

PHOSPHORUS COMPOUNDS WITH UNUSUAL COORDINATION - 20¹. 1,2,3,4-TRIAZAPHOSPHOLES BY
 [3+2]-CYCLOADDITION OF AZIDES TO A STABLE PHOSPHAALKYNE

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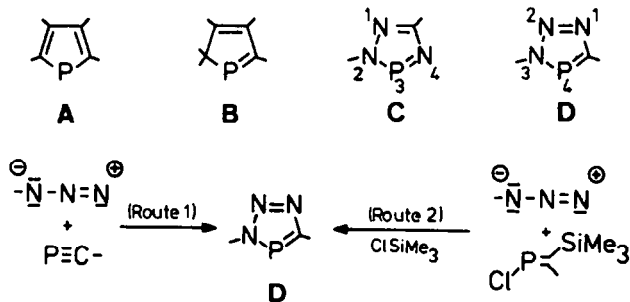
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Abstract: - The azides **2a-l** undergo regiospecific [3+2]-cycloaddition with the phosphalkyne **1** to form the 1,2,3,4-triazaphospholes **3a-l**; in the case of the reaction with **2j**, an additional silyl shift occurs resulting in the formation of **4j**. The latter product can be hydrolyzed to **6** which has also been prepared independently from **1** and hydrazoic acid (**7**). Flash vacuum pyrolyses of the 1,2,3,4-triazaphospholes **3c** and **3e** produce mixtures of the isomers **13a,b** and **14a,b**, respectively, from which the 1,2-azaphospholes **14** can be isolated as the major reaction products.

INTRODUCTION

Phospholes with trivalent, tricoordinated phosphorus atoms (**A**) are well known². In contrast to these heteroaromatic compounds, the isomeric 2H-phospholes (**B**) which contain $\lambda^3_o^2$ -phosphorus atoms have not yet been isolated. As a result of their 1,3-diene nature, they can, however, be trapped by Diels-Alder reactions³ or be stabilized by the formation of metal complexes⁴. By means of the successive exchange of up to 3 carbon atoms in **B** by nitrogen atoms, mono-, di-, and triazaphospholes can be prepared. The latter compounds play a significant role in the development of the chemistry of low-coordinated phosphorus compounds⁵.

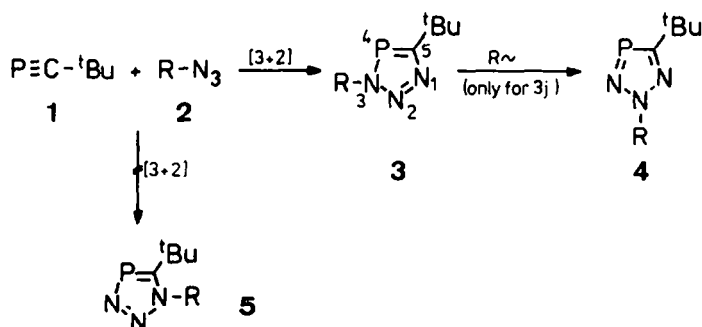


Of the triazaphospholes, only the 1,2,4,3-isomers **C** had been reported previously^{6,7}, whereas the 1,2,3,4-triazaphospholes **D** were unknown before the start of our investigations in

this field. Recently, two principle routes for the synthesis of heteroarenes of this type have been employed. Route 1 consists of the [3+2]-cycloaddition of azides to phosphoalkynes^{8,9}. Route 2 starts from chloro(trimethylsilylalkylidene)phosphanes and involves the initial addition of azides to the phosphane followed by the thermal elimination of chlorotrimethylsilane to furnish **D**¹⁰. In the present paper, we report our results on the synthesis of 1,2,3,4-triazaphospholes by Route 1 in detail and on some selected flash vacuum pyrolyses of these heterocycles.

CYCLOADDITION REACTIONS

When the phosphoalkyne **1** is allowed to react with the azides **3a-i** at 0 °C in diethyl ether, the 3H-1,2,3,4-triazaphospholes are obtained as liquids (**3a,f,h,i**) or as crystalline solids (**3b-e,g**) in 76-100% yields. Other phosphoalkynes (1, 1-adamantyl¹¹, isopropyl¹², neopentyl¹², 1-methyl-1-cyclohexyl¹², and 1-methyl-1-cyclopentyl¹² in place of *tert*-butyl) react analogously to give the corresponding 1,2,3,4-triazaphospholes in high yields. All of these cycloaddition reactions proceed regiospecifically, no evidence for the formation of adducts with the reversed dipole orientation as represented by the structure **5** was found.



2-5	a	b	c	d	e
R	Me	<i>t</i> Bu	Ph	(4)-EtO ₂ C-C ₆ H ₄	1-C ₁₀ H ₇
	f	g	h	i	j
	CH=CH ₂	CO ₂ Me	CH ₂ CN	CH ₂ SiMe ₃	SiMe ₃

Although the difference in the Pauling electronegativities between phosphorus and carbon (2.1 and 2.5, respectively) is not very large, the cycloaddition process is apparently electronically controlled. This is also valid for the 1,3-dipolar cycloadditions of diazo compounds to phosphoalkynes^{1,11,12}. The fact that the reaction of **1** + **2** leads to a product (**3**) with a minimal steric hindrance of the substituents of both reaction partners cannot

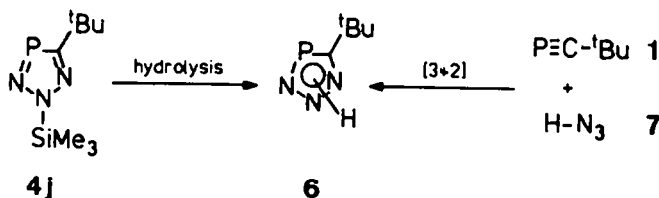
be attributed to the spatial requirements of these substituents. When this steric hindrance is minimized as, for example, in the reaction of methyl azide (**2a**) with methylidynephosphane (1, H in place of *tert*-butyl) - the first member of the phosphacetylene series - 3-methyl-1,2,3,4-triazaphosphole (**3a**, H in place of *tert*-butyl) is formed in spite of the lack of steric hindrance¹³. The parallels to the cycloadditions of azides to mono-acceptor substituted acetylenes with respect to dipole orientations cannot be overlooked¹⁴.

