Phosphorus–Nitrogen Compounds. Part XXXIX.[1] Friedel–Crafts Reactions of Chloro(piperidino)cyclotriphosphazatrienes with Benzene

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Chloro(piperidino)cyclotriphosphazatrienes, $N_3P_3Cl_{6-n}(NC_5H_{10})_n$, react with boiling benzene in the presence of anhydrous aluminium chloride to give phenylpiperidino-derivatives, $N_3P_3Ph_mCl_{6-n-m}(NC_5H_{10})_n$. Replacement of chlorine by phenyl occurs at $\equiv PCl(NC_5H_{10})$ but not at $\equiv PCl_2$ groups under the conditions investigated. Hydrocarbons are not observed as by-products except in reactions of chloro(dimethylamino)(piperidino)cyclotriphosphazatrienes. Differences in the behaviour of chloro(piperidino)- and chloro(dimethylamino)-cyclotriphosphazatrienes are discussed.

THE reaction patterns of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with dimethylamine [2] and piperidine [3] are similar, and corresponding aminochlorocyclotriphosphazatrienes have the same configurations. This resemblance is greater than between any other pair of amines so far investigated. Part XXXV of this Series [4] described Friedel–Crafts reactions of chloro(dimethylamino)cyclotriphosphazatrienes with benzene. The structures of the products were determined from their ^1H n.m.r. spectra, and it was established that the replacement of chlorine by phenyl occurs preferentially at $\equiv PCl(NMe_2)$ rather than at $\equiv PCl_2$ groups. Two hydrocarbons, triphenylmethane and diphenylmethane, were the main products in reactions of *cis*-nongeminal $N_3P_3Cl_2(NMe_2)_4$ and were by-products in the other reactions.

This paper describes Friedel–Crafts reactions with benzene of seven chloro(piperidino)cyclotriphosphazatrienes whose structures were determined by Keat and Shaw: [3] $N_3P_3Cl_5(NC_5H_{10})$ (I), m.p. 68°; *cis*-nongeminal-$N_3P_3Cl_4(NC_5H_{10})_2$ (II), m.p. 129°; *trans*-nongeminal-$N_3P_3Cl_4(NC_5H_{10})_2$ (III), m.p. 104—105°; *cis*-nongeminal-$N_3P_3Cl_3(NC_5H_{10})_3$ (IV), m.p. 190°; *trans*-nongeminal-$N_3P_3Cl_3(NC_5H_{10})_3$ (V), m.p. 114·5°; geminal-$N_3P_3Cl_3(NC_5H_{10})_3$ (VI), m.p. −17°; and *cis*-nongeminal-$N_3P_3Cl_2(NC_5H_{10})_4$ (VII), m.p. 111—112°; and two new nongeminal dichloro(dimethylamino)(piperidino)cyclotriphosphazatrienes: $N_3P_3Cl_2(NMe_2)_3(NC_5H_{10})$ (VIII), m.p. 122°; and $N_3P_3Cl_2(NMe_2)_2(NC_5H_{10})_2$ (IX), m.p. 95°. The reported derivative [5] $N_3P_3Cl(NC_5H_{10})_5$, m.p. 121—123·5°, has not been prepared in this laboratory.

RESULTS

The chloropiperidino-derivatives (I)—(IX) (1 mol) react with boiling benzene in the presence of anhydrous aluminium trichloride (6 mol) to give good yields of phenyl(piperidino)-derivatives (X)—(XVIII). The reaction patterns are summarised in Schemes 1 and 2. The only by-products observed are traces of triphenylmethane and diphenylmethane in reactions of the dichlorodimethylaminopiperidinocyclotriphosphazatrienes (VIII) and (IX). Replacement of chlorine by phenyl occurs at $\equiv PCl(NC_5H_{10})$ but not at $\equiv PCl_2$ groups under the conditions investigated. Thus $N_3P_3Cl_5(NC_5H_{10})$ (I), reacts to form $N_3P_3PhCl_4(NC_5H_{10})$ (X), which contains the $\equiv PPh(NC_5H_{10})$ group. The basicity [6] of the monophenylmonopiperidino-derivative (X) is low, as expected, $pK'_a < -6$.

