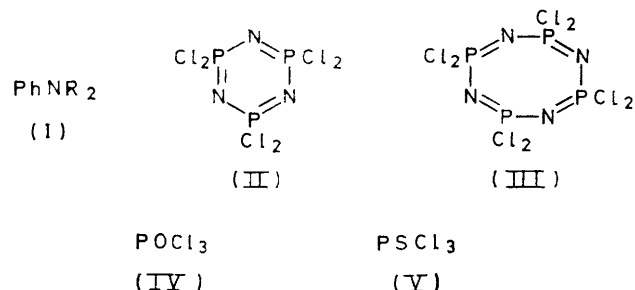


Phosphorus–Nitrogen Compounds. Part XLIII.¹ Reactions of *NN*-Dialkylanilines with Phosphorus(v) Chlorides; Examples of Ambident Nucleophilic Behaviour

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The reactions of hexachlorocyclotriphosphazatriene ($N_3P_3Cl_6$) with dialkylanilines ($PhNR_2$) yield 'carbon-' [$N_3P_3Cl_5(C_6H_4 \cdot NR_2)$] and 'nitrogen-substituted,' [$N_3P_3Cl_5(NRPh)$] derivatives, whereas the analogous reactions of octachlorocyclotetraphosphazetetrane ($N_4P_4Cl_8$) yield only 'nitrogen-substituted' derivatives [$N_4P_4Cl_7(NRPh)$ and $N_4P_4Cl_6(NRPh)_2$ ($R = Me$)]. The behaviour of phosphoryl chloride with *NN*-dialkylanilines is much more complex, but 'carbon-substitution' predominates. Products include $(R_2N \cdot C_6H_4)_2P(O)R'$, $(R_2N \cdot C_6H_4)_3P(O)$, $(PhNR)P(O)R'_2$, and $PhNHR$ ($R = Me$ or Et ; $R' = Cl, OH,$ or OEt) and $(R_2N \cdot C_6H_4)_2P(O)NRPh$, $(PhNR)_3P(O)$, $(PhNR)_2P(O)(NHPh)$, $(R_2N \cdot C_6H_4)_2CH_2$, and $(R_2N \cdot C_6H_4)_3CH$ ($R = Me$). From the analogous reactions of thiophosphoryl chloride only $(Me_2N \cdot C_6H_4)P(S)(OEt)_2$ and $(Et_2N \cdot C_6H_4)_3P(S)$ were isolated. The behaviour of phosphoryl and thiophosphoryl chlorides with *N*-methylaniline was briefly investigated. Possible mechanisms for the reactions of phosphorus(V) chlorides with *NN*-dialkylanilines are briefly discussed. The ambident behaviour of the latter with the former and with cyanuric chloride is compared. S_o Values are deduced from the 1H n.m.r. spectra of the 'carbon-substituted' compounds.

AMBIDENT nucleophiles have attracted a good deal of attention in recent years (for a review see ref. 2). Most of this work has been concerned with anionic nucleophiles, but a few examples of neutral nucleophiles have also been investigated (*cf.* refs. 3–5). *NN*-Dialkylanilines behave as neutral ambident nucleophiles towards cyanuric chloride.⁶ In view of the number of similarities between 1,3,5-triazines and cyclophosphazenes,⁷ we have investigated the reactions of *NN*-dialkylanilines (I) with



hexachlorocyclotriphosphazatriene (II) and octachlorocyclotetraphosphazetetrane (III). These reactions were extended to include other, more reactive, phosphorus(v)

philic centre was carbon in our earlier studies⁶ and is phosphorus(v) in the present one.

Cyanuric chloride ($N_3C_3Cl_3$) reacts with *NN*-dimethylaniline to yield exclusively mono- and di-'nitrogen-substituted' products together with methyl chloride [reaction (i)].⁸ (For a definition of 'nitrogen-' and 'carbon-substitution' see ref. 8.) Even with *N*-ethyl-*N*-methylaniline only a trace of 'carbon-substituted' derivative, (*p*-NMeEt- C_6H_4) $N_3C_3Cl_2$, is observed, the overwhelming part of the reaction taking place at the nitrogen atom. Only when *NN*-diethylaniline is the nucleophile are the yields of 'nitrogen-' (70%) and 'carbon-substituted' (30%) products of comparable magnitude.⁸

When hexachlorocyclotriphosphazatriene (II) reacts at 160 °C for 14 h with *NN*-dimethylaniline in the molar proportions 1 : 2, a 60% conversion into pure phosphazene derivatives is achieved; 'carbon-' (VI; $R = Me$) and 'nitrogen-substituted' (VII; $R = Me$) derivatives can be isolated in the ratio 1 : 10, in addition to amine hydrochloride and methyl chloride. Spectroscopic investigations (see later) prove that in the 'carbon-substituted' compound the phosphazeryl grouping has



chlorides, *viz.* phosphoryl (IV) and thiophosphoryl chloride (V).

The chlorocyclophosphazenes (II) and (III) require considerably higher temperatures (160 °C) than cyanuric chloride (90 °C) to react at similar rates with *NN*-dialkylanilines. Steric factors undoubtedly play a part, as the chlorine-bearing atoms have different co-ordination numbers [three in cyanuric chloride, four in the phosphorus(v) compounds]. Additionally, the electro-

¹ Part XLII, M. Biddlestone and R. A. Shaw, *J.C.S. Dalton*, 1975, 2527.