In the ¹H-NMR spectra of **3a-i**, similar resonances for the signals of the *tert*-butyl groups in the 5 positions ($\delta = 1.32\text{--}1.55$ ppm) with small ⁴J_{H,P} coupling constants (0.6-1.8 Hz) are observed. The resonance for the 3-methyl or 3-methylene substituents, as in **3a,h,i** ($\delta = 3.85$, 4.73, and 3.82 ppm) have more diagnostic value; the coupling constants with phosphorus (³J_{H,P} = 7.2, 5.8, and 6.5 Hz) are not in accord with a dipole orientation as represented by the structure **5**. ⁴J_{H,P} Coupling constants (see also above) are considerably smaller.

The ¹³C-NMR spectra of **3a,c,g**, and **i** were recorded. The C-5 ring carbon atoms absorb at $\delta = 197.6\text{--}199.4$ ppm with ¹J_{C,P} coupling constants of 54.9-57.3 Hz. The resonances of the substituents in the 3-position or the magnitudes of their coupling with phosphorus, respectively, are of major importance for differentiating between the possible regioisomers **3** and **5**. Thus, the ²J_{C,P} coupling constants of 15.9, 11.9, 21.0, and 10.9 Hz observed for the carbon atoms directly bonded to N-3 in **3a,f,g** and **i** are unequivocally in accord with the 3H-1,2,3,4-triazaphosphole structure. The corresponding ³J_{C,P} coupling constants that would be expected for the isomers **5** are considerably smaller (compare with, for example, the phosphorus splittings of the tertiary and primary carbon atoms in the *tert*-butyl groups of **3**). Furthermore, these observations exclude with certainty an R group shift to N-2 as represented by the formula **4**.

The transition from a $\lambda^3_{\sigma^1}$ -phosphorus atom to a $\lambda^3_{\sigma^2}$ -phosphorus atom in the conversion of **1** to **3** is also reflected in the enormous low-field shifts of the ³¹P resonances. For **3a-i** these occur at $\delta = 161.8\text{--}180.7$ ppm (for comparison, **1**: $\delta = -69.2$ ppm in C₆D₆)¹⁵ and thus are of the same order of magnitude as those of the 1,2,3-diazaphospholes¹⁶.

In the reaction of the phosphacetylene **1** with trimethylsilyl azide (**2j**), the cycloaddition to give **3j** is followed by a [1,5]-shift of the trimethylsilyl group to yield **4j**. Evidence for this rearrangement is given by the absence of a ⁴J_{H,P} and a ³J_{C,P} coupling with the corresponding nuclei of the silyl group in the ¹H- and ¹³C-NMR spectra, respectively, as would be expected for **3j**. Silyl shifts of this type in 1,2,3-triazoles are well known¹⁷.



The 2-silyl-1,2,3,4-triazaphosphole **4j** is rather sensitive to hydrolysis and is even desilylated to give **6** by simple stirring with diethyl ether over silicagel (without exclu-

sion of moisture). Silyl substituted 1,2,3-triazoles behave analogously¹⁷. The same compound can be obtained independently by the reaction of **1** with hydrazoic acid (**7**). The NMR spectroscopic data of **4j** (see experimental section) are in accord with those of other members of the same series and require no further interpretation.

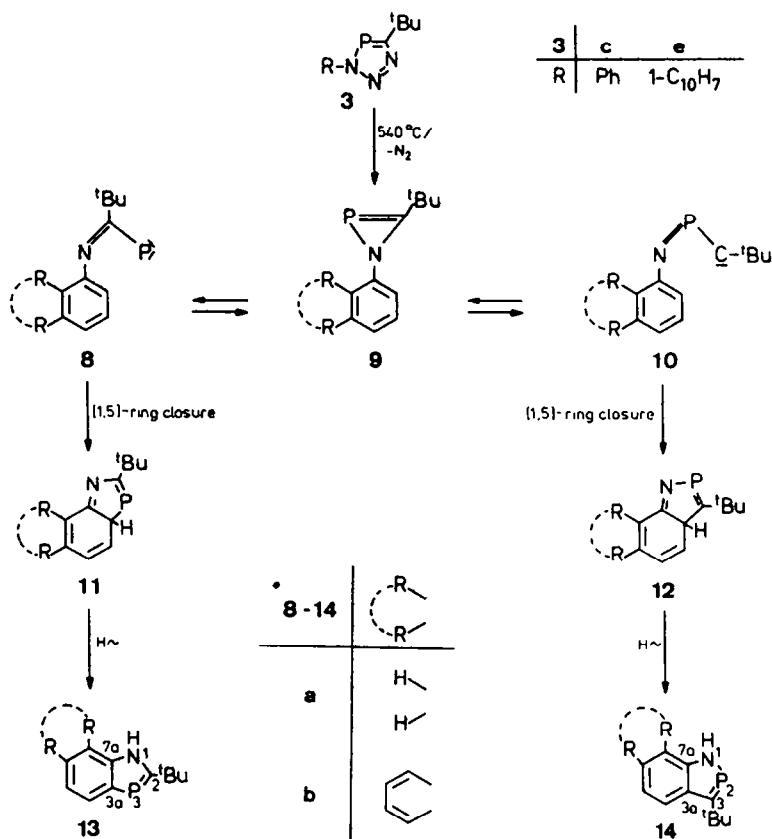
FLASH VACUUM PYROLYSES OF **3c** AND **3e**