cis-Nongeminal (II) and *trans*-nongeminal $N_3P_3Cl_4(NC_5H_{10})_2$ (III) give mixtures of a monophenyl (XI), pK'_a found [6] −4·8, calc. −5·0; and diphenyl derivative (XII), pK'_a found [6] −0·8, calc. −0·8. Comparison with the basicities of *cis*-nongeminal (IV), *trans*-nongeminal (V), and geminal $N_3P_3Cl_3(NC_5H_{10})_3$ (VI), pK'_a −5·1, −5·3, and −3·9 respectively,[7] confirms that the monophenyl-derivative (XI) contains $\equiv PPh(NC_5H_{10})$, $\equiv PCl(NC_5H_{10})$, and $\equiv PCl_2$ groups. Comparison with the basicities of of *cis*-nongeminal $N_3P_3Cl_2(NC_5H_{10})_4$ (VII) and 2,2:4,6:4,6-$N_3P_3Ph_2Cl_2(NC_5H_{10})_2$, pK'_a −0·9 and −3·6 respectively,[7,8] confirms that the diphenyl derivative (XII) contains one $\equiv PCl_2$ and two $\equiv PPh(NC_5H_{10})$ groups.

The products (XI) and (XII) are pure compounds. The geometrical relationships between the phenyl and piperidino-groups have not been established; corresponding Friedel–Crafts reactions of *cis*- and *trans*-nongeminal $N_3P_3Cl_4(NMe_2)_2$, give 2-*cis*-4:6,6:2,4-$N_3P_3Ph_2Cl_2(NMe_2)_2$.

cis-Nongeminal (IV) and *trans*-nongeminal $N_3P_3Cl_3(NC_5H_{10})_3$ (V) react to give $N_3P_3Ph_3(NC_5H_{10})_3$ (XIV), pK'_a found [6] 5·0, calc. 4·8, which is obtained also from the reaction of *cis*-nongeminal $N_3P_3Ph_3Cl_3$, m.p. 191—192°, with piperidine.[9] The diphenyl derivative (XIII), pK'_a found [6] 1·9, calc. 2·0, is an intermediate in the reaction of *trans*-nongeminal $N_3P_3Cl_3(NC_5H_{10})_3$ (V). Both (XIII) and (XIV) contain $\equiv PPh(NC_5H_{10})$ groups, and again, the *cis–trans*-relationships have not been established. Geminal $N_3P_3Cl_3(NC_5H_{10})_3$ (VI) reacts to form $N_3P_3PhCl_2(NC_5H_{10})_3$ (XV), which contains $\equiv PPh(NC_5H_{10})$, $\equiv P(NC_5H_{10})_2$, and $\equiv PCl_2$ groups.

cis-Nongeminal $N_3P_3Cl_2(NC_5H_{10})_4$ (VII) reacts to form the nongeminal diphenyltetrakispiperidino-derivative (XVI), pK'_a 6·1,[6] which as expected is less basic than isomeric geminal $N_3P_3Ph_2(NC_5H_{10})_4$, m.p. 195—197°,[10] pK'_a 6·7.[8] This is a striking difference in behaviour from *cis*-

