Friedel-Crafts Reactions of Some Aminochlorocyclotriphosphazatrienes*

Earlier parts of this series discussed the reactions of chlorodimethylamino derivatives [2], N₅P₃Cl₆-ₙRₙ [R = NHMe (n = 2), NHEt (n = 1, 2), NHPr (n = 1, 4), NHBut (n = 2, 4), NHC₆H₅Ph (n = 1), NEt₂ (n = 1, 2, 3), N(CH₂Ph)₂ (n = 1)] react with benzene in the presence of anhydrous aluminium chloride to give phenylated products: phosphazenes and/or hydrocarbons. The structures of the phenylphosphazenes are assigned from their NMR spectra. Reactions of N₅P₃Cl₅R (R = NMe₂, NC₆H₅) have been reinvestigated. The influence of the amino groups on rates and products is discussed. This paper describes reactions of chloroamino cyclotriphosphazatrienes [3], N₅P₃Cl₆-ₙRₙ [R = NHMe (n = 2), NHEt (n = 1, 2), NHPr (n = 1, 4), NHBut (n = 2, 4), NHC₆H₅Ph (n = 1), NEt₂ (n = 1, 2, 3), N(CH₂Ph)₂ (n = 1)] with boiling benzene in the presence of aluminium chloride (6 mole). Phenylated products were obtained from all reactions except that of cis-N₅P₃Cl₅NMe₂. In some cases, phenylation was incomplete because =PC₃Cl₂ groups are less reactive than =PCR groups (R = NM₂, NC₆H₅). An interesting feature of the reactions of the chlorodimethylamino cyclotriphosphazatrienes with benzene was the formation of hydrocarbon by-products [2].

This paper describes reactions of chloroamino derivatives, N₅P₃Cl₆-ₙRₙ [R = NHMe (n = 2), NHEt (n = 1, 2), NHPr (n = 1, 4), NHBut (n = 2, 4), NHC₆H₅Ph (n = 1), NEt₂ (n = 1, 2, 3), N(CH₂Ph)₂ (n = 1)] with boiling benzene in the presence of anhydrous aluminium chloride. In addition, the reactions of N₅P₃Cl₅R (R = NMe₂, NC₆H₅) have been reinvestigated in order to find the optimum conditions for phenylation.

Aminochlorocyclotriphosphazatrienes were prepared by literature methods [3-12]. Light petroleum, b.p. 60-80 °C, was used for column chromatography and recrystallisation. * Represented at the 2nd International Symposium on Inorganic Ring Systems, Göttingen, August 21-24, 1978. Requests for reprints should be sent to Prof. Dr. R. A. Shaw, Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX, U. K.
Table I. Friedel-Crafts reactions of some aminochlorocyclophosphazenes.

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</thead>
<tbody>
<tr>
<td>Na₃P₃Cl₄(NHMe)₂</td>
<td>103</td>
<td>6</td>
<td>55-60</td>
<td>96</td>
<td>Na₃P₃Ph₃Cl₃(NHMe)₂ (1)</td>
<td>20</td>
</tr>
<tr>
<td>Na₃P₃Cl₄(NHEt)</td>
<td>35</td>
<td>3</td>
<td>55-60</td>
<td>72</td>
<td>Na₃P₃PhCl₄(NHEt) (2)</td>
<td>17⁴</td>
</tr>
<tr>
<td>Na₃P₃Cl₄(NHEt)₂</td>
<td>85</td>
<td>6</td>
<td>55-60</td>
<td>48</td>
<td>Na₃P₃PhCl₄(NHEt)₂ (3)</td>
<td>20</td>
</tr>
<tr>
<td>Na₃P₃Cl₅(NMe₂)</td>
<td>liq.</td>
<td>1</td>
<td>55-60</td>
<td>288</td>
<td>Na₃P₃PhCl₄(NMe₂) (9)</td>
<td>46</td>
</tr>
<tr>
<td>Na₃P₃Cl₅(NEt₂)</td>
<td>liq.</td>
<td>1</td>
<td>55-60</td>
<td>4</td>
<td>Na₃P₃PhCl₅(NEt₂) (5)</td>
<td>0.2⁴</td>
</tr>
<tr>
<td>Na₃P₃Cl₅(NEt₂)₂</td>
<td>liq.</td>
<td>6</td>
<td>55-60</td>
<td>72</td>
<td>Na₃P₃PhCl₅(NEt₂)₂ (6)</td>
<td>41</td>
</tr>
<tr>
<td>Na₃P₃Cl₅(NEt₂)₃</td>
<td>43</td>
<td>6</td>
<td>55-60</td>
<td>72</td>
<td>Na₃P₃PhCl₅(NEt₂)₃ (7)</td>
<td>26</td>
</tr>
<tr>
<td>Na₃P₃Cl₅(NC₅H₁₀)⁵</td>
<td>68</td>
<td>1</td>
<td>55-60</td>
<td>288</td>
<td>Na₃P₃PhCl₅(NC₅H₁₀) (10)</td>
<td>51⁴</td>
</tr>
</tbody>
</table>