1,2,3,4-Triazaphospholes (**3**) are potential precursors for the generation of azaphosphirenes (**9**) or their isomeric phosphinidenes (**8**) and/or carbenes (**10**) by photolysis or thermolysis. As no evolution of nitrogen occurs on irradiation with UV light ($\lambda \geq 280$ nm) and as the heterocyclic compounds are thermally stable (compare with the purification of some members of the series by bulb-to-bulb distillation), we have concentrated on the flash vacuum pyrolysis technique¹⁸. It was found that **3c** does not decompose even at 400 °C/10⁻⁴ mbar. The expected nitrogen cleavage only occurs at temperatures above 500 °C under otherwise identical conditions. The two isomeric benzo-condensed azaphospholes **14a** and **13a** are formed in a ratio of 4:1 (by ³¹P-NMR spectroscopy) and the mixture is characterized by a correct elemental analysis. The 1,2-azaphosphole **14a** can be separated (62% yield) by medium pressure chromatography on silicagel whereas **13a** can only be enriched in the mixture with **14a** (up to a ratio of 1:1).

A decisive proof for the constitutions of the two azaphospholes is given by the ³¹P-NMR spectra: that of **14a** is characterized by a resonance at $\delta = 210.3$ ppm; this low-field position is indicative of a $\lambda^3\sigma^2$ -phosphorus atom with an adjacent nitrogen atom (compare with the ³¹P-resonances of **3**). In contrast, the phosphorus atom of **13a** absorbs at rather high field ($\delta = 66.3$ ppm) which is in harmony with the corresponding resonances of benzo-1,3-azaphosphole (**13**, R=H and H in place of *tert*-butyl)¹⁹ and of the 1,2,4-diazaphospholes¹.

The fact that the phosphorus atom in **14a** has only one neighbouring carbon atom is shown by the ¹³C-NMR spectrum. The resonance of C-3 at $\delta = 190.1$ ppm is split by phosphorus with a coupling constant of 58.0 Hz whereas that of C-3a has a phosphorus coupling constant of 11.2 Hz. In the spectrum of the isomeric **13a** (the resonances were determined from the isomeric mixture) by contrast, both neighbouring carbon atoms C-2 and C-3a ($\delta = 175.3$ and 140.3 ppm, respectively) exhibit $^1J_{C,P}$ coupling constants of comparable magnitudes (49.9 and 41.1 Hz, respectively).

Flash vacuum pyrolysis of **3e** gives rise to a similar product pattern as that of **3c**. The naphtho-condensed azaphospholes **14b** and **13b** are formed in a ratio of 3:1 (by ¹H-NMR spectroscopy on the basis of the signals of the *tert*-butyl groups). Product **14b** can be isolated in the pure state by fractional crystallization of the mixture. The assignment of the two isomers as 1,2- and 1,3-azaphospholes, respectively, is again based on ³¹P-NMR spectroscopy (**14b**: $\delta = 180.1$ and **13b**: $\delta = 74.4$ ppm).



For the interpretation of the reaction $3 \rightarrow 13 + 14$, it must be assumed that, in the final analysis, a phosphinidene (**8**) and a carbene (**10**) are responsible for the respective product formation. The two species can undergo interconversion through the azaphosphirine **9**²⁰. Access to this system of reactive intermediates by nitrogen extrusion proceeds by way of the anti-aromatic system **9** or the carbene **10**. [1,5]-Electrocyclization²¹ of the sextet intermediates (**8** \rightarrow **11** and **10** \rightarrow **12**) followed by a hydride shift to nitrogen (**11** \rightarrow **13** and **12** \rightarrow **14**) gives rise to the product patterns mentioned. To the best of our knowledge, ring closures of the type **8** \rightarrow **11** are not known for phosphinidenes. It is known from the literature, however, that styrylcarbenes undergo isomerization to indenenes²² and α -aryliminocarbenes to indoles²³ by analogous mechanisms.

EXPERIMENTAL SECTION

Melting points (not corrected): Mettler FP 61 (heating rate: 3 °C/min).- Elemental analyses: Perkin-Elmer Analyser 240.- IR spectra: Perkin-Elmer 397, Beckman IR 20A.- ¹H-NMR spectra: Varian EM 390, Bruker WP 200 (tetramethylsilane as internal standard).- ¹³C-NMR spectra: Bruker WP 200 (tetramethylsilane as internal standard).- ³¹P-NMR spectra: Bruker WP 200 (85% orthophosphoric acid as external standard).- All reactions with **1** were performed in an argon atmosphere (Schlenk tube technique); before use the reaction vessels were evacuated, baked out, and purged with argon. The solvents used were anhydrous and were distilled and stored under argon.

General Procedure for the Reaction of Phosphaalkyne **1** with Azides. A stirred solution of 0.50 g (5.0 mmol) of the phosphaalkyne **1**²⁴ in 10 ml of diethyl ether is cooled to 0 °C and 5.0 mmol of the azide **2** or **7**, respectively, in 5 ml of diethyl ether are added dropwise. The reaction is exothermic. After 30 min (or 60 min in the case of **2c**) the mixture is evaporated at 30 °C/14 mbar. Further purification by recrystallization or bulb-to-bulb distillation is as described below for the individual products. Temperatures given are bath temperatures.

