phospholes. Schmidpeter et al.[2] synthesized spirobitriazaphospholes **6** from PCl_5 and *N*-methylbenzamidrazone and



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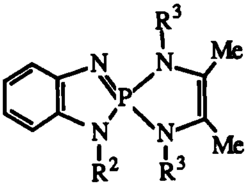
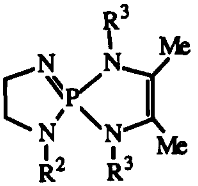


5a



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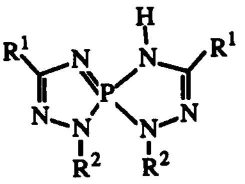
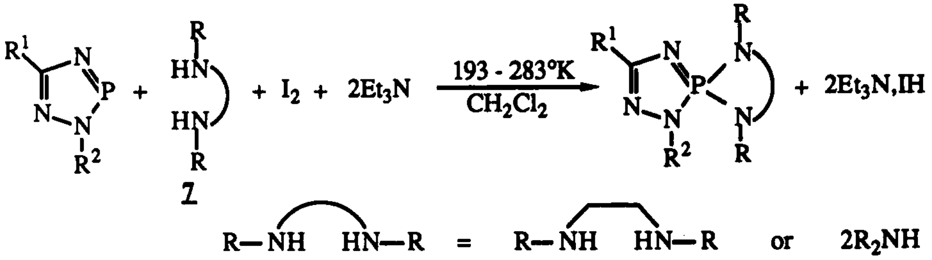


6

Et_3N. Although **4, 5** and **6** are not prepared in the same way they resemble each other very much as far as **4** and **6** are concerned. These spiro compounds consist of two unsaturated rings. This structural fact can be expected to influence their reactivity and stability. Therefore it becomes interesting to synthesize spirophosphazenes such as **2** with one saturated ring. To make further comparisons easier it appears necessary to synthesize spirocompounds such as **2** and **3** which maintain the triazaphosphole ring **1**. For this purpose we carried out the following reaction[3]:

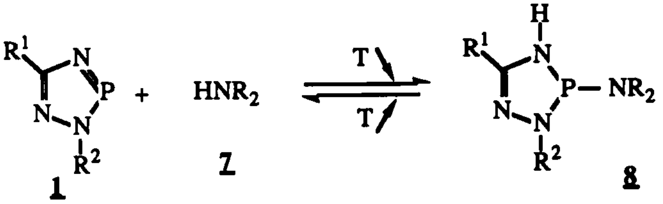


This oxydative reaction is original as far as dicoordinated phosphorus compounds and amines are concerned.

RESULTS AND DISCUSSION

1°) The reaction does not proceed completely in the absence of triethylamine. This is accounted for by the trapping of hydrogen iodide by **7** and **2** and **3**. In fact, analysis of the reaction medium ^{31}P NMR spectra, before and after adding the stoechiometric amount of Et_3N, shows a change of chemical shift of **2** or **3** (ca. 17 ppm). e.g., the signal corresponding to **2a** lies at 38 ppm before adding Et_3N and moves to 55 ppm after addition. The spiro structure of the compound corresponding to the signal lying at 38 ppm was determined on the ground of its ^{13}C NMR spectrum.

2°) An intermediate was identified. It is the three coordinated $\lambda^3\sigma^3$ phosphorus compound **8** resulting from the addition of one amino group on **1** P=N bond. That is easily accounted for by the fact that triazaphospholes react reversibly with amines.[4] The equilibrium is displaced entirely towards the product on cooling:

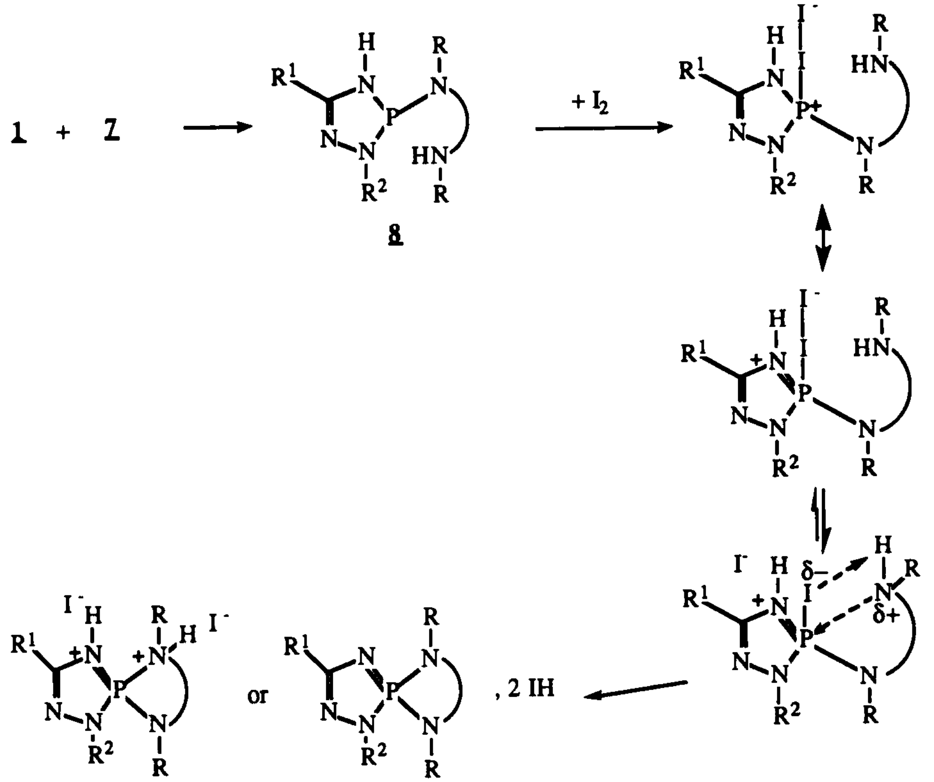


So when a mixture of **1** and **7** is cooled to −40°C or less its ^{31}P NMR spectrum shows a unique signal lying at about 80 ppm. This signal disappears progressively to the advantage of the one attributed to **2** or **3**. No other signal except those of **8** and **2** or **3** were present in the ^{31}P NMR spectra scanned during the process. **2** and **3** structures were determined from their ^{1}H, ^{13}C and ^{31}P NMR data and elemental analysis.

A mechanism which is in good agreement with the observed fact is shown below. It is readily understandable if it is taken into account that:
-anion I^- is a base softer than $>N-$
-cation I^+ and molecule I_2 are acids softer than H^+

That means that abstraction of the proton from neutral amine >NH by I^- is unlikely. On the other hand I^+ or I_2 could be expected to react preferentially with a tricoordinated $\lambda^3\sigma^3$ phosphorus atom which is a base softer than alkylamine. In fact tricoordinated phosphorus compounds are well known to react with iodine molecule, the reactive site being the phosphorus atom.[5]

It should be noticed that whatever the way of mixing the reactants no pentacoordinated phosphorus species has ever been detected in the reaction media. Therefore it should be considered that all the steps involving iodine are faster than the one corresponding to the addition of the first amino group on the P=N bond.



2 (or 3) + 2IH

EXPERIMENTAL DATA

All NMR spectra were run in CD_2Cl_2 on a Brucker spectrometer AC80.

2, *R^1=Ph R^2=Me R^3=Me (3-phenyl-1,6,9-trimethyl-1,3,4,6,9-pentaza-5-phospha(spiro 4,4)-2,4-nonadiene)* **2a**: *preparation*: A mixture of triazaphosphole **1a** (R^1=Ph, R^2=Me; 6.3 mmol) and *N,N'*-dimethylethylenediamine (6.3 mmol) and triethylamine (12.6 mmol) in dichloroethane (30 mL) is stirred at 0°C. To this solution is added dropwise iodine (6.3 mmol) dissolved in ether (50 mL). Triethylammonium iodide precipitates. After addition, the mixture is allowed to warm to room temperature and the stirring is continued for two hours. Then the precipitate is filtered. Concentration to dryness of the filtrate, under reduced pressure ($7.5\ 10^{-4}$ Torr), yields a highly hygroscopic white powder which is washed with ether.