a Estimated by gle, b data from ref. [2], c data from ref. [3].

C₁₈H₂₂Cl₂N₅P₃ (MW 448)

Calcd C 42.9 H 4.9 N 15.6.
Found C 42.5 H 4.8 N 15.4.

The second product [eluant: benzene/diethyl ether (9:1)] was recrystallised from light petroleum to give an isomer of 3.

2-cis-4:6,6:2,4-Na₃P₃Ph₂Cl₄(NHEt)₂ (4), m. p. 124°C (2.3 g, 18%).

Found C 43.0 H 4.9 N 15.4.

c) Na₃P₂Cl₃(NEt₂), liq., lit. [7] m. p. 18°C (11.5 g, 0.03 mole) and anhydrous aluminium chloride (12 g, 0.09 mole) were heated in benzene at 55-60°C for 3 d. After hydrolysis and subsequent work-up, an oily material (11 g) was obtained. The oil was dissolved in light petroleum and the solution was kept at 0°C for several days. Several crops of crystals were obtained. These were combined and recrystallised from light petroleum to give 2:4,4,6,6:2-Na₃P₃PhCl₄(NEt₂) (5), m. p. 70°C (9.6 g, 75%).

C₁₉H₂₃Cl₄N₅P₃ (MW 370)

Calcd C 28.2 H 3.5 N 13.2 Cl 33.3.
Found C 28.3 H 3.1 N 13.2 Cl 33.3.

d) 2-trans-4:6,6:2,4-Na₃P₃Cl₄(NEt₂) liq., lit. [7] m. p. 22°C (18.5 g, 0.044 mole) and anhydrous aluminium chloride (35.2 g, 0.264 mole) were heated in boiling benzene (500 ml) for 3 d. After the usual work-up procedure, an oil (18 g) was obtained. The oil was chromatographed over silica gel (350 g). The first fraction [eluant: light petroleum/benzene (1:1)] was identified as 2:4,4,6:2-cis-4-Na₃P₃PhCl₃(NEt₂)₂ (6), liq., b. p. 145°C/0.01 mm (8.4 g, 41%).

C₁₉H₂₅Cl₃N₃P₃ (MW 462.5)

Calcd C 36.4 H 5.4 N 15.2.
Found C 36.8 H 5.6 N 15.4.

Elution with benzene gave 2-trans-4:6,6:2,4-Na₃P₃PhCl₃(NEt₂) (7), liq., b. p. 150°C/0.01 mm (5.8 g, 26%).

C₂₀H₃₀Cl₄N₅P₃ (MW 439)

Calcd C 47.6 H 5.9 N 13.9.
Found C 47.2 H 5.7 N 13.6.