5-tert-Butyl-3-methyl-3H-1,2,3,4-triazaphosphole (**3a**)²⁵. Reaction of 0.29 g of methyl azide (**2a**)²⁵. Yield: 0.71 g (91%) colourless liquid with b.p. 48 °C/10⁻² mbar.- IR(Film): ν = 2950 cm⁻¹ (CH), 1475, 1450, 1360, 1185, 1115, 785.- ¹H-NMR(CDCl₃): δ = 1.37 (d, ⁴J_{P,H} = 0.9 Hz, 9H, tBu), 3.85 (d, ³J_{P,H} = 7.2 Hz, 3H, Me).- ¹³C-NMR(CDCl₃): δ = 31.6 [d, ³J_{P,C} = 7.5 Hz, (H₃C)₃C], 35.0 [d, ²J_{P,C} = 16.8 Hz, (H₃C)₃C], 38.1 (d, ²J_{P,C} = 15.9 Hz, N-CH₃), 198.3 (d, ¹J_{P,C} = 54.9 Hz, C-5).- ³¹P-NMR(CDCl₃): δ = 173.5.- C₆H₁₂N₃P (157.16) calc. C,45.85; H,7.69; N,26.74. Found C,46.0; H,7.47; N,26.7%.

3,5-Di-tert-butyl-3H-1,2,3,4-triazaphosphole (**3b**)²⁶. Reaction of 0.50 g of tert-butyl azide (**2b**)²⁶. Yield: 1.0 g (100%) oil with b.p. 150 °C/5·10⁻² mbar that slowly crystallizes. Colourless crystals with m.p. 73 °C (from diethyl ether).- IR(KBr): ν = 2980 cm⁻¹ (CH), 1465, 1370, 1210, 1120, 840, 800.- ¹H-NMR(CDCl₃): δ = 1.45 (d, ⁴J_{P,H} = 1.8 Hz, 9H, C-tBu), 1.75 (d, ⁴J_{P,H} = 0.9 Hz, 9H, N-tBu).- ³¹P-NMR(C₆D₆): δ = 161.8.- C₉H₁₈N₃P (199.24) calc. C,54.26; H,9.11; N,21.09. Found C,54.1; H,9.10; N,21.1%.

5-tert-Butyl-3-phenyl-3H-1,2,3,4-triazaphosphole (**3c**)²⁷. Reaction of 0.59 g of phenyl azide (**2c**)²⁷. Yield: 1.02 g (93%) colourless crystals with m.p. 61 °C (from cyclopentane).- IR(KBr): ν = 3040 cm⁻¹ (CH-aromat.), 2950 (CH-aliph.), 1590, 1485, 1455, 1360, 1270, 1150, 1050, 770.- ¹H-NMR(CDCl₃): δ = 1.51 (d, ⁴J_{P,H} = 0.6 Hz, 9H, tBu), 7.2-7.3 (m, 5H, aromatic-H).- ¹³C-NMR(CDCl₃): δ = 31.0 [d, ³J_{P,H} = 7.9 Hz, (H₃C)₃C], 34.9 [d, ²J_{P,C} = 16.6 Hz, (H₃C)₃C], 121.7, 121.8, 128.2, 129.3 (aromatic-C), 140.6 (d, ²J_{P,C} = 10.3 Hz, aromatic-C), 198.0 (d, ¹J_{P,C} = 55.6 Hz, C-5).- ³¹P-NMR(CDCl₃): δ = 168.6.- C₁₁H₁₄N₃P (219.22) calc. C,60.24; H,6.44; N,19.17. Found C,60.2; H,6.44; N,19.3%.

5-tert-Butyl-3-(4-ethoxycarbonylphenyl)-3H-1,2,3,4-triazaphosphole (**3d**)²⁸. Reaction of 0.96 g of 4-ethoxycarbonylphenyl azide (**2d**)²⁸. Yield: 1.30 g (90%) oil with b.p. 150 °C/5·10⁻² mbar that slowly crystallizes. Colourless crystals with m.p. 65 °C (from diethyl ether).- IR(KBr):

$\nu = 2980 \text{ cm}^{-1}$ (CH), 1730 (CO), 1620, 1520, 1470, 1430, 1380, 1280, 1180, 1110, 1020, 870, 780.- $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1.41$ (t, $^3\text{J}_{\text{H,H}} = 7.2$ Hz, 3H, $\text{H}_3\text{C-Ethyl}$), 1.50 (d, $^4\text{J}_{\text{P,H}} = 1.1$ Hz, 9H, tBu), 4.38 (q, $^3\text{J}_{\text{H,H}} = 7.2$ Hz, 2H, $\text{H}_2\text{C-Ethyl}$), 7.8-8.2 (m, 4H, aromatic-H).- $^{13}\text{C-NMR}(\text{C}_6\text{D}_6)$: $\delta = 13.9$ (q, $^1\text{J}_{\text{C,H}} = 127.0$ Hz, CH_2-CH_3), 31.0 [dq, $^3\text{J}_{\text{P,C}} = 7.6$ Hz, $^1\text{J}_{\text{H,C}} = 128.2$ Hz, $(\text{H}_3\text{C})_3\text{C}$], 35.0 [d, $^2\text{J}_{\text{P,C}} = 15.4$ Hz, $(\text{H}_3\text{C})_3\text{C}$], 60.9 (t, $^1\text{J}_{\text{H,C}} = 148.6$ Hz, CH_2-CH_3), 121.2 (dd, $^3\text{J}_{\text{P,C}} = 8.8$ Hz, $^1\text{J}_{\text{H,C}} = 165.5$ Hz, aromatic-C-2,6), 130.1 (s, aromatic-C-4), 130.5 (d, $^1\text{J}_{\text{H,C}} = 166.1$ Hz, aromatic-C-3,5), 144.0 (d, $^2\text{J}_{\text{P,C}} = 9.9$ Hz, aromatic-C-1), 165.4 (s, CO), 198.7 (d, $^1\text{J}_{\text{P,C}} = 55.7$ Hz, C-5).- $^{31}\text{P-NMR}(\text{C}_6\text{D}_6)$: $\delta = 170.8$.- $\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}_2\text{P}$ (291.29) calc. C,57.73; H,6.23; N,14.43. Found C,57.8; H,6.26; N,14.5%.