² R. Gompper, *Angew. Chem. Internat. Edn.*, 1964, **3**, 525.

³ N. S. Isaacs, *J. Chem. Soc. (B)*, 1966, 1053.

⁴ B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Hoffman, and H. F. Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2806.

entered the *para*-position of the aniline. [In an earlier study using an excess of the amine (I; $R = Me$) and forcing conditions, a small yield of hexa-'nitrogen-substituted' derivative, $N_3P_3(NRPh)_6$ ($R = Me$) was obtained.⁹]

When a reaction similar to the above was carried out with octachlorocyclotetraphosphazetetrane (III), no 'carbon-substitution' was observed. Mono- (VIII;

⁵ C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1960, **82**, 6132.

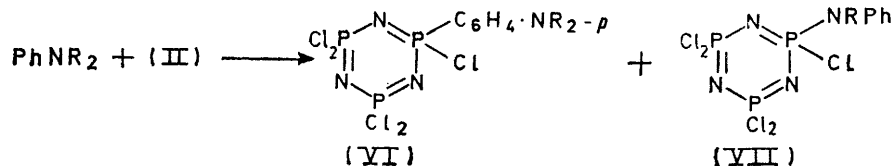
⁶ R. C. Golesworthy, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1962, 1507.

⁷ R. A. Shaw, *Endeavour*, 1968, 74.

⁸ R. A. Shaw and P. Ward, *J. Chem. Soc.*, 1965, 5446.

⁹ I. D. Knight and R. A. Shaw, quoted in ref. 10.

R = Me) and di-'nitrogen-substituted' (IX; R = Me) derivatives could be isolated in the ratio of 5 : 4 (total yield *ca.* 85%). Thus, in its behaviour with *NN*-dimethylaniline the octachloride (III) resembles cyanuric chloride⁸ more closely than does its lower homologue (II). The greater reactivity of the octachloride (III) than of the hexachloride (II) towards many nucleophiles is well



established.¹⁰ Whereas the 'carbon-substituted' derivatives of cyanuric chloride are bright yellow,^{6,8,11} and the 'nitrogen-substituted' ones colourless,^{6,8,11} both types [*e.g.* (VI) and (VII)] of phosphazenylium derivative are



colourless. The disubstituted derivative (IX) could have one of five possible structures,¹⁰ one geminal and four nongeminal. The apparent phosphorus-hydrogen spin-spin coupling constants $^3J_{\text{PH}}$ of compounds (VIII) and (IX) (15.0 and 15.3 Hz) suggest similar nongeminal environments and are similar to those of nongeminal chloro-dimethylamino-derivatives of both cyclotriposphazatrienes¹² and cyclo-tetraphosphazatetraenes.¹³ A recent publication suggests that compound (IX) has a 2,6-*trans*-structure.¹⁴ A detailed investigation of the reactions of compounds (II) and (III) with *N*-methylaniline is in progress.¹⁵

The reactions of *NN*-dialkylanilines (I) with mono-nuclear phosphorus compounds such as (IV) and (V) (*a*) provide systems uncomplicated by the possibilities of isomerism, (*b*) proceed at lower temperature (130 °C), and (*c*) give some insight into the effects of changing the nature of the heteroatom multiply bonded to phosphorus, *i.e.* >PCl:N- ; >PCl:O ; >PCl:S .

The reaction of *NN*-dimethylaniline with phosphoryl chloride (IV) has received attention from time to time.^{16,17} Unlike the chlorophosphazenes, in most phosphoryl or thiophosphoryl chloride derivatives, any remaining phosphorus-chlorine bonds tend to undergo hydrolysis during work-up. Hence, the reaction mixtures were solvolysed to obtain stable derivatives of the original products. Like earlier workers,^{16,17} we used initially hydrolytic methods but subsequently found that ethanolysis was a far more useful procedure. Occasionally, a 'non-solvolytic' work-up procedure was employed when the isolation of species still containing phosphorus-chlorine bonds seemed feasible and desirable.

¹⁰ R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.

¹¹ R. A. Shaw and P. Ward, *J. Chem. Soc. (B)*, 1967, 123.

¹² R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 1965, 7193.

¹³ D. Millington and D. B. Sowerby, *J.C.S. Dalton*, 1972, 2035.

The reaction between phosphoryl chloride (IV) and *NN*-dimethylaniline was studied in greatest detail. Up to nine products, (X)—(XVIII) (see Scheme), were identified in some reactions (*e.g.* reaction 7 in Table 1). Earlier workers^{16,17} reported three of these products, (X; R = Me, R' = OH), (XI; R = Me), and (XVII; R = Me). Six products, (X)—(XV), contain phosphorus,

consisting of two 'carbon-', one mixed 'carbon-' and 'nitrogen-' and three 'nitrogen-substituted' derivatives. (See Table 1). Work-up procedures based on hydrolysis or ethanolysis give, in general, the same results. The same yields of the same products (or of solvolysis products from a common precursor) are found, *e.g.* reactions 2 and 3, and 6 and 7. However only in the ethanolysis procedure do we find evidence of the mono-'nitrogen-substituted' derivative (XIII; R = Me, R' = Cl), here isolated as the diester (XIII; R = Me, R' = OEt).

