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Azidophosphanes: Attractive Starting Materials for the Preparation of Phosphazenes

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ABSTRACT

Azidophosphanes are versatile reactants in the Staudinger reaction. The azides Cl_2PN_3 (**1**), *$(Et_2N)ClPN_3$* (**2**), *and $(Et_2N)_2PN_3$* (**3**) *react with phosphanes to give the N-phosphanyl phosphazenes* **4–10**. *$(Et_2N)P(N_3)_2$ is oxidized by PhN_3 yielding $(Et_2N)P(N_3)_2{=}NPh$* (**11**), *which with PPh_3 yields the di- and triphosphazenes* **12** *and* **13**.

INTRODUCTION

In recent times azidophosphanes R_2PN_3 have been a subject of interest, especially for the intermediate formation of monomeric phosphonitriles, $R_2P{\equiv}N$ [1–4]. Their photolysis or thermolysis in the absence of trapping agents yields oligomers or polymers [1, 2, 5]. Irradiation in the presence of suitable agents leads to addition products of the transient phosphonitriles [3, 4]. Covalent azides generally oxidize phosphanes (Staudinger reaction), and although phosphorylazides have been frequently used for synthesizing *N*-phosphoryl phosphazenes [6–9], surprisingly only very little information exists on azidophosphanes for the synthesis of defined phosphanyl phosphazenes. It is even reported [2] that the azidophosphanes $RR'PN_3$ (R = *t*-Bu, R′ = *t*-Bu, N(*i*-PR)$_2$; R = NMe_2, R′ = N(*i*-Pr)$_2$) don't react with PBu_3. On the other hand Gusar et al. [10], Horn et al. [11], and Paciorek [12] describe the reaction of azidophosphanes with phosphites [10] or PPh_3 [11, 12], respectively. The methods for preparing *N*-phosphanyl phosphazenes, known in the literature, are rather complicated [13, 14]. Therefore, we studied the possibility and the conditions for preparing compounds of this type using azidophosphanes as reactants. The use of halogeno azidophosphanes for this synthesis has not yet been described in the literature.

RESULTS AND DISCUSSION

The azidophosphanes Cl_2PN_3 (**1**), $(Et_2N)ClPN_3$ (**2**), and $(Et_2N)_2PN_3$ (**3**) can be obtained in good yields by nucleophilic exchange of chloride by azide with trimethylsilylazide (TMSA) or sodium azide, NaN_3, at low temperatures [18]. Solutions <1M in mixtures of acetonitrile and toluene are sufficiently stable at room temperature to allow the use of compounds **1–3** for the synthesis of novel mono-, di-, and triphosphazenes. They may react both as azide and as phosphane components in the Staudinger reaction.

Azidodichlorophosphane, Cl_2PN_3 (**1**), prepared in situ from PCl_3 and TMSA, reacts with tertiary phosphanes at room temperature forming the *N*-phosphanyl phosphazenes **4–8** (Table 1):

$$Cl_2PN_3 + PR_3 \longrightarrow Cl_2P{-}N{=}PR_3 + N_2$$

Whereas the reaction with triphenylphosphane is quantitative, in the case of the other phosphanes the yields are decreased due to redox reactions between the educts PCl_3 and PR_3 [15].

Compounds **4** and **5** have already been prepared in a different way by Fluck and Hösle [13]. Compound **4** can be isolated from the reaction mixture

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TABLE 1 ^{31}P NMR Data for *N*-phosphanyl Phosphazenes **4–10**, $R^1R^2P{-}N{=}P'R_3$, and for the di- and triphosphazenes **12** and **13** $Et_2N(N_3)_n(Ph_3P'{=}N{-})_{2-n}P{=}NPh$

Comp.	R^1	R^2	R_3	δP	$\delta P'$	$^2J(PP')$/Hz
4	Cl	Cl	Ph_3	165.8	15.4	74.7
5	Cl	Cl	*n*-Bu_3	156.9	39.9	89.4
6	Cl	Cl	Et_2Ph	162.0	38.0	90.0
7	Cl	Cl	$EtPh_2$	165.0	24.0	86.5
8	Cl	Cl	$(c\text{-}C_6H_{11})_3$	158.0	42.0	115.0
9	Cl	NEt_2	Ph_3	186.5	13.5	76.1
10	NEt_2	NEt_2	$(NEt_2)_3$	180.8	24.6	96.6
12	$n = 1$	(AB)		18.5	6.4	24.2
13	$n = 0$	(AB_2)		−2.9	8.3	26.4

as a well-crystallized solid, while compounds **5–8** are obtained only as impure viscous liquids, which cannot be distilled in a vacuum.