^{31}P NMR $\delta = 55.8$ ppm; ^1H NMR δ 2.1(*d*, 6H, $C\underline{H}_3$-N-CH_2, $^3J_{H\text{-}P} = 10.4$ Hz) 2.4(*d* (AB), 4H, CH_3-N-$C\underline{H}_2$, $^3J_{H\text{-}P} = 9.4$ Hz) 3.1(*d*, 3H, $C\underline{H}_3$-N-N, $^3J_{H\text{-}P} = 6.5$ Hz) 7.2 and 8.7 ($C_6\underline{H}_5$); ^{13}C NMR δ 30.8 (*d*, $\underline{C}H_3$-N-CH_2, $^2J_{C\text{-}P} = 6.5$ Hz) 32.3(*d*, $\underline{C}H_3$-N-N, $^2J_{C\text{-}P} = 7.5$ Hz) 46.4 (*d*, CH_3-N-$\underline{C}H_2$, $^2J_{C\text{-}P} = 7.4$ Hz) 135.6(*d*, $\underline{C}$=N, $^2J_{C\text{-}P} = 17.3$ Hz) 125.4 through 128.3 ($\underline{C}_6H_5$)

Elemental analysis:	calculated	C 54.74	H 6.89	N 26.6	P 11.76
	found	C 54.52	H 6.85	N 26.33	P 12.3
		C 54.56	H 6.90	N 26.19	P 12.39

R^1=Ph R^2=Me R^3=Me **2a** + 2 **IH**: ^{31}P NMR δ = 38 ppm; ^{13}C NMR δ 31.2(*d*, $\underline{C}H_3$-N-CH_2, $^2J_{C\text{-}P}$ = 6.05 Hz) 32.9(*d*, $\underline{C}H_3$-N-N, $^2J_{C\text{-}P}$ = 11.5 Hz) 46(*d*, CH_3-N-$\underline{C}H_2$, $^2J_{C\text{-}P}$ = 16.3 Hz) 125 through 132 (C_6H_5) 145.4(*d*, C=N, $^2J_{C\text{-}P}$ = 22 Hz).

R^1=iPr R^2=Me R^3=Me: (3-isopropyl-1,6,9-trimethyl-1,2,4,6,9-pentaza-5-phospha(spiro 4,4)-2,4-nonadiene) **2b**: ^{31}P NMR δ = 60.3 ppm; ^{1}H NMR δ 0.7(*d*, 6H, H—C(C$\underline{H}_3$)2, $^3J_{HC\text{-}CH}$ = 6.8 Hz) 2(*d*, 6H, C$\underline{H}_3$-N-CH_2, $^3J_{H\text{-}P}$ = 10.3 Hz) 2.6(*d*, 3H, C$\underline{H}_3$-N-N, $^3J_{H\text{-}P}$ = 6.2 Hz) 2.8(*d*, 4H, CH_3-N-C$\underline{H}_2$, $^3J_{H\text{-}P}$ = 9.3 Hz); ^{13}C NMR δ 30.7(*d*, $\underline{C}H_3$-N-CH_2, $^2J_{C\text{-}P}$ = 6.3 Hz) 31.8(*d*, $\underline{C}H_3$-N-N, $^2J_{C\text{-}P}$ = 13.8 Hz) 31.8(*d*, $\underline{C}$H-C-N, $^2J_{C\text{-}P}$ = 7.4 Hz) 45.7(*d*, CH_3-N-$\underline{C}H_2$, $^2J_{C\text{-}P}$ = 12.3 Hz) 166.3(*d*, P=N-$\underline{C}$=N, $^2J_{C\text{-}P}$ = 7 Hz).