We could readily obtain the di-'carbon-' (X; R = Me, R' = OH or OEt) and tri-'carbon-substituted' (X; R = Me) derivatives, but even under the most favourable circumstances investigated [chloride (IV) and amine (I, R = Me) in the molar ratio 4 : 1 (reaction 8)], we were unable to isolate any mono-'carbon-substituted' derivative (XIX; R = Me, R' = Cl, OH, or OEt). [In the crude reaction mixture after 4 h, we were able to detect a trace of the diester (XIX; R = Me, R' = OEt) by mass spectrometry.]

Although the mono-'carbon-substituted' derivative, (XIX; R = Me, R' = Cl, OH, or OEt) was not isolated, the mono-'nitrogen-substituted' derivative (XIII; R = Me, R' = OEt) could readily be obtained by the ethanolysis procedure. Its absence, when the hydrolytic procedure was used, can be attributed either to unfavourable solubility properties, or to its speedier decomposition by aqueous alkali, than by alcoholic alkoxide. Hydrolysis or alcoholysis of compounds such as (XIII; R = Me) is however not the only feasible route to dealkylation products such as the secondary amine (XVI; R = Me). The occurrence of the mixed tri-'nitrogen-substituted' derivative (XV; R = Me) in similar proportions to the homogeneously substituted tri-'nitrogen-substituted' derivative (XIV; R = Me) suggests that dealkylation processes are probably proceeding in the original reaction mixture. They are usually observed when either prolonged reaction times or an excess of phosphoryl chloride is employed. Such

¹⁴ R. Keat, S. S. Krishnamurthy, M. N. S. Rao, A. C. Sau, R. A. Shaw, A. R. Vasudeva Murthy, and M. Woods, *Z. Naturforsch.*, 1974, **29b**, 701.

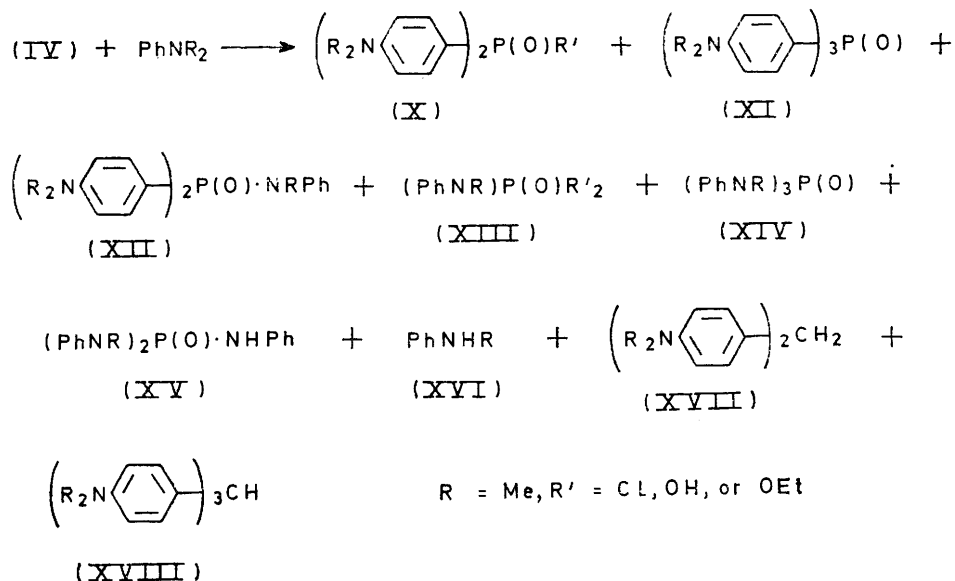
¹⁵ S. S. Krishnamurthy, M. N. S. Rao, R. A. Shaw, A. R. Vasudeva Murthy, and M. Woods, unpublished results.

¹⁶ M. Bourneuf, *Bull. Soc. chim. France*, 1923, **133**, 1808.

¹⁷ R. K. Robins and B. E. Christensen, *J. Org. Chem.*, 1951, 324.

dealkylated species containing nitrogen-hydrogen bonds have been shown in separate experiments to react with phosphorus-chlorine bonds much faster than their tertiary amine analogues, *e.g.* (I; R = Me). The phosphinic amide (XII; R = Me) has probably arisen *via* the phosphinic chloride (X; R = Me, R' = Cl) and not from other possible precursors such as (XIII; R = Me,

between cyanuric chloride and *NN*-dialkylanilines that although the effect of increasing the size of the two alkyl-groups from methyl to ethyl is profound, further increase in the length of these alkyl chains causes only relatively small changes in the proportion of 'carbon-' to 'nitrogen-substituted' compounds. In the reaction between phosphoryl chloride and *NN*-dimethylaniline



SCHEME

TABLE I
Products and yields in the reactions of *NN*-dialkyl- and *N*-alkyl-anilines with phosphoryl chloride