The reactivity of the azidophosphanes $[(Et_2N)_{2-n}PCl_nN_3$ (n = 0, 1, 2)] against triphenylphosphane decreases with increasing n. Whereas compound **4** is obtained in almost quantitative yield, *N*-chloro(diethylamino)phosphanyl triphenylphosphazene, $(Et_2N)ClP{-}N{=}PPh_3$ (**9**), is only formed in about 70% yield from **2** under similar conditions. Compound **3** does not react with triphenylphosphane even at higher temperatures (80°C). Instead, oligomeric and polymeric products were detected in the reaction mixtures, indicating a decomposition of **3** (see, e.g., [2, 5]):

$$n(Et_2N)_2PN_3 \longrightarrow 1/n[(Et_2N)_2PN]_n + nN_2$$

However, the use of the more nucleophilic tris(diethylamino)phosphane produces the *N*-phosphanyl phosphazene **10** in good yields:

$$(Et_2N)_2PN_3 + P(NEt_2)_3 \longrightarrow (Et_2N)_2P{-}N{=}P(NEt_2)_3 + N_2$$

The ^{31}P NMR spectra of all the *N*-phosphanyl phosphazenes obtained in this manner show an AX spin system (see Table 1).

That azidophosphanes give the Staudinger reaction with sufficiently reactive azides has already been shown in the literature, e.g., [16, 17]. We used $Et_2NP(N_3)_2$ prepared from Et_2NPCl_2 and TMSA in the molar ratio 1:2:

$$Et_2NPCl_2 + 2\ Me_3SiN_3 \longrightarrow Et_2NP(N_3)_2 + 2\ Me_3SiCl$$

Its reaction with phenyl azide yields the bis(azido)phosphazene **11** ($\delta^{31}P$: −11):

$$Et_2NP(N_3)_2 + PhN_3 \longrightarrow Et_2N(N_3)_2P{=}NPh + N_2$$

11

Even at room temperature compound **11** reacts with triphenylphosphane:

$$Et_2N(N_3)_2P{=}NPh + (2 - x)PPh_3 \longrightarrow x\ Et_2N(N_3)(PhN{=})P{-}N{=}PPh_3$$

12

$$+ (1 - x)\ Et_2N(PhN{=})P(-N{=}PPh_3)_2 + (2 - x)N_2$$

13

If $x > 0$, a mixture of the products **12** and **13** is formed. In the case of $x = 0$, the pure product **13** can be isolated. The NMR data are given in Table 1.

EXPERIMENTAL

The ^{31}P NMR spectra were measured on a Bruker FT spectrometer AM 300. The chemical shifts are relative to 85% phosphoric acid as external standard. A positive sign indicates a low field shift.

The mass spectra were obtained with a Varian spectrometer MAT CH-6 at 70 eV.

All investigations were carried out with careful exclusion of moisture and oxygen by working in a dry nitrogen atmosphere.

Preparation of the Azidophosphanes **1–3**

To the solution of 6 mmol of the corresponding chloride (PCl_3, Et_2NPCl_2, $(Et_2N)_2PCl$) in 2 mL of toluene and 2 mL of acetonitrile 6 mmol of TMSA (trimethylsilylazide) or NaN_3 was added at temperatures of 0–15°C. To complete the conversion of the chlorides into the azides, the reaction mixture was stirred for about 2 h at the same temperature. *In order to avoid explosions, maximum care has to be taken in preparing and handling the solutions of azidophosphanes. Particularly, the phosphorus chlorides must be free of HCl, which is easily formed by*

hydrolysis. For removing HCl, the phosphorus chlorides were treated with CaH_2 and freshly distilled before use.

The azidophosphanes were characterized by ^{31}P NMR: Cl_2PN_3 (**1**): δ = 160.8 (literature [18]: 161.6); $(Et_2N)ClPN_3$ (**2**): δ = 149.5; $(Et_2N)_2PN_3$ (**3**): δ = 120.8.

N-*Dichlorophosphanyl triphenylphosphazene*, **4**

In a 250 mL three-necked flask equipped with a thermometer, a powder addition funnel and a gas burette, 13.75 g (0.1 mol) of PCl_3 and 26.2 g (0.1 mol) of PPh_3 were dissolved in 40 mL toluene and 22 mL acetonitrile at room temperature. Then, within 3 h, 6.5 g (0.1 mol) NaN_3 was added gradually while the mixture was stirred magnetically. The reaction mixture became slightly warm and nitrogen was produced continuously. The temperature in the reaction vessel had to be kept at 20–25°C by cooling in a water bath. After nitrogen evolution has ceased, the mixture was allowed to stand for 12 h at room temperature. Then NaCl was separated and the vessel containing the filtrate was stored at −30°C. Compound **4** crystallized from this solution as a colorless solid of high purity. Mp: 129–132°C (literature [13]: 115–117°C). Yield: 26.5 g (70%). Analysis: C: Found: 58.2% (Calc.: 57.2%); H: 4.1 (4.0); Cl: 18.5 (18.8); N: 3.7 (3.7); P: 16.7 (16.4). MS: *m/e* = 381 (intensity: 1.3%) (M^+ + 4); 380 (1.4) (M^+ + 3); 379 (6.2) (M^+ + 2); 378 (2.0) (M^+ + 1); 377 (9.3) (M^+); 345 (2.4) (380 − ^{35}Cl); 344 (11.6) (379 − ^{35}Cl); 343 (7.3) (378 − ^{35}Cl); 342 (33.9) (M^+ − ^{35}Cl); 307 (2.1) (M^+ − 2(^{35}Cl)); 278 (17.7) ($Ph_3PNH_2^+$); 277 (43.9) (Ph_3PNH^+) and additional fragments of lower value.