5-tert-Butyl-3-(1-naphthyl)-3H-1,2,3,4-triazaphosphole (3e). Reaction of 0.85 g of 1-naphthyl azide (2e)²⁹. Yield: 1.02 g (76%) colourless crystals with m.p. 131 °C (from diethyl ether).- IR(KBr): $\nu = 3060 \text{ cm}^{-1}$ (CH-aromat.), 2990 (CH-aliphatic.), 1610, 1520, 1470, 1400, 1370, 1290, 1120, 1040, 810, 790, 770.- $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1.55$ (d, $^4\text{J}_{\text{P,H}} = 1.2$ Hz, 9H, tBu), 7.5-8.0 (m, 7H, aromatic-H).- $^{13}\text{C-NMR}(\text{C}_6\text{D}_6)$: $\delta = 31.4$ [dq, $^3\text{J}_{\text{P,C}} = 7.4$ Hz, $^1\text{J}_{\text{H,C}} = 125.7$ Hz, $(\text{H}_3\text{C})_3\text{C}$], 35.2 [d, $^2\text{J}_{\text{P,C}} = 15.5$ Hz, $(\text{H}_3\text{C})_3\text{C}$], 122.5-136.6 (m, aromatic-C), 198.9 (d, $^1\text{J}_{\text{P,C}} = 57.3$ Hz, C-5).- $^{31}\text{P-NMR}(\text{C}_6\text{D}_6)$: $\delta = 180.7$.- $\text{C}_{15}\text{H}_{16}\text{N}_3\text{P}$ (269.29) calc. C,66.90; H,5.99; N,15.60. Found C,67.0; H,6.06; N,15.6%.

5-tert-Butyl-3-vinyl-3H-1,2,3,4-triazaphosphole (3f). Reaction of 0.35 g of vinyl azide (2f)³⁰. Yield: 0.79 g (93%) colourless liquid with b.p. 70 °C/5·10⁻³ mbar.- IR(Film): $\nu = 3080 \text{ cm}^{-1}$ (CH-vinyl.), 2960 (CH-aliphatic.), 1630 (C=C), 1475, 1360, 1250, 1205, 1115, 815.- $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1.47$ (d, $^4\text{J}_{\text{P,H}} = 1.5$ Hz, 9H, tBu), 5.11 (dd, A-part of an ABMX-system, $^2\text{J}_{\text{H,H}} = 1.7$ Hz, $^3\text{J}_{\text{H,H(cis)}} = 8.8$ Hz, 1H), 5.76 (m, B-part of an ABMX-system, $^2\text{J}_{\text{H,H}} = 1.7$ Hz, $^3\text{J}_{\text{H,H(trans)}} = 15.8$ Hz, $^4\text{J}_{\text{P,H}} = 2.2$ Hz, 1H), 7.63 (m, M-part of an ABMX-system, $^3\text{J}_{\text{H,H(cis)}} = 8.8$ Hz, $^3\text{J}_{\text{H,H(trans)}} = 15.8$ Hz, $^3\text{J}_{\text{P,H}} = 5.4$ Hz, 1H).- $^{13}\text{C-NMR}(\text{CDCl}_3)$: $\delta = 31.4$ [d, $^3\text{J}_{\text{P,C}} = 7.8$ Hz, $(\text{H}_3\text{C})_3\text{C}$], 35.3 [d, $^2\text{J}_{\text{P,C}} = 16.2$ Hz, $(\text{H}_3\text{C})_3\text{C}$], 105.5 (d, $^2\text{J}_{\text{P,C}} = 11.9$ Hz, $\text{CH}=\text{CH}_2$), 135.3 (d, $^3\text{J}_{\text{P,C}} = 11.9$ Hz, $\text{CH}=\text{CH}_2$), 198.3 (d, $^1\text{J}_{\text{P,C}} = 55.6$ Hz, C-5).- $^{31}\text{P-NMR}(\text{CDCl}_3)$: $\delta = 175.2$.- $\text{C}_7\text{H}_{12}\text{N}_3\text{P}$ (169.17) calc. C,49.69; H,7.15; N,24.84. Found C,48.9; H,7.02; N,25.0%.