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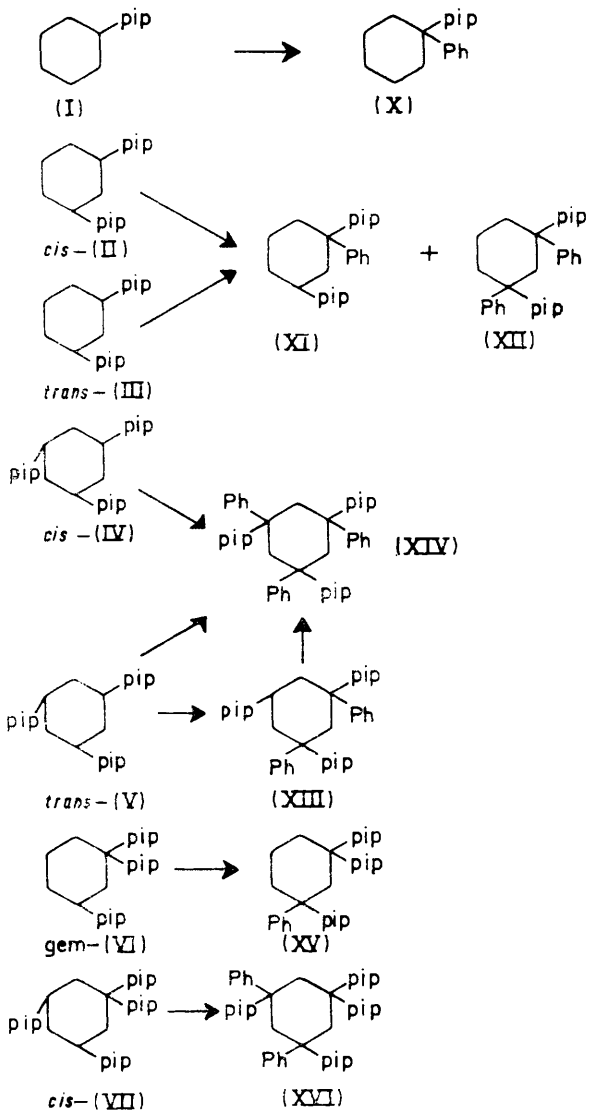
[7] D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1831.
[8] D. Feakins, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc.* (*A*), 1968, 10.
[9] R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 1962, 5004.
[10] K. Hills and R. A. Shaw, *J. Chem. Soc.*, 1964, 130.

nongeminal $N_3P_3Cl_2(NMe_2)_4$ which decomposes under these conditions.[4]

Dimethylaminopiperidino-derivatives.— *trans*-Nongeminal $N_3P_3Cl_3(NMe_2)_3$ (XIX), m.p. 105°,[2] reacts with piperidine

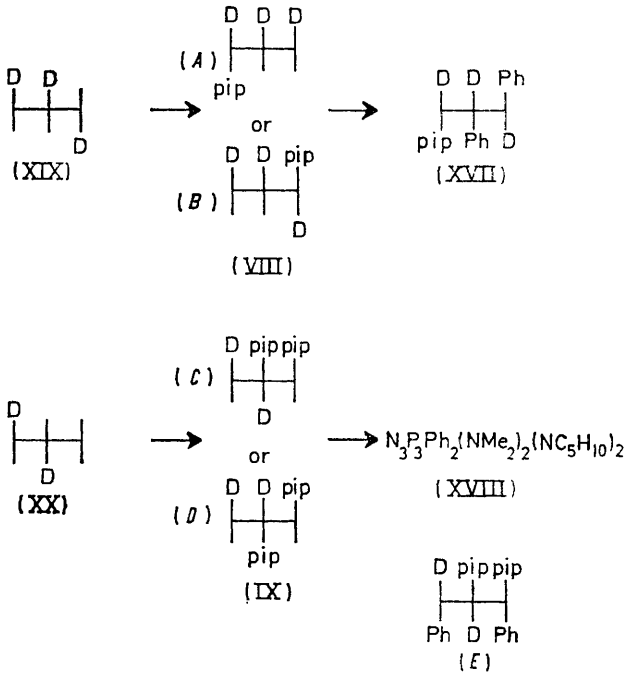


SCHEME 1

Preparation of phenylpiperidino-derivatives (pip = NC_5H_{10}, Cl omitted)

(2 mol) to give $N_3P_3Cl_2(NMe_2)_3(NC_5H_{10})$ (VIII). *trans*-Nongeminal $N_3P_3Cl_4(NMe_2)_2$ (XX), m.p. 103°, reacts with piperidine (4 mol) to give $N_3P_3Cl_2(NMe_2)_2(NC_5H_{10})_2$ (IX). The basicities of the products, pK'_a −1·5 and −1·1 respectively,[7] are characteristic of dichlorotetrakisamino-cyclotriphosphazatrienes with chlorine atoms in non-geminal positions. Friedel–Crafts reaction of the products (VIII) and (IX) gives the diphenyl derivatives (XVII) and (XVIII).