Preparation of the N-*phosphanyl Phosphazenes* **5–8**

A solution of 1.1 g (8 mmol) of PCl_3, dissolved in 8 mL of acetonitrile and 4 mL of toluene, was placed in the same device as described for the preparation of **4** and was magnetically stirred. At first, within 1 h, 0.52 g (8 mmol) of NaN_3 was added and then the calculated amount of PR_3 (**5**: 1.62 g P(*n*-Bu)$_3$; **6**: 1.33 g PEt_2Ph; **7**: 1.71 g $PEtPh_2$; **8**: 2.24 g P(*c*-C_6H_{11})$_3$ dissolved in 6 mL of toluene). The temperature must not rise above 10°C. The reaction mixtures were stirred for about 2.5 h, then they were filtered and the solvents removed under reduced pressure. The products **5–8** were obtained as viscous liquids, which decomposed when distillation was attempted. Yields: 50–60%. For ^{31}P NMR data see Table 1.

N-*Chlorodiethylaminophosphanyl Triphenylphosphazene*, **9**

A solution of 1.4 g (8.1 mmol) of Et_2NPCl_2 and 2.1 g (8 mmol) of PPh_3 was dissolved in a mixture of 2 mL of toluene and 2 mL of acetonitrile; 0.93 g TMSA was then added dropwise at 20–25°C. The reaction was finished after about 2.5 h. After removal of the volatile compounds, **9** remained as an oily liquid in a yield of 70%.

N-*Bis(diethylamino)phosphanyltris-(diethylamino)phosphazene*, **10**

To a freshly prepared solution of 4.6 mmol of $(Et_2N)_2PN_3$ (**3**) in 4 mL of toluene 1.12 g (4.5 mmol) of $P(NEt_2)_3$ was added at 40°C. The reaction was complete after about 2 h. The solvent was removed in vacuo. Compound **10** remained as an oily residue. Yield: 1.1 g (56%).

N-*Phenyl Diazido(diethylamido)phosphazene*, **11**

To a stirred solution of 2.48 g (14.3 mmol) of Et_2NPCl_2 in 4 mL of toluene 3.3 g (28.7 mmol) of TMSA was added dropwise at 0°C. After being warmed to 20°C, 1.7 g (14.3 mmol) PhN_3 was added. After 1 h the mixture was heated to 40°C for 4 h. According to the ^{31}P NMR spectrum the reaction mixture contained no other P compounds except **11**. This solution was used for preparing compounds **12** and **13**. The isolation of **11** was not attempted.

N-*Phenyl Azido(diethylamido)-(triphenylphosphazenyl)phosphazene*, **12**, *and* N-*phenyl Diethylamido-bis(triphenylphosphazenyl)phosphazene*, **13**

A solution of 3.7 g (14.2 mmol) of PPh_3 in 4 mL of toluene was added at room temperature to a solution of 7.1 mmol of **11** in 2 mL of toluene. A vigorous evolution of nitrogen took place, and the reaction mixture became very warm. After completion of the N_2 evolution the mixture was stirred for a further 2 h at 50°C. Then the solution was reduced to about half its volume by evaporating the solvent in vacuo. Compound **13** was obtained as a colorless solid in a yield of 75% (5.3 g). By using a smaller amount of PPh_3 a mixture of the compounds **12** and **13** was obtained. The NMR data are given in Table 1.

13: Mp: 242–245°C; MS: *m/e* = 748 (intensity: 0.8%) (M^+ + 2); 747 (3.5) (M^+ + 1); 746 (6.9) (M^+); 745 (2.4) (M^+ − H); 719 (2.1) (748 − Et); 718 (7.8) (747 − Et); 717 (17.5) (M^+ − Et); 676 (1.8) (748 − Et_2N); 675 (7.9) (747 − Et_2N); 674 (16.2) (M^+ − Et_2N); 585 (8.6) (748 − Et_2N–PhN); 584 (44.1) (747 − Et_2N–PhN); 583 (100) (M^+ − Et_2N–PhN) and additional fragments of lower value.

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