e) 2-trans-4:6,6:2,4-Na₃P₃Cl₃(NEt₂), m. p. 43°C, lit. [13] m. p. 43°C (18.8 g, 0.041 mole) and anhydrous aluminium chloride (32.8 g, 0.246 mole) were heated in boiling benzene (500 ml) for 3 d. After hydrolysis and subsequent removal of benzene, a crude solid was obtained which was recrystallised from light petroleum to give 2-trans-4:6,6:2,4,6-Na₃P₃Ph₃(NEt₂) (8), m. p. 140°C (15.8 g, 66%).
Table II. Hydrogen-1 NMR data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{CH_2}$</th>
<th>$\delta_{CH_3}$</th>
<th>Proposed structure</th>
<th>$3J^*$ (P-H)</th>
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<tr>
<td>N$_3$P$_2$PhCl$_2$(NHEt)$_2$</td>
<td>3.12$^a$</td>
<td>1.14</td>
<td>2:4:4:6:6;2</td>
<td>13.0 Hz</td>
</tr>
<tr>
<td>N$_3$P$_2$PhCl$_2$(NHEt)</td>
<td>2.66$^b$</td>
<td>0.92</td>
<td>2:trans-4;4:6:6:2</td>
<td></td>
</tr>
<tr>
<td>N$_3$P$_3$Ph$_2$Cl$_2$(NHEt)$_2$</td>
<td>2.83</td>
<td>1.18</td>
<td>2: cis-4:6:6:2:4</td>
<td></td>
</tr>
<tr>
<td>N$_3$P$_2$EtCl$_2$(NHEt)</td>
<td>3.04$^a$</td>
<td>1.22</td>
<td>2:4:4:6:6:2</td>
<td></td>
</tr>
<tr>
<td>N$_3$P$_2$EtCl$_2$(NPh$_2$)</td>
<td>3.15$^b$</td>
<td>1.10, 1.07</td>
<td>2:4:6:6:2:2: cis-4</td>
<td></td>
</tr>
<tr>
<td>N$_3$P$_2$EtCl$_2$(NPh$_2$)</td>
<td>3.00$^b$</td>
<td>0.81</td>
<td>2:trans-4:6:6:2:4</td>
<td></td>
</tr>
<tr>
<td>N$_3$P$_2$P(Ph$_3$)(NPh)</td>
<td>2.90$^b$</td>
<td>0.91, 0.65</td>
<td>2:trans-4:6:2:4,6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 3J* (P-H) ~ 14.0 Hz, $^b$ centre of multiplet, $^c$ relative intensities in brackets.
(R = NAlk₂ or Ph) are usually close to the resonance of \( =PCl_2 \) [16], this compound is assigned a geminal structure \( [=PPh(NEt_2)\,\text{group}] \).

The reaction of trans-\( N_2P_3Cl_4(NEt_2)_2 \) in boiling benzene gives the mono-phenyl derivative, \( N_2P_3PhCl_4(NEt_2)_2 \) (6) and a diphenyl-derivative, \( N_2P_3PhCl_4(NEt_2)_2 \) (7). The tris-trans-diethylamino-compound, \( N_2P_3Cl_4(NEt_2)_3 \), reacts with boiling benzene to give \( N_2P_3Ph(NEt_2)_3 \) (8). Compound 6 has previously been assigned a 2:4,4,6:2,6-structure from basicity data [15]. NMR data for this compound clearly indicate that the diethylamino-groups are cis to one another (Table II). The structures of the remaining phenyldiethylamino compounds are also deduced from NMR data by considering the shielding effect of the phenyl groups(s) [2].

**Discussion**

It is clear from Table I that the phenylation of aminochlorocyclophosphazenes takes place even when only one mole of aluminium chloride per mole of phosphazene is used. Yields are increased by increasing the amount of aluminium chloride or by an increase in reaction time. The effect of temperature is more complex because there are at least two competing reactions with different temperature coefficients: (a) phenylation at phosphorus (without decomposition of the phosphazene) and (b) phenylation at carbon and subsequent decomposition to give phenylated hydrocarbons.

The nature of the phosphorus centre plays an important part in these reactions. Six centres can be distinguished: (i) \( =PCl_2 \), (ii) \( =PCl(NRR') \), (iii) \( =P(NRR')_2 \), (iv) \( =PClPh \), (v) \( =PPh_2 \), (vi) \( =PPh(NRR') \). Phenylation at phosphorus proceeds most readily for (ii) \( =PCl(NRR') \) [2, 3, 17] and (iv) \( =PClPh \) groups [18, 19]. Phenylation at carbon (b) can occur with (ii) \( =PCl(NRR') \) groups and this is the only reaction that has been observed for (iii) \( =P(NRR')_2 \) or (v) \( =PPh(NRR') \) groups. For example, the only new product when 2:4,4,6:2-\( N_2P_3PhCl_4(NEt_2)_2 \) was boiled with benzene (12 h) (6 mole aluminium trichloride) was a small amount of diphenylmethane (0.3%). Hydrocarbon formation is not observed during Friedel-Crafts reactions of cyclophosphazenes containing only (i) \( =PCl_2 \) and/or (iv) \( =PClPh \), and/or (v) \( =PPh_2 \) groups [18, 19].