Methyl 5-tert-Butyl-3H-1,2,3,4-triazole-3-carboxylate (3g). Reaction of 0.51 g of methoxy-carbonyl azide (2g)³¹. Yield: 0.92 g (92%) colourless crystals with m.p. 41 °C (from pentane).- IR(KBr): $\nu = 2960 \text{ cm}^{-1}$ (CH), 1785 (CO), 1475, 1455, 1320, 1195, 1125, 790.- $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1.37$ (d, $^4\text{J}_{\text{P,H}} = 1.2$ Hz, 9H, tBu), 3.70 (s, 3H, OMe).- $^{13}\text{C-NMR}(\text{CDCl}_3)$: $\delta = 32.1$ [d, $^3\text{J}_{\text{P,C}} = 7.5$ Hz, $(\text{H}_3\text{C})_3\text{C}$], 38.2 [d, $^2\text{J}_{\text{P,C}} = 15.5$ Hz, $(\text{H}_3\text{C})_3\text{C}$], 172.4 (d, $^2\text{J}_{\text{P,C}} = 21.0$ Hz, CO), 199.4 (d, $^1\text{J}_{\text{P,C}} = 55.2$ Hz, C-5).- $^{31}\text{P-NMR}(\text{CDCl}_3)$: $\delta = 177.1$.- $\text{C}_7\text{H}_{12}\text{N}_3\text{O}_2\text{P}$ (201.17) calc. C,41.79; H,6.01; N,20.89. Found C,41.8; H,5.90; N,20.8%.

5-tert-Butyl-3-cyanomethyl-3H-1,2,3,4-triazaphosphole (3h). Reaction of 0.41 g of azido-acetonitrile (2h)³². Yield: 0.78 g (86%) colourless oil with b.p. 72 °C/5·10⁻³ mbar.- IR (Film): $\nu = 2960 \text{ cm}^{-1}$ (CH), 2210 (CN), 1475, 1455, 1360, 1215, 1120.- $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1.32$ (d, $^4\text{J}_{\text{P,H}} = 1.4$ Hz, 9H, tBu), 4.73 (d, $^3\text{J}_{\text{P,H}} = 5.8$ Hz, CH_2).- $^{31}\text{P-NMR}(\text{CDCl}_3)$: $\delta = 175.8$.- $\text{C}_7\text{H}_{11}\text{N}_4\text{P}$ (182.17) calc. C,46.15; H,6.09; N,30.76. Found C,46.0; H,6.00; N,31.1%.

5-tert-Butyl-3-trimethylsilylmethyl-3H-1,2,3,4-triazaphosphole (3i). Reaction of 0.65 g of trimethylsilyl azide (**2i**)³³. Yield: 1.10 g (96%) colourless oil with b.p. 75 °C/5·10⁻² mbar).- IR(Film): $\nu = 2950 \text{ cm}^{-1}$ (CH), 1475, 1360, 1250, 1115, 855.- ¹H-NMR(C₆D₆): $\delta = -0.01$ (s, 9H, Tms), 1.45 (d, ⁴J_{P,H} = 1.2 Hz, 9H, tBu), 3.82 (d, ³J_{P,H} = 6.5 Hz, CH₂-Tms).- ¹³C-NMR(CDCl₃): $\delta = -2.3$ [s, (H₃C)₃Si], 31.8 [d, ³J_{P,C} = 7.5 Hz, (H₃C)₃C], 35.3 [d, ²J_{P,C} = 16.5 Hz, (H₃C)₃C], 43.9 (d, ²J_{P,C} = 10.9 Hz, CH₂-Tms), 197.6 (d, ¹J_{P,C} = 56.3 Hz, C-5).- ³¹P-NMR(CDCl₃): $\delta = 173.2$.- C₉H₂₀N₃PSi (229.34) calc. C,47.13; H,8.79; N,18.32. Found C,47.2; H,8.61; N,18.3%.

5-tert-Butyl-2-trimethylsilyl-2H-1,2,3,4-triazaphosphole (3j). Reaction of 0.58 g of trimethylsilyl azide (**2j**)³⁴. Yield: 0.79 g (73%) colourless, moisture-sensitive liquid with b.p. 50 °C/5·10⁻³ mbar that slowly crystallizes at 0 °C (m.p. 48 °C).- IR(KBr): $\nu = 2960 \text{ cm}^{-1}$ (CH), 1475, 1360, 1255, 1075, 850.- ¹H-NMR(C₆D₆): $\delta = 0.35$ (s, 9H, Tms), 1.49 (d, ⁴J_{P,H} = 1.2 Hz, 9H, tBu).- ¹³C-NMR(C₆D₆): $\delta = 0.54$ [s, (H₃C)₃Si], 34.8 [d, ³J_{P,C} = 7.6 Hz, (H₃C)₃C], 36.9 [d, ²J_{P,C} = 13.9 Hz, (H₃C)₃C], 204.6 (d, ¹J_{P,C} = 58.4 Hz, C-5).- ³¹P-NMR(C₆D₆): $\delta = 183.2$.- C₉H₁₈N₃PSi (215.31) calc. C,44.62; H,8.42; N,19.51. Found C,44.3; H,8.36; N,19.5%.

5-tert-Butyl-1,2,3,4-triazaphosphole (6). Reaction of 0.21 g of hydrazoic acid (**7**)³⁵. Yield: 0.62 g (86%) colourless crystals with m.p. 76 °C (from pentane).- IR(KBr): $\nu = 3030 \text{ cm}^{-1}$ (NH), 2950 (CH), 1475, 1455, 1360, 1260, 680.- ¹H-NMR(CDCl₃): $\delta = 1.43$ (d, ⁴J_{P,H} = 1.4 Hz, 9H, tBu), 14.6 (s, breit, 1H, NH).- ¹³C-NMR(CDCl₃): $\delta = 31.8$ [d, ³J_{P,C} = 7.0 Hz, (H₃C)₃C], 35.3 [d, ²J_{P,C} = 13.7 Hz, (H₃C)₃C], 190.0 (d, ¹J_{P,C} = 60.9 Hz, C-5).- ³¹P-NMR(CDCl₃): $\delta = 160.8$.- C₅H₁₀N₃P (143.13) calc. C,41.94; H,7.04; N,29.36. Found C,41.9; H,7.02; N,29.2%.