Dimethylamino ^1H n.m.r. spectra of the dimethylamino-piperidino-derivatives are summarised in Table 1. The spectrum of the diphenyl derivative (XVII) contains three doublets characteristic of three different dimethylamino-groups. The spectrum of $N_3P_3Cl_2(NMe_2)_3(NC_5H_{10})$ (VIII) contains two doublets of relative intensities 2 : 1, which in the absence of further resolution suggests either structure (*A*) or (*B*) (Scheme 2). The spectrum of $N_3P_3Cl_2(NMe_2)_2$-$(NC_5H_{10})_2$ (IX) contains two doublets of equal intensities, consistent with structure (*C*) or (*D*) with chlorines in *cis*-positions. The spectrum of the diphenyl derivative



SCHEME 2

Preparation of phenyl(dimethylamino)(piperidino)cyclotriphosphazatrienes (D represents NMe_2, pip represents NC_5H_{10}, Cl omitted)

(XVIII), pK'_a 5·3, contains two doublets, one at very high field, which would be consistent with structure (*E*).

DISCUSSION

Dimethylamino-groups in different chemical environments can usually be distinguished by their ^1H n.m.r. spectra.[2] The protons within each dimethylamino-group give rise to one signal. Small differences in chemical shifts arising from piperidino-groups in different chemical environments are not readily observed; the α-, β-, and γ-protons, some in axial and some in equatorial positions, give complex signals.[3] This hinders the complete assignment of structures of piperidino-derivatives. The assignment of structures by analogy is dangerous, particularly in the phosphazene field.

The main differences between Friedel–Crafts reaction patterns of chloropiperidino- and chlorodimethylamino-cyclotriphosphazatrienes are: (*a*) *cis*-nongeminal (II) and *trans*-nongeminal $N_3P_3Cl_4(NC_5H_{10})_2$ (III) give mixtures of the same monophenyl derivative (XI) and the same diphenyl derivative (XII), whereas the

corresponding *cis*- and *trans*-nongeminal $N_3P_3Cl_4(NMe_2)_2$ give the same diphenyl derivative, 2-*cis*-4:6,6:2,4-$N_3P_3Ph_2Cl_2(NMe_2)_2$, but not a monophenyl intermediate under the conditions investigated; (*b*) *cis*-nongeminal (IV) and *trans*-nongeminal $N_3P_3Cl_3(NC_5H_{10})_3$ (V) give a nongeminal triphenyl derivative (XIV) and the latter (V) gives also a diphenyl derivative (XIII), whereas the corresponding *cis*- and *trans*-nongeminal $N_3P_3Cl_3(NMe_2)_3$ give mixtures of *cis*- and *trans*-nongeminal $N_3P_3Ph_3(NMe_2)_3$, but not a diphenyl intermediate under the conditions investigated; (*c*) *cis*-nongeminal $N_3P_3Cl_2(NC_5H_{10})_4$ (VII) gives high yields of $N_3P_3Ph_2(NC_5H_{10})_4$ (XVI), whereas *cis*-nongeminal $N_3P_3Cl_2(NMe_2)_4$ decomposes under similar conditions; (*d*) hydrocarbons are not observed in reactions of chloropiperidinocyclotriphosphazatrienes, whereas dimethylamino-derivatives give triphenylmethane and diphenylmethane.

There are no obvious differences in properties between chlorodimethylamino- and chloropiperidino-cyclotriphosphazatrienes in their ground states. Piperidino, like dimethylamino and phenyl, is electron-releasing with respect to chlorine, and the lengthening of P–Cl bonds in such compounds can be correlated with ^{35}Cl n.q.r. measurements.[11] Basicity measurements confirm that corresponding chlorodimethylamino- and chloropiperidino-cyclotriphosphazatrienes have similar electron releasing properties with respect to perchloric acid acid in nitrobenzene. Significant differences in reactivity may depend on different steric requirements of dimethylamino- and piperidino-groups, particularly in bimolecular reactions.

