Studies in Cyclophosphazenes. Part 10.[1] The Mechanism for *trans*-Isomer Preference in the Non-geminal Diamination of Hexachlorocyclotriphosphazene

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With the aim of elucidating the mechanistic origins of *trans* preference as observed in the amination reactions of chlorocyclophosphazenes, a kinetic study of the reactions of pentachloro(dimethylamino)cyclotriphosphazene, $N_3P_3Cl_5(NMe_2)$, with NMe_2H in tetrahydrofuran to produce *cis*- and *trans*-$N_3P_3Cl_4(NMe_2)_2$ has been undertaken. Gas chromatographic analysis was employed to follow the changes in the concentrations of the components of the product mixture with time, from which rate constants for both the *cis* and the *trans* reactions at various temperatures, as well as the values of the enthalpies and entropies of activation of both reactions, have been evaluated. The data show that the *trans* preference is due solely to the fact that $\Delta S^{\ddagger}_{trans} > \Delta S^{\ddagger}_{cis}$. To explain the origin of *trans* preference the operation of a modified substituent-solvating effect is postulated, according to which the substituent, after protonation, functions as a neighbouring group that by intramolecular acid catalysis facilitates departure of the chloride ion. This mechanism specifically favours the formation of the *trans* isomer as for steric reasons it cannot aid the formation of the *cis* isomer.

THE predominant formation of one isomer in reactions that can lead to many, a phenomenon that we name stereoselectivity,† has frequently been observed in the substitution reactions of the halogenocyclophosphazenes and it is typically very prevalent in their much studied amination reactions.[3,4] Studies of these reactions have permitted delineation of geminal, non-geminal, and mixed replacement patterns, but the substitution pattern that is observed in any particular reaction is influenced, if not determined, by many factors such as the type of amine (primary or secondary), the steric requirements of the alkyl groups, the basicity of the amine, the solvent used, the presence of excess of amine (or other base), and the temperature.[3] Considerable effort has been directed to elucidating the roles played by these factors and to rationalizing their influence, but many questions remain unanswered.

This paper concerns *trans* preference, a stereoselective effect that has been reported in replacement reactions of chlorocyclotriphosphazenes with amines. We define it as favoured attack *trans* to the maximum number of amino-substituents, all reactions being assumed to occur with inversion. It is important to note that *trans* preference is not defined with reference to the configurations of the major products of the substitution reactions. Table 1 presents the four general non-geminal aminations for each of which two alternative possibilities of *cis*- or *trans*-isomer formation exist. *trans* Preference has unequivocally been demonstrated in examples of the first three of these reactions, although in reaction (3) it is the *cis* isomer which is produced. For the last reaction of Table 1 the results reported using dimethylamine,[5] the only amine studied, are inconclusive as they preceded detection and characterization of the product expected for *trans* preference.[6]

Two explanations for *trans* preference have been advanced. Keat and Shaw [7] invoked the '*cis* effect' (c.e.) according to which electron density is transferred more readily between two groups situated on neighbouring phosphorus atoms which are *cis* to one another, than between two such groups *trans* to one another. This transfer of electronic charge is presumably most important between groups that are respectively able to release and attract electrons. Then, according to this theory, in a chlorocyclotriphosphazene partially substituted by electron-releasing substituents, the c.e. will induce a greater negative charge on the chlorine atoms *cis* to the maximum number of such substituents, and in bimolecular nucleophilic displacement, assuming inversion, both approach of the nucleophile and departure of the chloride ion will be favoured when the reagent approaches *trans* to the maximum number of substituents present. For dimethylamino-substituents, n.m.r. evidence was cited in support of the preferential *cis* transfer

TABLE 1

Configurations of products of non-geminal monoaminations of aminochlorocyclotriphosphazenes

	Starting material					Product						
Reaction	Degree of substitution	Configuration	Numbering for NR_2 [a]	Numbering for Cl	Formula [a]	Degree of substitution	Major product	Minor product	Numbering for NR_2 [a]	Numbering for Cl	Formula [a]	Ref.
(1)	1		2	2,4,4,6,6	$N_3P_3Cl_5(NR_2)$	2	*trans*	*cis*	2,4	2,4,6,6	$N_3P_3Cl_4(NR_2)_2$	28
(2)	2	*cis*	2,4	2,4,6,6	$N_3P_3Cl_4(NR_2)_2$	3	*trans*	*cis*	2,4,6	2,4,6	$N_3P_3Cl_3(NR_2)_3$	5
(3)	3	*trans*	2,4,6	2,4,6	$N_3P_3Cl_3(NR_2)_3$	4	*cis*	*trans*	2,2,4,6	4,6	$N_3P_3Cl_2(NR_2)_4$	6*a*
(4)	3	*gem*	2,2,4	4,6,6	$N_3P_3Cl_3(NR_2)_3$	4	*trans* [b]	*cis* [b]	2,2,4,6	4,6	$N_3P_3Cl_2(NR_2)_4$	

[a] R = Alkyl or H. [b] Predicted assuming *trans* preference. See text for detailed discussion of this reaction.