Both competing reactions, (a) and (b), can occur at (ii) \( =PCl(NRR') \) groups. Steric effects influence reactions involving secondary amino groups. The derivatives, \( N_2P_3Cl_4(NRR') \), react with benzene in the presence of one mole of aluminium chloride at 55–60 °C (12 d) to give the phenylated products, \( N_2P_3Ph(NRR') \), in yields of 46% (NMe₂), 51% (NC₃H₇), and 0.2% (NEt₂) (Table I). Similarly, dimethyamine [6] and piperidine [8] differ from diethylamine [7] in reaction rate with \( N_2P_3Cl_4 \) and in product distribution. Thus, the major nongeminal dialkylamino-isomer, \( N_2P_3Cl_4(NRR') \), has a cis-configuration when \( NRR' = NMe_2 \) [6] and a trans-configuration when \( NRR' = NEt_2 \) [7]. Results obtained in this and an earlier study [2] can be compared with the above observations: phenylation of nongeminal-\( N_2P_3Cl_4(NRR') \) gives \( N_2P_2PhCl_5(NRR')_2 \) \( [NRR' = NMe_2 \) (dimethylamino-groups cis to one another), \( NRR' = NEt_2 \) (diethylamino-groups trans to one another)]. The tris-compound, \( N_2P_3Cl_4(NRR')_3 \), gives a mixture of cis- and trans-triphenyl-isomers, \( N_2P_3Ph_3(NRR')_3 \), when \( NRR' = NMe_2 \), but only the trans-isomer when \( NRR' = NEt_2 \). Drastic differences in behaviour have also been reported for the reactions of dimethylaniline, PhNMe₂, and diethylamine, PhNEt₂, with \( N_2C_3Cl_3 \) [20].

When a primary amino-group is involved, the \( =PCl(NRR') \) group reacts predominantly by phenylation at phosphorus (a) if the alkyl group is unbranched \( (R = H, R' = Me, Et) \) and by phenylation at carbon (b) when the alkyl group is branched \( (R = H, R' = Pr) \). Steric factors may be responsible for the differences. If the amino group \( NRR' \) is either benzylamino, NHC₂H₂Ph, or dibenzylamino, N(CH₂Ph)_₂, only reaction (b) is observed. Those amino groups, \( NRR' \), which tend to give hydrocarbons exclusively also behave anomalously in the thermolysis of phenylphosphonothioic diamides, \( PhP(S)(NRR')_2 \) \( (R = H, R' = alkyl) [21] \); loss of the alkyl group, \( R' \), is observed rather than the formation of cyclodiphosphazanes, \( [PhP(S)(NRR')]_2 \), the characteristic behaviour of these diamides with unbranched amino-groups.

Non-geminal cyclotriporphosphazatrienes, \( N_2P_3Cl_4-n(NRR')_n \), generally undergo reaction (a) when \( n = 1 \), though at greatly varying rates. When \( n = 2 \), reaction (a) can occur at both \( =PCl(NRR') \) groups; for \( NRR' = NMe_2 \), no monophenyl derivative, \( N_2P_3Cl_4Ph(NMe_2)_2 \), was observed, and the same diphenyl derivative, cis-\( N_2P_3Cl_2Ph_2(NMe_2)_2 \), was isolated from the reactions.
of both cis- and trans-NaP3Cl4(NMe2)2 [2]; for NRR′ = NC5H10, both geometric isomers, NaP3Cl4(NC5H10)2, gave the same monophenyl, NaP3Cl2Ph(NC5H10)2, and the same diphenyl derivatives, NaP3Cl2Ph4(NC5H10)2. Their respective isomers were not observed. For NRR′ = NEt2 (trans), monophenylation, NaP3Cl2Ph(NEt2)2 (NEt2 groups cis to one another), and diphenylation, trans-NaP3Cl2Ph2(NEt2)2, were observed. The primary amino compounds, trans-NaP3Cl4(NHMe)2 and trans-NaP3Cl4(NHEt)2, gave diphenyl derivatives, NaP3Cl2Ph2(NR′Et)2(NR′Et)2. The former (NR′ = NHMe) gave only the cis-isomer; the latter (NR′ = NEt2) gave both geometric isomers. A monophenyl derivative, NaP3Cl2Ph(NEt2)2, was isolated by earlier workers but its structure is uncertain [14].