Reaction no.	Reactants and their ratio ^a	Reaction Temp. (°C)	Reaction Time (h)	Work-up procedure ^b	Relative % yields of products ^c										
					(XVI) (R = Me)	(X) (R' = OEt)	(XI) (R' = OH)	(XII)	(XIII) (R' = OEt)	(XX)	(XIV)	(XV)	(XVII)	(XVIII)	
1	(IV) 1 (I; R = Me) 2	130	9	B	²⁴ <i>d</i>	⁴² (R' = OEt)	1.5		⁶ (R' = OEt)					1.4	
2	1	4	130	9	B	<i>d</i>	⁴² (R' = OEt)	3		^{1.5} (R' = OEt)				0.3	
3	1	4	130	9	A	<i>d</i>	⁴⁵ (R' = OH)	2						0.3	0.2
4	1	4	130	9	A	<i>d</i>	⁴⁶ (R' = OH)	2						0.2	0.1
5	1	4	130	36	A	<i>d</i>	⁷⁵ (R' = OH)	4	2					0.5	0.2
6	1	6	130	72	A	<i>d</i>	⁴⁶ (R' = OH)	19	12			2	1	0.7	0.3
7	1	6	130	72	B	<i>d</i>	⁴² (R' = OEt)	18	13	⁶ (R' = OEt)		2	1.5	0.8	0.2
8	4	1	130	6	B	<i>d</i>	¹ (R' = OEt)	0.5		^{0.2} (R' = OEt)					
9	(IV) 1 (I; R = Et) 2	130	9	B	(R = Et) <i>d</i>	²² (R' = OEt)	1			² (R' = OEt)					
10	1	4	130	9	A	<i>d</i>	⁵³ (R' = OH)	7							
11	(IV) 1 (XVI; R = Me) 4	50	2.5	C							51	4	0.5		

^a The actual figures are multiples of 1/6 mol. ^b See text. ^c Yields of compounds (X)—(XVI) and (XX) based on (IV); of (XVII) and (XVIII) on (I). ^d Compounds observed, but experimental procedures made quantitative estimation not feasible.

R' = Cl), as shown by the fact that the phosphinic amide (XII) is formed, and its yield increases, under conditions which favour further reaction of (X), to *e.g.* (XI) (Table I). Experience with the system cyanuric chloride-dialkylaniline suggests that replacement of chlorine atoms by amino-groups decreases the reactivity of the resulting amino-chloro-1,3,5-triazines towards tertiary arylamines and appears to suppress 'carbon-substitution' altogether.¹⁸

We have shown in an earlier study⁸ of the reaction

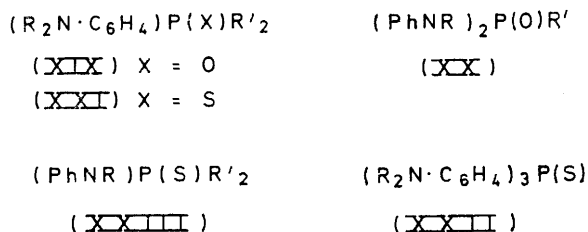
the products belong overwhelmingly to the 'carbon-substituted' types. Predictably, in replacing *NN*-dimethyl- with *NN*-diethyl-aniline relatively little change occurs; the phosphinic (X; R = Et, R' = OH or OEt) and phosphine oxide derivatives (XI; R = Et) are formed to a slightly larger degree, and the mono-'nitrogen-substituted' derivative (XIII) [again only obtained with the ethanolysis procedure (R = Et, R' = OEt)] to a lesser extent. *N*-Ethylaniline (XVI; R = Et) was

¹⁸ R. A. Shaw and P. Ward, unpublished results.

found in the products from both solvolysis procedures. No trace was found, however, of purely organic compounds related to the diphenyl- (XVII) or triphenylmethane bases (XVIII).

For comparison purposes the reaction between *N*-methylaniline (XVI; R = Me) and phosphoryl chloride (IV) was investigated. The reaction proceeds readily at considerably lower temperature and in a shorter time. Three products were observed: a diamidic chloride (XX; R = Me, R' = Cl), a product type not observed with the corresponding tertiary amine (I; R = Me), the phosphoric triamide (XIV; R = Me), and its partially dealkylated analogue (XV; R = Me). The last two are also obtained from *NN*-dimethylaniline under much more drastic conditions. The presence of compound (XV; R = Me) shows that dealkylation also occurs with the secondary amine. No 'carbon-substituted' derivative was observed in our study with *N*-methylaniline (but *cf.* ref. 4).

Reactions between thiophosphoryl chloride (V) and *NN*-dialkylanilines (I; R = Me or Et) are accompanied by much decomposition and only a portion (sometimes small) of the reactants could be accounted for. The reaction between the chloride (V) and the amine (I; R = Me) gave as sole, identified product the phosphonic derivative (XXI; R = Me, R' = OEt), in fair yield, a structural type we have been unable to isolate in the corresponding oxide series (XIX; R = Me or Et,



R' = Cl, OH, or OEt). From the reaction of the chloride (V) and the amine (I; R = Et), a small yield of the phosphine sulphide (XXII; R = Et) was obtained.

The reaction of thiophosphoryl chloride (V) with a secondary amine (XVI; R = Me), was also briefly investigated. As anticipated, it proceeds slower than with phosphoryl chloride (IV). By utilising the greater stability to hydrolysis of the thioic derivatives, the amidic dichloride (XXIII; R = Me, R' = Cl) could be isolated.