Olah has shown that different types of transition state are possible in Friedel–Crafts reactions.[12] The phenylation of chlorophosphazenes must involve polarisation or ionisation of P–Cl bonds by aluminium trichloride. Possible donor sites in chloroaminophosphazenes and their phenyl derivatives have been discussed,[4] but the structures of intermediate complexes are unknown. The hydrocarbons triphenylmethane and diphenylmethane must be formed as a result of nucleophilic attack on α-carbon in a dimethylamino-group. The absence of hydrocarbons in the chloropiperidino-series can be attributed to steric hindrance to attacking benzene and/or the cyclic nature of the organic group, which would require cleavage of both C–N bonds. Preliminary results suggest that hydrocarbons are not formed in reactions of chloro(diethylamino)cyclotriphosphazatrienes.

TABLE 1

Dimethylamino ^1H n.m.r. spectra in CCl_4

Compound	τ (CH_3)	^3J *(P–H)/Hz	Relative intensities
(VIII) $N_3P_3Cl_2(NMe_2)_3(NC_5H_{10})$	7·37, 7·47	17·0, 12·5	2, 1
(IX) $N_3P_3Cl_2(NMe_2)_2(NC_5H_{10})_2$	7·37, 7·50	16·3, 12·2	1, 1
(XVII) $N_3P_3Ph_2(NMe_2)_3(NC_5H_{10})$	7·43, 7·50, 7·56	12·4, 12,2, 12·4	1, 1, 1
(XVIII) $N_3P_3Ph_2(NMe_2)_2(NC_5H_{10})_2$	7·43, 7·62	11·5, 12·2	1, 1

TABLE 2

Friedel–Crafts reactions

Reagent	(mmol)	$AlCl_3$ (mmol)	Benzene (ml)	Time (days)	Products	(%)		(%)
(I)	20	120	300	7	(X)	73		
(II)	9	54	200	15	(XI)	50	(XII)	30
(III)	34	200	350	7·5	(XI)	75	(XII)	10
(III)	9	54	200	15	(XI)	60	(XII)	15
(IV)	1·6	9·6	100	20	(XIV)	41		
(V)	16	96	300	7	(XIII)	65		
(XIII)	9	54	200	4	(XIV)	40	(XIII)	46 [a]
(V)	8	48	150	15	(XIV)	70		
(VI)	3	36	200	6	(XV)	50	(VI)	20 [a]
(VII)	28	170	350	7	(XVI)	80		
(VIII)	9	54	200	3	(XVII)	70		
(IX)	10	60	250	3	(XVIII)	70		

[a] Unreacted starting material.

EXPERIMENTAL

Chloro(piperidino)cyclotriphosphazatrienes (I)—(VII),[3] *trans*-nongeminal-$N_3P_3Cl_3(NMe_2)_3$, m.p. 105°,[2] and *trans*-nongeminal-$N_3P_3Cl_4(NMe_2)_2$, m.p. 103°,[2] were prepared by conventional methods and characterised by m.p., mixed m.p., and i.r. spectra.

Piperidine (4·6 g, 54 mmol) was added slowly to stirred *trans*-nongeminal-$N_3P_3Cl_3(NMe_2)_3$ (XIX), m.p. 105° (10 g, 26 mmol), in ether (200 ml) at −78°. The mixture was

[11] R. Keat, A. L. Porte, D. A. Tong, and R. A. Shaw, *J.C.S. Dalton*, 1972, 1648; W. Dagliesh, R. Keat, A. L. Porte, R. A. Shaw, and D. A. Tong, unpublished results.