R^1=Me R^2=Me R^3=Ph: (6,9-diphenyl-1,3-dimethyl-1,2,4,6,9-pentaza-5-phospha(spiro 4,4)-2,4-nonadiene) **2c**: ^{31}P NMR δ = 40.4 ppm.

R^1=Ph R^2=Ph R^3=Ph: (1,3,6,9-tetraphenyl-1,2,4,6,9-pentaza-5-phospha (spiro 4,4)-2,4-nonadiene) **2d**: ^{31}P NMR δ = 39.8 ppm.

R^1=Ph R^2=Ph R^3=Me: (1,3-diphenyl-6,9-dimethyl-1,2,4,6,9-pentaza-5-phospha(spiro 4,4)-2,4-nonadiene) **2e**: ^{31}P NMR δ = 56 ppm.

3, *R^1=Ph R^2=Ph: (3-bis(diethylamino)-2,5-diphenyl-1,2,4,3-cyclotriazaphosphorane)* **3a**: *preparation*: A mixture of triazaphosphole **1b** (R^1=R^2=Ph; 1.1 mmol) and diethylamine (8.8 mmol) in dichloromethane (3 mL) is stirred at −85°C. To this mixture is added at once iodine (1.1 mmol). When iodine is entirely dissolved the mixture is allowed to warm to room temperature overnight. On addition of Et_2O (5 mL) diethylammonium iodide precipitates and is filtered. The filtrate is then concentrated to dryness under reduced pressure (7.5 10^{-4} Torr).

Elemental analysis:					
	calculated	C 63.49	H 8.41	N 19.48	P 8.62
	found	C 63.47	H 8.38	N 19.47	P 8.7

^{31}P NMR δ = 56 ppm; ^{1}H NMR δ 1.04(*t*, 6H, C$\underline{H}_3$—CH_2 $^3J_{HCCH}$ = 7.1 Hz) 3.19(*m*, 4H, CH_3—C$\underline{H}_2$, $^2J_{H\text{-}P}$ = 11.45 Hz) 6.8 and 8.2 (*m*, 10H, 2C_6H_5); ^{13}C NMR δ 13.2(*d*, $\underline{C}H_3CH_2$, $^3J_{P\text{-}C}$ = 3.63 Hz) 39.8(*d*, CH_3—$\underline{C}H_2$, $^2J_{P\text{-}C}$ = 3.42 Hz) 110 to 160 (2 $\underline{C}_6H_5$).

R^1=Ph R^2=Me: (3-bis(diethylamino)-5-phenyl-2-methyl-1,2,4,3-cyclotriaza phosphorane) **3b**: ^{31}P NMR δ = 60 ppm; ^{1}H NMR δ 0.86(*t*, 6H, C$\underline{H}_3$—CH_2, $^3J_{HCCH}$ = 8Hz) 2.8(*m*, 4H, CH_3—C$\underline{H}_2$) 3.05(*d*, 3H, CH_3—N, $^3J_{H\text{-}P}$ = 6 Hz) 7.2 and 8.6(*m*, 5H, C_6H_5); ^{13}CNMR δ 13.56(*d*, $\underline{C}H_3$—CH_2, $^3J_{P\text{-}C}$ = 3.22 Hz) 33.77(*d*, NCH_3 $^2J_{P\text{-}C}$ = 10.48 Hz) 41.2(*d*, CH_3—$\underline{C}H_2$, $^2J_{P\text{-}C}$ = 4.3 Hz) 146.1(*d*, C=N, $^2J_{P\text{-}C}$ = 20.35 Hz).

R^1=Ph R^2=Me: **3b** + 2 **IH**: ^{31}P NMR δ = 40 ppm.

This work is part of Dr. O. S. Diallo's thesis: "Thèse de Doctorat d' Etat n° 1409 Université Toulouse III, 1990.

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