It is at present not easy to rationalise all the above findings. In the reactions of dimethylaniline (I; R = Me) with phosphoryl chloride (IV), we isolated (in keeping with earlier findings^{16,17}), only di-'carbon-' (X; R = Me, R' = Cl, OH, or OEt) and tri-'carbon-substituted' (XI; R = Me) derivatives. The absence or near absence of the mono-'carbon-substituted' derivative (XIX; R = Me, R' = Cl, OH, or OEt) is all the more remarkable, as a related compound (XIX; R = H, R' = OH)¹⁹ has

been reported to be obtained by another route. Furthermore, the corresponding sulphur analogue (XXI; R = Me, R' = OEt) has been obtained during the present study. Whether (XIX; R = Me, R' = Cl) reacts faster than (IV) with further amine (I; R = Me), whether it is rapidly decomposed, or whether it is lost owing to the experimental procedures employed, is not clear. We somewhat favour the first of these possibilities, as indications are that ionisation increases in the order $P(O)Cl_3 < PhP(O)Cl_2 < Ph_2P(O)Cl$.²⁰ If this plays a part in the mechanism of the system reported here, one would expect an acceleration of the reaction on replacement of the first chlorine atom. This should be even more pronounced on replacement of the second chlorine atom, but here steric effects may play a retarding role.

Equally noteworthy is that although mono-'nitrogen-' (XIII; R = Me, R' = OEt), and tri-'nitrogen-substituted' (XIV and XV; R = Me) compounds are observed in the reactions with tertiary amines, di-'nitrogen-substituted' derivatives (XX; R = Me, R' = Cl, OH, or OEt) are apparently absent. These are however readily accessible from the secondary amine (XVI; R = Me) and phosphoryl chloride (IV).

We will defer detailed discussion of the reaction mechanisms, but the following observations are pertinent. In the related system cyanuric chloride-*NN*-dialkylanilines, charge-transfer complexes, as well as quaternary salts, have been observed.²¹ The former are likely precursors of the 'carbon-substituted' derivatives, the latter of the 'nitrogen-substituted' derivatives.

The ¹H n.m.r. spectra of organic derivatives of phosphorus show a pronounced solvent shift [$\delta(CCl_4) - \delta(PhH)$] which indicates a fairly specific interaction of the phosphorus compound with the π -electrons of the benzene ring.²² With *NN*-dialkylanilines this type of interaction and/or a similar one with the lone pair of electrons of the amino-group is possible.

'Nitrogen-substitution' may result from the direct reaction of *NN*-dialkylanilines with the phosphorus halides, giving rise to alkyl halides; it can also occur from the reaction of *N*-alkylanilines with phosphorus halides with elimination of hydrogen halide. The formation of the latter arises *inter alia* from the reaction leading to 'carbon-substituted' compounds.

Chambers and Pearson²³ have shown that *NN*-dialkylanilines are dealkylated smoothly at 156 °C to secondary amines. Further dealkylation (at convenient rates) of the latter to anilines requires temperatures of the order of 195 °C. As the reaction temperatures in our study were in the range 130–160 °C, the hydrogen halide arising could have produced significant quantities of *N*-alkylanilines, together with small quantities of anilines. This could account for part of the yield of 'nitrogen-substituted' compounds, as secondary and primary amines react much faster than tertiary amines

¹⁹ A. Michaelis and E. Benzinger, *Annalen*, 1877, **188**, 275.

²⁰ V. Gutmann, *Angew. Chem. Internat. Edn.*, 1970, **7**, 843.

²¹ R. A. Shaw and P. Ward, *J. Chem. Soc. (B)*, 1969, 596.

²² R. Keat and R. A. Shaw, *J. Chem. Soc. (A)*, 1968, 703.

²³ R. A. Chambers and D. E. Pearson, *J. Org. Chem.*, 1963, **28**, 3144.

with phosphorus halides. Silicon tetrabromide has been reported to act as a dealkylating agent; it is likely that this applies also to phosphorus halides. Evidence for the latter comes from the reaction of the chlorophosphazenes (II) and (III) with *NN*-dimethylaniline, where the proportion of 'carbon-substituted' compounds is small or negligible. Hydrogen chloride-induced dealkylation could therefore account for only a small proportion of the 'nitrogen-substituted' compounds

TABLE 2

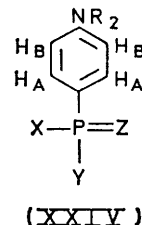
Effect of structural changes in ambident nucleophilic reactions on the relative numbers of bonds formed at different reaction sites

Reaction system	Reaction temp. (°C)	Relative % formation of bonds	
		C-C	C-N
$N_3C_3Cl_3 + (I; R = Me)$	90	0	100
$N_3C_3Cl_3 + (I; R = Et)$	90	30	70
		P-C	P-N
(II) + (I; R = Me)	160	10	90
(III) + (I; R = Me)	160	0	100
(IV) + (I; R = Me)	130	85-90	10-15
(IV) + (I; R = Et)	130	97-99	1-3

with these substrates [(II) and (III)]. With the mono-nuclear phosphorus halides, because of their overwhelming preference for 'carbon-substitution', the source of the 'nitrogen-substituted' derivatives is less clear. Dealkylated amines (XVI; R = Me or Et), isolated after completion of the reaction may have

Et) affect cyanuric chloride, and phosphoryl chloride in the same manner: the proportion of product derived by attack at the softer and sterically less demanding centre increases. Overall the phosphorus(v) chlorides, in comparison with cyanuric chloride, seem to have a greater preference for attack at the aromatic carbon atom; this is particularly pronounced for phosphoryl chloride (IV). Part of this effect may again be steric in origin, as the electrophilic centre is 3-co-ordinate for cyanuric chloride and 4-co-ordinate in the phosphorus(v) chlorides.