Hydrolysis of 4j to 6. A solution of 0.54 g (2.5 mmol) of **4j** in 20 ml of diethyl ether is stirred with 2 g of silicagel for 30 min without protection from moisture. Filtration, evaporation of the filtrate, and recrystallization of the residue from pentane give 0.33 g (91%) of **6** with m.p. 76 °C. Mixture melting point as well as IR and ³¹P-NMR spectral data are identical with those of the product obtained from the reaction of **1** with **7** (see above).

Flash Vacuum Pyrolysis of the Triazaphosphole 3c. 0.55 g (2.5 mmol) of the triazaphosphole **3c** are subjected to flash vacuum pyrolysis at 540 °C/10⁻⁴ mbar (quartz tube, 1.0 X 30 cm) for a period of 3 h. The pyrolysis product is frozen out on a cold finger at -196 °C. On warming to room temperature 0.45 g (95%) of an isomer mixture consisting of 3-tert-butyl-1H-1,2-benzazaphosphole (14a) and 2-tert-butyl-1H-1,3-benzazaphosphole (13a) in a ratio of 4:1 (by ³¹P-NMR spectroscopy) is obtained. The yellow, viscous oil gave a correct elemental analysis.

Medium pressure chromatography (Büchi MPLS-681, glass column 46 X 2.6 cm) of the isomeric mixture on silicagel (Merck, 15-20 μm) with 500 ml of chloroform/hexane 3:1 gives in succession:

a) 0.30 g (62%) of **14a** as pale yellow crystals with m.p. 86 °C (from cyclopentane).- IR(KBr): $\nu = 3220 \text{ cm}^{-1}$ (NH), 3000 (CH-aromat.), 2950 (CH-aliphatic), 1580, 1480, 1210, 730.- ¹H-NMR(CDCl₃): $\delta = 1.57$ (d, ⁴J_{P,H} = 2.2 Hz, 9H, tBu), 7.1-7.8 (m, 4H, aromatic-H), 9.1 (s, broad, 1H, NH).- ¹³C-NMR(CDCl₃): $\delta = 31.7$ [d, ³J_{P,C} = 13.6 Hz, (H₃C)₃C], 35.2 [d, ²J_{P,C} = 17.2 Hz,

(H_3C) $_3\text{C}$], 113.6, 119.2, 121.0, 123.1 (aromatic-C), 120.1 (d, $^2\text{J}_{\text{P,C}} = 11.2$ Hz, C-3a), 147.5 (d, $^2\text{J}_{\text{P,C}} = 2.3$ Hz, C-7a), 190.1 (d, $^1\text{J}_{\text{P,C}} = 58.0$ Hz, C-3).- $^{31}\text{P-NMR}(\text{CDCl}_3)$: $\delta = 210.3$.- $\text{C}_{11}\text{H}_{14}\text{NP}$ (191.21) calc. C,69.09; H,7.38; N,7.33. Found C,69.0; H,7.24; N,7.2%.

b) 0.11 g (23%) of the isomeric mixture **14a/13a** in a ratio of 1:1 (by $^{31}\text{P-NMR}$ spectroscopy). The NMR spectroscopic data of **13a** were determined from this mixture.- $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1.40$ (d, $^4\text{J}_{\text{P,H}} = 1.2$ Hz, 9H, tBu), 7.0-7.8 (m, 4H, aromatic-H).- $^{13}\text{C-NMR}(\text{CDCl}_3)$: $\delta = 31.1$ [d, $^3\text{J}_{\text{P,C}} = 8.5$ Hz, (H_3C) $_3\text{C}$], 35.8 [d, $^2\text{J}_{\text{P,C}} = 13.8$ Hz, (H_3C) $_3\text{C}$], 113.2, 124.3, 128.5, 129.9 (aromatic-C), 140.3 (d, $^1\text{J}_{\text{P,C}} = 41.1$ Hz, C-3a), 142.5 (d, $^2\text{J}_{\text{P,C}} = 8.2$ Hz, C-7a), 175.3 (d, $^1\text{J}_{\text{P,C}} = 49.9$ Hz, C-2).- $^{31}\text{P-NMR}(\text{CDCl}_3)$: $\delta = 66.3$.

Flash Vacuum Pyrolysis of the Triazaphosphole 3e. From the flash vacuum pyrolysis of 0.67 g (2.5 mmol) of the triazaphosphole **3e** at $580^\circ\text{C}/2 \cdot 10^{-4}$ mbar as described above 0.60 g (99%) of an isomer mixture consisting of 3-tert-butyl-1H-naphtho[1,2-d]-1,2-azaphosphole (14b) and 2-tert-butyl-1H-naphtho[1,2-d]-1,3-azaphosphole (13b) in a ratio of 3:1 (by $^1\text{H-NMR}$ spectroscopy) are obtained. Fractional crystallization from diethyl ether gives 0.19 g (32%) of analytically pure **14b** as colourless crystals with m.p. 135°C .- IR(KBr): $\nu = 3420$ cm^{-1} (NH), 2970 (CH), 1520, 1460, 1400, 1370, 1300, 1220, 820, 755.- $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1.59$ (d, $^4\text{J}_{\text{P,H}} = 2.3$ Hz, 9H, tBu), 7.2-7.8 (m, 6H, aromatic-H).- $^{13}\text{C-NMR}(\text{CDCl}_3)$: $\delta = 31.8$ [d, $^3\text{J}_{\text{P,C}} = 12.6$ Hz, (H_3C) $_3\text{C}$], 35.2 [d, $^2\text{J}_{\text{P,C}} = 17.2$ Hz, (H_3C) $_3\text{C}$], 120.4-130.4 (aromatic-C), 143.6 (s, C-7a), 177.0 (d, $^1\text{J}_{\text{P,C}} = 40.5$ Hz, C-3).- $^{31}\text{P-NMR}(\text{CDCl}_3)$: $\delta = 180.1$.- $\text{C}_{15}\text{H}_{16}\text{N}$ (241.12) calc. C,74.67; H,6.68; N,5.81. Found C,75.0; H,6.68; N,5.9%.