Both cis- and trans-isomers of NaP3Cl5(NR′Et)3 gave mixtures of geometric triphenyl-isomers, NaP3Ph3(NR′Et)3 [2]. No mono- or di-phenyl precursors were detected. In contrast, the analogous piperidino isomers, NaP3Cl5(NC5H10)2, both gave the same triphenyl derivative, NaP3Ph3(NC5H10)2; a diphenyl derivative, NaP3ClPh2(NC5H10)3, was isolated from the reaction of the trans-tris-precursor. The trans-diethylamino derivative, NaP3Cl5(NEt2)3, gave a single product, trans-NaP3Ph3(NEt2)3. For n = 4, the nongeminal cis-derivatives, NaP3Cl4(NR′Et)4, gave very different results. Whereas NaP3Cl4(NMe2)4 reacted to give hydrocarbons exclusively [2] [reaction (b)], NaP3Cl2(NC5H10)4 gave excellent yields of the diphenyl derivative, NaP3Ph2(NC5H10)4. However, the nongeminal tetra-amino derivatives, NaP3Cl4(NMe2)2(NC5H10)2, and NaP3Cl4(NMe2)2(NC5H10)2, still gave excellent yields of the corresponding diphenyl derivatives (one isomer only in both cases) [3]. This observation provides an excellent example of the fine balance that exists between reaction paths (a) and (b).

Various hydrocarbons were detected in many of our reactions (see Experimental) but it is not clear whether all of these are primary reaction products. Hydrocarbons such as alkylbenzenes undergo a variety of transformations in the presence of aluminium chloride, even under milder conditions than those described here [22].

It is clear that =PCl(NR′)2 (and =PPPhCl) groups always react faster by route (a) than =PCl2 groups [2, 3, 17-19]. However, the presence of two or more =PCl(NR′)2 groups does not always permit a confident prediction of the reaction path.

In some cases stepwise phenylation of the =PCl(NR′)2 groups is observed; in others, phenylation appears to accelerate and only fully phenylated derivatives are isolated. Also, pairs of geometric isomers were observed in some instances; in others, only one isomer was isolated.

It seems likely that two major, competing processes are involved in the Friedel-Crafts phenylation of phosphazenes:

1. Complex formation via a nitrogen donor function of the phosphazene substrate and aluminium chloride (chloride ion departure hindered) and

2. complex formation via the chlorine atom facilitating the departure of the chloride ion. This effect is enhanced in the presence of electron-releasing groups (amino and/or phenyl). The overall effect of these processes is difficult to quantify.

Crystallographic and spectroscopic data provide useful insights. For example, the P–Cl bond of the =PCl(NR′Et)2 group is longer than the P–Cl bonds of the =PCl2 group in geminal NaP3Cl5(NR′Et)3 and the 35Cl signal from the =PCl(NR′Et)2 group occurs at a lower frequency than the =PCl2 signal. Both techniques suggest that the P–Cl bond is more ionic in the =PCl(NMe2)2 group than in the =PCl2 group [23]. In Friedel-Crafts reactions, a chlorine atom is envisaged departing as a chloride ion. In a recent paper on the mass spectra of geminal and non-geminal phenylchlorocyclophosphazenes, it was demonstrated that chlorine atoms are lost more readily from =PClPh groups than from =PCl2 groups [24].

Under controlled conditions, selective phenylation [2] can be carried out as shown above.