The 1H n.m.r. spectra (see Table 3) of the 'carbon-substituted' derivatives are of the AA'BB' type, and



thus prove unambiguously that all these derivatives are *para*-substituted dialkylanilines (XXIV), analogous to the products derived from the cyanuric chloride reaction.¹¹ A comparison of S_o values²⁴ (Table 3) shows the triazine moiety to be a more effective electron-withdrawing substituent [$N_3C_3Cl_2$ -78, $N_3C_3(NMe_2)Cl$ -71,

TABLE 3

1H N.m.r. data (τ values; J in Hz) of 'carbon-substituted' derivatives

Compound	S_o (p.p.m.)	$\tau(H_A)$	$\tau(H_B)$	$J(P, H_A)$	$J(P, H_B)$	$J(H_A, H_B)$
(X; R = Me, R' = OH)	-53	2.40	3.40	11.7	2.7	8.8
(X; R = Me, R' = OEt)	-63	2.32	3.30	11.5	2.8	8.9
(X; R = Et, R' = OH)	-51	2.43	3.42	11.6	2.7	8.9
(X; R = Et, R' = OEt)	-61	2.34	3.35	11.4	2.9	9.0
(XIII; R = Me)	-57	2.38	3.38	11.0	2.6	8.8
(XI; R = Me)	-47	2.48	3.32	11.2	2.3	9.0
(XI; R = Et)	-47	2.48	3.32	11.1	2.3	8.9
(VI) †	-66	2.29	3.33	16.2	4.7	9.0
(XXI; R = Me, R' = OEt)	-68	2.27	3.30	13.3	3.3	8.8
(XXII; R = Me)	-47	2.48	3.40	12.5	2.5	8.8

† In CCl_4 ; others in $CDCl_3$.

arisen in part from the decomposition of the 'nitrogen-substituted' compounds during work-up.

In the general context of the behaviour of neutral ambident nucleophiles, it is appropriate to compare the reactions of *NN*-dialkylanilines (I; R = Me or Et) with cyanuric chloride⁸ and the various phosphorus(v) chlorides. The 'cleanness' of the reactions, and hence the degree of reliability placed on deductions based on these, decreases rapidly in the order: $N_3C_3Cl_3 > N_3P_3Cl_6 \sim N_4P_4Cl_8 > P(O)Cl_3 > P(S)Cl_3$. Table 2 summarises the overall findings with respect to changes in the structure of the reaction partners and their effect on the relative proportions of bonds formed (bonds rather than molecules, as in some cases more than one bond is formed per molecule) at the more electronegative, 'harder' atom, nitrogen (C-N and P-N), and at the 'softer' centre, aromatic carbon (C-C and P-C). Greater steric demands by the nucleophile, (I) (R = Me \rightarrow

$N_3C_3(NMe_2)_2$ -63],¹¹ than the phosphorus(v) grouping $PXY(Z)$ (-68 to -47). A more detailed examination of the S_o values of the latter group reveals that these are little affected by the nature of R (Me or Et) or Z (formally multiply bonded O, S, or N). S_o Values have the highest negative magnitudes (-66 to -68) if the two substituents X and Y are both electronegative groups (Cl, N, O), the least negative (-47) if both X and Y are aromatic carbon residues, with intermediate S_o values (-51 to -63) if X and Y belong one each to the two above groups. The considerably more negative S_o values for corresponding derivatives where the OEt group replaces an OH group are noteworthy.

EXPERIMENTAL

Phosphoryl chloride (May and Baker Ltd.) and thiophosphoryl chloride (Alfa Inorganic Inc.) were purified by

²⁴ G. W. Smith, *J. Mol. Spectroscopy*, 1964, 12, 146.

fractional distillation. Aromatic amines (B.D.H. Ltd. or Eastman Kodak Ltd.) were purified by distillation under reduced pressure and the purity, checked by g.l.c. analysis, was found to be >99.7%. The chlorophosphazenes (Albright and Wilson Ltd.) were recrystallised to constant m.p. Light petroleum used had b.p. 60–80 °C unless otherwise stated.

¹H N.m.r. spectra were recorded with a Varian A 60 and a Varian HA 100 spectrometer (Me₄Si as internal standard). Mass spectra were obtained with an A.E.I. MS9 spectrometer (at the London School of Pharmacy under the ULIRS scheme).