† For differentiation, stereospecificity is defined as the exclusive formation of only one isomer in a reaction that can produce several. Compare these definitions with those of specificity and selectivity of analytical reagents.[2]

of charge. However, most of the crystallographic determinations of P–Cl bond lengths in aminochlorocyclotriphosphazenes that have since been reported [8] do not support the c.e.

An alternative explanation called the ' substituent-solvating effect ' (s.s.e.) was proposed by one of us [9] on the basis of a predicted difference in $\Delta S^{\ddagger}$ calculated for the reactions producing *cis*- and *trans*-tetrachlorobis(dimethylamino)cyclotriphosphazenes. Since in these reactions chloride-ion release is rate determining, the effect assumed participation of the amino-substituent in solvation of the released chloride ion through a 2,4 interaction that should result in only a small loss in the degrees of freedom of the system compared to a far greater loss by the system as a whole on solvation by solvent molecules. This ' internal solvation ' leads to higher values of $\Delta S^{\ddagger}$ for these reactions than for those in which this effect is absent. Assuming displacement with inversion, this substituent-solvating effect can only come about if the ring is attacked from the side opposite the substituent in a reaction that leads to the *trans* isomeric product with respect to the solvating substituent. Attack from the same side of the ring as the substituent, leading to the *cis* isomer, cannot be aided by this effect.

Since these proposals were made it appears that no additional experimental findings, direct or indirect, that are relevant to the above explanations have been reported.

Our aim in this study was to adduce new evidence that has a bearing on this problem of *trans* preference. Because this phenomenon is clearly of kinetic origin, roughly equal amounts of *cis* and *trans* isomers existing in equilibrium,[10,11] it was felt that kinetic evidence would best provide new, relevant, and meaningful insights into the problem. Furthermore, since the reactions are stereoselective, with reactions leading to both isomers being in competition, a study of both rates appeared to be necessary.

We argued that a critical test of the two explanations could be made by measuring the activation parameters of the reactions leading to formation of both isomers: the c.e. would appear to predict that $\Delta H^{\ddagger}_{cis} > \Delta H^{\ddagger}_{trans}$, whilst the s.s.e. requires that $\Delta S^{\ddagger}_{trans} > \Delta S^{\ddagger}_{cis}$. We therefore measured k values for reaction (1) at several temperatures and calculated the relevant activation

$$N_3P_3Cl_5(NMe_2) + 2NMe_2H \longrightarrow \textit{cis}\text{- and } \textit{trans}\text{-}N_3P_3Cl_4(NMe_2)_2 + [NMe_2H_2]Cl \quad (1)$$

parameters. The results obtained are at variance with those predicted for the c.e., but although they are consistent with the s.s.e. as originally suggested a modified version of the s.s.e. is proposed, based on a new interpretation of the results that better fits more of the known facts. Moreover, in contrast with the original s.s.e. theory, the new rationalization does have precedents in other reactions. Part of the data reported in this paper have been presented previously.[12]

EXPERIMENTAL

Materials.—The reagents used and the methods for their purification have been described previously.[13] The toluene-*p*-sulphonic acid was a Merck *pro analysi* product.

Preparations.—Hexachlorocyclotriphosphazene was prepared by Emsley and Udy's method [14] using fine ammonium chloride precipitated by adding a large excess of chilled acetone to a hot saturated solution of the salt in water and filtering rapidly. The trimeric oligomer was separated from the other cyclic chlorocyclophosphazenes by vacuum sublimation at 70—80 °C: its m.p. was 111—112 °C (lit.,[15] 114 °C).

Pentachloro(dimethylamino)cyclotriphosphazene was synthesized by a previously described method.[16] After preliminary separation by column chromatography on silica, the final purification was by vacuum distillation (0.05 mmHg) * at 85 °C. Gas chromatography (g.c.) showed no peaks arising from the starting material or from more highly substituted derivatives.