The following data for **13b** were determined from the original isomeric mixture: $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1.50$ (d, $^4\text{J}_{\text{P,H}} = 1.2$ Hz, 9H, tBu), 7.3-8.1 (m, 6H, aromatic-H).- $^{31}\text{P-NMR}(\text{CDCl}_3)$: $\delta = 74.4$.

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REFERENCES AND FOOTNOTES

- 1 Part 19: W. Rösch, U. Hees, M. Regitz, Chem. Ber. **120** (1987) in press.
- 2 Review: F. Mathey, Top. Phosphorus Chem. **10** (1980) 1.
- 3 F. Mathey, F. Mercier, C. Charrier, J. Am. Chem. Soc. **103** (1981) 4595.
- 4 C. Charrier, H. Bonnard, G. DeLauzon, S. Holand, F. Mathey, Phosphorus Sulfur **18** (1983) 51.- S. Holand, C. Charrier, F. Mathey, J. Fischer, A. Mitschler, J. Am. Chem. Soc. **106** (1984) 826.

- 5 A. Schmidpeter, K. Karaghiosoff, Nachr. Chem. Techn. Lab. **33** (1985) 793.
- 6 Y. Charbonnel, J. Barrans, Tetrahedron **32** (1976) 2039.
- 7 A. Schmidpeter, H. Tautz, Z. Naturforsch. **35b**(1980) 1222.
- 8 Preliminary communication: W. Rösch, M. Regitz, Angew. Chem. **96**(1984) 898; Angew. Chem., Int. Ed. Engl. **23** (1984) 900.
- 9 Preliminary communication: Y. Y. C. Yeung Lam Ko, R. Carrié, A. Muench, G. Becker, J. Chem. Soc., Chem. Commun. **1984**, 1634.
- 10 Y. Y. C. Yeung Lam Ko, R. Carrié, J. Chem. Soc., Chem. Commun. **1984**, 1640.
- 11 T. Allspach, M. Regitz, G. Becker, W. Becker, Synthesis **1986**, 31.
- 12 W. Rösch, U. J. Vogelbacher, T. Allspach, M. Regitz, J. Organomet. Chem. **306**(1986) 39.
- 13 M. Hermesdorf, H. Heydt, M. Regitz, unpublished results, University of Kaiserslautern 1986.
- 14 W. Lwowski in 1,3-Dipolar Cycloaddition Chemistry (A. Padwa, ed.) 1st. Edn., Vol.1, p.628ff., Wiley, New York 1984.
- 15 G. Becker, G. Gresser, W. Uhl, Z. Naturforsch. **36b**(1981) 16.
- 16 J. Högel, A. Schmidpeter, W. S. Sheldrick, Chem. Ber. **116** (1983) 549.
- 17 L. Birkofer, P. Wegner, Chem. Ber. **99**(1966) 2512; ibid **100**(1967) 3485.
- 18 The first experiments were performed in 1985 by Professor Wentrup's group at the University of Marburg. We take this opportunity to thank Professor Wentrup for his help.
- 19 K. Issleib, R. Vollmer, Z. Anorg. Allg. Chem. **481**(1981) 22.
- 20 On the problem of 1H-azirines, see: M. Regitz, B. Arnold, D. Danion, H. Schubert, G. FuBer, Bull. Soc. Chim. Belg. **90**(1981) 615.
- 21 Review: R. Huisgen, Angew. Chem. **92** (1980) 979; Angew. Chem., Int. Ed. Engl. **19** (1980) 947.
- 22 W. Welter, A. Hartmann, M. Regitz, Chem. Ber. **111**(1978) 3068.
- 23 G. Mitchell, C. W. Rees, J. Chem. Soc., Perkin Trans. I **1987**, 413.
- 24 Compare with Ref. ¹⁵; for an improved procedure, see: Ref. ¹.
- 25 O. Dimroth, W. Wislicenus, Ber. Dtsch. Chem. Ges. **38**(1905) 1573.
- 26 J. A. Miller, Tetrahedron Lett. **1975**, 2959; in place of carbon disulfide as solvent, dimethylformamide was used and the tert-butyl azide (**2b**) was distilled out of the reaction mixture.
- 27 H. Bretschneider, H. Rager, Monatsh. Chem. **81** (1950) 970.
- 28 M. O. Forster, H. E. Fierz, J. Chem. Soc. **91**(1907) 1942.
- 29 O. Dimroth, K. Pfister, Ber. Dtsch. Chem. Ges. **43** (1910) 2757.
- 30 R. H. Wiley, J. Moffat, J. Org. Chem. **22**(1957) 995.
- 31 M. O. Forster, H. E. Fierz, J. Chem. Soc. **93**(1908) 72.
- 32 K. Freudenberg, E. Eichel, F. Leutert, Ber. Dtsch. Chem. Ges. **65**(1932) 1183.
- 33 K. Nishiyama, N. Tanaka, J. Chem. Soc., Chem. Commun. **1983**, 1322.
- 34 S. S. Washburne, W. R. Peterson, J. Organomet. Chem. **33**(1971) 153.
- 35 Collective of Authors, Organikum, 15th. Edn., p.807, VEB-Verlag der Wissenschaften, Berlin 1981.