General Procedure.—The amine and the phosphorus chloride were placed in a two-necked flask (250 ml) previously flushed with dry, oxygen-free nitrogen. Reaction mixtures were heated for 9 h at 130 °C (oil-bath). The

material was boiled with ether for 15 min; the mixture was filtered and the filtrate cooled to yield a violet precipitate. Part of this could be recrystallised from light petroleum to give bis(dimethylaminophenyl)methane (XVII; R = Me), m.p. 86 °C. The rest was recrystallised from ether to give tris(dimethylaminophenyl)methane (XVIII; R = Me), m.p. 177 °C. The ether-insoluble material was boiled with ethanol to give on cooling tris(dimethylaminophenyl)phosphine oxide (XI; R = Me), m.p. 286 °C (from ethanol–light petroleum). Alternatively the alkali-insoluble material was chromatographed on a column packed with silica gel and the compounds were eluted with ethyl acetate in the following order: (i) unchanged *NN*-dimethylaniline; (ii) a mixture of (XVII) and (XVIII) (R = Me); (iii) (XV; R = Me), m.p. 151 °C; (iv) (XIV), m.p. 132 °C; (v) (XII; R = Me), m.p. 126 °C; (vi) (XI; R = Me). The aqueous solution

TABLE 4
Analytical data

Formula	Compound	M.p. (°C)	Found (%)					Required (%)				
			C	H	N	P	M ^a	C	H	N	P	M
C ₈ H ₁₀ N ₂ P ₂ Cl ₅	(VI)	137–138	22.0	2.5	13.2	21.6 ^a	432	22.1	2.3	13.0	21.5	432
C ₁₇ H ₂₀ N ₄ P ₂ Cl ₅	(VII)	58–60	20.0	2.0	13.5	22.0 ^b	418	20.1	1.9	13.4	22.2	418
C ₇ H ₈ N ₂ P ₂ Cl ₅	(VIII)	64–66	15.9	1.7	13.0	23.2 ^c	534	15.8	1.5	13.1	23.2	534
C ₁₄ H ₁₈ N ₄ P ₂ Cl ₆	(IX)	144–146 (lit., ¹⁴ 146)	27.7	2.6	14.0	20.3 ^d	604	27.8	2.7	14.0	20.2	604
C ₁₆ H ₂₁ N ₃ P ₂ O ₂	(X; R = Me, R' = OH)	209–210 (lit., ¹⁵ 209–211; lit., ¹⁶ 199, 249–250)	63.1	7.0	9.0	10.45	304	63.2	7.0	9.2	10.2	304
C ₁₈ H ₂₅ N ₃ P ₂ O ₂	(X; R = Me, R' = OEt)	128–129	65.3	7.7	8.25	9.5	332	65.1	7.6	8.4	9.3	332
C ₂₀ H ₂₉ N ₃ P ₂ O ₂	(X; R = Et, R' = OH)	215–217 (lit., ¹⁶ 195, 253–254)	66.9	8.3	7.6	8.6	360	66.6	8.1	7.8	8.6	360
C ₂₂ H ₃₃ N ₃ P ₂ O ₂	(X; R = Et, R' = OEt)	105–106	68.0	8.7	7.1	8.1	388	68.0	8.6	7.2	8.0	388
C ₂₄ H ₃₇ N ₃ P ₂ O	(XI; R = Me)	285–286 (lit., ¹⁶ 262; lit., ¹⁷ 305–306)	70.85	7.2	10.4	7.85	407	70.8	7.4	10.3	7.6	407
C ₃₀ H ₄₁ N ₃ PO	(XI; R = Et)	236–237	73.4	8.5	8.7	6.5	491	73.4	8.6	8.55	6.3	491
C ₃₂ H ₄₅ N ₃ PO	(XII; R = Me)	125–126	70.3	7.25	10.6	8.0	393	70.2	7.2	10.7	7.9	393
C ₁₁ H ₁₃ NPO ₂	(XIII; R = Me, R' = OEt)	–17 to –19	54.3	7.25	5.7	12.7	243	54.3	7.4	5.8	12.8	243
C ₁₃ H ₁₇ NPO ₂	(XIII; R = Et, R' = OEt)	–23 to –24	55.9	7.9	5.6	12.2	257	56.0	7.8	5.45	12.0	257
C ₁₅ H ₁₉ NPO	(XIV; R = Me)	130–132	69.2	6.6	11.3	8.7	305	69.0	6.6	11.5	8.5	305
C ₂₀ H ₂₅ N ₂ PO	(XV; R = Me)	150–151	68.2	6.1	11.8	9.0	351	68.4	6.3	12.0	8.8	351
C ₁₁ H ₁₃ N ₂	(XVII; R = Me)	85–86 (lit., ¹⁸ 90)	80.1	8.5	11.1		254	80.3	8.7	11.0		254
C ₁₁ H ₁₃ N ₂	(XVIII; R = Me)	175–177 (lit., ¹⁸ 175)	80.7	8.5	11.5		373	80.4	8.4	11.25		373
C ₁₄ H ₁₆ N ₂ PClO	(XX; R = Me, R' = Cl)	–26 to –27	56.7	5.5	9.7	10.7 ^e	294	56.9	5.4	9.5	10.5	294
C ₁₅ H ₁₉ N ₂ PO ₂ S	(XXI; R = Me, R' = OEt)	51–52	52.6	7.3	5.3	11.5 ^f	273	52.7	7.4	5.1	11.3	273
C ₁₅ H ₁₉ N ₂ PS	(XXII; R = Et)	265–266	70.9	8.1	8.2	6.2 ^g	507	71.0	8.3	8.3	6.1	507
C ₇ H ₉ N ₂ PCl ₂ S	(XXIII; R = Me, R' = Cl)	–11 to 13	35.1	3.5	5.7	13.1 ^h	240	35.0	3.4	5.8	12.9	240

^a Found: Cl, 40.8. Reqd. 41.1%. ^b Found: Cl, 42.2. Reqd. 42.4%. ^c Found: Cl, 46.5. Reqd. 46.6%. ^d Found: Cl, 35.3. Reqd. 35.2%. ^e Found: Cl, 11.9. Reqd. 12.1%. ^f Found: Cl, 11.6. Reqd. 11.7%. ^g Found: S, 6.7. Reqd. 6.3%. ^h Found: Cl, 29.3; S, 13.3. ⁱ Reqd. Cl, 29.5; S, 13.4%.