[12] G. A. Olah, S. Kobayashi, and M. Tashiro, *J. Amer. Chem. Soc.*, 1972, **94**, 7448.

boiled under reflux (4 h), and piperidine hydrochloride was removed by filtration. T.l.c. of the oily product (10 g) showed a trace of starting material and one new product. Recrystallisation from light petroleum gave 2,4:2,4,6:6-*dichlorotris(dimethylamino)(piperidino)cyclotriphosphazatriene* (VIII) (8 g, 70%), m.p. 122° (Found: C, 31·4; H, 6·3; Cl, 16·8. $C_{11}H_{28}Cl_2P_3N_7$ requires C, 31·4; H, 6·6; Cl, 16·8%).

A similar reaction of piperidine (18·7 g, 220 mmol) with *trans*-nongeminal-$N_3P_3Cl_4(NMe_2)_2$ (XX), m.p. 103°, (20·9 g, 54 mmol) gave an oily product (22 g), which recrystallised to form 2,4:4,6:2,6-*dichlorobis(dimethylamino)bis(piperidino)cyclotriphosphazatriene* (IX) (15 g, 60%), m.p. 95° (Found: C, 36·1; H, 7·3; Cl, 15·6; N, 20·9. $C_{14}H_{32}Cl_2N_7P_3$ requires C, 36·3; H, 7·0; Cl, 15·3; N, 21·2%).

Friedel–Crafts Reactions.—The general procedure was as before.[4] Reaction conditions and yields of products are summarised in Table 2. Structures, m.p.s, and analytical data are recorded in Table 3.

TABLE 3

Phenyl(piperidino)cyclotriphosphazatrienes

No.	Compound	M.p. (b.p.)	Found (%) C	H	Cl	N	Formula	Required (%) C	H	Cl	N
(X)	2:4,4,6,6:2-$N_3P_3PhCl_4(NC_5H_{10})$	68°	30·0	3·3	32·3	12·6	$C_{11}H_{45}Cl_4N_4P_3$	30·1	3·4	32·4	12·8
(XI)	2:4,4,6:2,6-$N_3P_3PhCl_3(NC_5H_{10})_2$	132	39·1	5·2	21·4	14·5	$C_{16}H_{25}Cl_3N_5P_3$	39·5	5·1	21·8	14·4
(XII)	2,4:6,6:2,4-$N_3P_3Ph_2Cl_2(NC_5H_{10})_2$	136	49·7	5·6	13·1	13·3	$C_{22}H_{30}Cl_2N_5P_3$	50·0	5·6	13·4	13·2
(XIII)	2,4:6:2,4,6-$N_3P_3Ph_2Cl(NC_5H_{10})_3$	166	56·3	7·0	6·2	14·5	$C_{27}H_{40}ClN_6P_3$	56·2	6·9	6·1	14·5
(XIV)	2,4,6:2,4,6-$N_3P_3Ph_3(NC_5H_{10})_3$	187 [a]	64·2	7·1		13·5	$C_{33}H_{45}N_6P_3$	64·0	7·2	0·0	13·5
(XV)	2:4,4:2,6,6-$N_3P_3PhCl_2(NC_5H_{10})_3$	(160, 0·01 mmHg)	46·9	6·4	13·1		$C_{21}H_{35}Cl_2N_6P_3$	47·1	6·5	13·2	15·7
(XVI)	2,4:2,4,6,6-$N_3P_3Ph_2(NC_5H_{10})_4$	210	61·5	8·0		15·8	$C_{32}H_{50}N_7P_3$	61·4	8·0	0·0	15·7
(XVII)	2,4:2,4,6:6-$N_3P_3Ph_2(NMe_2)_3(NC_5H_{10})$	(150, 0·01 mmHg)	55·0	7·7		19·1	$C_{23}H_{38}N_7P_3$	54·6	7·6	0·0	19·4
(XVIII)	2,4:2,6:4,6-$N_3P_3Ph_2(NMe_2)_2(NC_5H_{10})_2$	(155, 0·01 mmHg)	57·3	7·6		17·9	$C_{26}H_{42}N_7P_3$	57·2	7·7	0·0	18·0

[a] Lit.[9] m.p. 187°.

We thank the Ministry of Aviation for financial support.

[3/2573 *Received*, 20*th December*, 1973]