* E. Bamberger and L. Rudolf, *Ber.*, 1908, **41**, 1908.

effluent gases were condensed in two traps cooled with acetone–CO₂ and liquid air, respectively. Crude reaction mixtures were treated by one of the following procedures:

(A) *Alkaline hydrolysis.* The crude mixture was treated with 6*N*-sodium hydroxide and unchanged amines were removed by steam distillation. Alkali-insoluble material was filtered off and the solution was acidified with glacial acetic acid to obtain acid-insoluble materials.

(B) *Sodium ethoxide treatment.* Sodium ethoxide (freshly prepared) in ethanol was added and the mixture heated under reflux for 2–3 h, then diluted with water and extracted with ether; the extracts were separated, dried (Na₂SO₄), and evaporated and the resultant oil was chromatographed.

(C) *Non-solvolytic method.* The crude mixture was treated with carbon tetrachloride and amine hydrochlorides were filtered off. The filtrate was concentrated and chromatographed.

Some reactions are described in some detail below: the rest are summarised in Table 1. Analytical data are given in Table 4.

(1) *Reaction of NN-Dimethylaniline with Phosphoryl Chloride.*—(A) *Hydrolysis.* After hydrolysis of the crude mixture, unchanged amine was removed by steam distillation. G.l.c. analysis of the distillate showed that it was a mixture of *NN*-dimethylaniline (I; R = Me) and a trace of *N*-methylaniline (XVI; R = Me). The alkali-insoluble

was acidified to yield compound (X; R = Me, R' = OH), m.p. 210 °C.

(B) *Sodium ethoxide treatment.* Ethyl acetate was used to elute the compounds in the following order: (i) *NN*-dimethylaniline (I; R = Me); (ii) a mixture of (XVII) and (XVIII) (R = Me); (iii) (XIII; R = Me, R' = OEt), m.p. –19 °C; (iv) (XV; R = Me); (v) (XIV; R = Me); (vi) (XII; R = Me); (vii) (X; R = Me, R' = OEt), m.p. 129 °C; (viii) (XI; R = Me).

(2) *Reaction of NN-Diethylaniline with Phosphoryl Chloride.*—Sodium ethoxide treatment was carried out and the compounds were eluted through a silica gel column by ethyl acetate in the following order: (i) a mixture of *NN*-diethylaniline (I; R = Et) and *N*-ethylaniline (XVI; R = Et) in the ratio 10:1, respectively, as determined by g.l.c.; (ii) (XIII; R = Et, R' = OEt), m.p. –23 °C; (iii) (X; R = Et, R' = OEt), m.p. 106 °C; (iv) (XI; R = Et), m.p. 237 °C.

(3) *Reaction of N-Methylaniline with Phosphoryl Chloride.*—A non-solvolytic work-up was used. The compounds were eluted with ethyl acetate from a silica gel column in the following order: (i) (XX; R = Me, R' = Cl), m.p. –26 °C; (ii) (XV; R = Me); (iii) (XI; R = Me).

(4) *Reaction of Thiophosphoryl Chloride with NN-Dimethylaniline.*—Sodium ethoxide treatment was carried out. Only (XXI; R = Me, R' = OEt), was isolated, m.p.

52 °C. Compounds (XVII) and (XVIII) (R = Me) were also detected in minute quantities.

(5) *Reaction of Thiophosphoryl Chloride with N-Methylaniline.*—A non-solvolytic work-up was applied. Ethyl acetate–benzene (1 : 9) was used as eluant. Only compound (XXIII; R = Me, R' = Cl) was isolated, m.p. –11 °C.

(6) *Reaction of Thiophosphoryl Chloride with NN-Diethylaniline.*—The sodium ethoxide method was used. Only (XXII; R = Et), m.p. 266 °C, was eluted from a silica gel column (CCl₄ as eluant).

(7) *Reaction of Hexachlorocyclotriphosphazatriene with NN-Dimethylaniline.*—A non-solvolytic work-up was applied. Carbon tetrachloride–benzene (3 : 2) was used as eluant. The compounds were eluted in the order: (i) (II);

(ii) (XXIV; R = Me), m.p. 58–60 °C; (iii) (XXV; R = Me), m.p. 137–138 °C.

(8) *Reaction of Octachlorocyclotetraphosphazetraene with NN-Dimethylaniline.*—A non-solvolytic method was used. Carbon tetrachloride was used as eluant and the compounds were eluted from a silica gel column in the following order: (i) (III); (ii) (XXVI; R = Me), m.p. 64–66 °C; (iii) (XXVII; R = Me), m.p. 144–146 °C.

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