Pure *trans*-tetrachlorobis(dimethylamino)cyclotriphosphazene was prepared as described previously,[16] m.p. 103 °C (lit.,[5] 103 °C). Mixed *cis*- and *trans*-tetrachlorobis(dimethylamino)cyclotriphosphazenes in a ratio of *ca.* 1 : 1 were prepared in acetonitrile.[17] After two recrystallizations from light petroleum (b.p. 40—60 °C), gas chromatography indicated that the product only contained these two compounds.

Instrumentation.—Quantitative g.c. analysis was performed on an ' all-glass ' Packard model 873 gas chromatograph attached to an Autolab System IV integrator as described previously.[11] The glass columns (length 3 m, internal diameter 3 mm) were filled with Chromosorb W (60—80 mesh) (Johns Manville) loaded with 5% (w/w) SE 30 (Applied Science Laboratories Inc.). The inlet and detector were held at 180 °C, and the column temperature was 150 °C. The flow rate of the nitrogen carrier gas was 30 $cm^3\ min^{-1}$. The size of the flame was of the utmost importance and the hydrogen and air were supplied to the detector at 40 and 400 $cm^3\ min^{-1}$ respectively.

Under the conditions specified above, g.c. separation of the mono(dimethylamino)-substituted and *cis*- and *trans*-bis-(dimethylamino)-substituted chlorocyclophosphazenes was complete with a full return to baseline between signals. The integrations of the peak areas were reproducible to $\pm 2\%$ of total area. By appropriate control experiments it was shown that within the experimental error the relative peak areas were independent of the absolute quantities injected, the ratios of the compounds, the solvents, the presence of excess of dimethylamine hydrochloride, and of excess of toluene-*p*-sulphonic acid.

Using the exact *cis* : *trans* isomer ratio of the mixed di-substituted product as determined by comparison with the pure *trans* isomer, a calibration solution was prepared by weighing samples of the mono- and the mixed di-substituted products and dissolving them in tetrahydrofuran (thf).

The relative sensitivity of the detector to the three phosphazenes varied slightly from day to day, probably because of differences in the size of the flame, so the integrator was calibrated daily. Regular checks in the course of each day's work, and at the end of the day, demonstrated the stability of the instrument.

Kinetic Measurements.—The preparation of the thf solutions of pentachloro(dimethylamino)cyclotriphosph-

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

azene and of dimethylamine and their equilibration, the apparatus used, and the method of conducting the kinetic experiments have all been described in detail.[13] Samples (*ca.* 4 cm^3) of the reaction mixture were removed at intervals and quenched by adding them to a thf solution containing a small excess of dried toluene-*p*-sulphonic acid dissolved in thf. The quenched solutions, which were stable for several days, were concentrated by evaporation before being analysed by g.c. Each sample was analysed not less than twice, the average values of the relative areas were determined, and from them the concentrations were calculated using the calibration factors determined.

RESULTS AND DISCUSSION

Table 2 lists full details of the kinetic experiments carried out on reaction (1). The reactions leading to both the *cis*- and the *trans*-isomeric products obeyed second-order rate laws that were first order in the concentrations of both phosphazene and amine.

also presents rate data and activation parameters for the combined *cis* and *trans* reactions, as determined in the present study (line 3). It is reassuring to note the very satisfactory agreement between the results obtained by the two totally independent methods.

The relative values of k_{cis} and k_{trans} at all temperatures clearly confirm *trans* preference as found in preparative experiments. The values of the activation parameters for the *cis* and *trans* reactions show that both of these reactions are controlled by the entropy of activation and that both operate by the same basic mechanism proposed previously [13] in which chloride-ion departure is the rate-limiting step. Importantly, the *difference* between the rates of the reactions producing the *cis* and *trans* isomers, *i.e.* the source of the observed *trans* preference, stems solely from the fact that $\Delta S^{\ddagger}_{trans}$ is larger (*i.e.* less negative) than $\Delta S^{\ddagger}_{cis}$, as $\Delta H^{\ddagger}_{trans}$ actually exceeds $\Delta H^{\ddagger}_{cis}$. This result is clearly incompatible with predictions that follow from the c.e. and consequently this effect appears to be untenable as a rationalization of *trans* preference.

Although the results obtained in this study are in agreement with predictions implied by the s.s.e. as

TABLE 2

Details of the kinetic experiments for reactions (1)

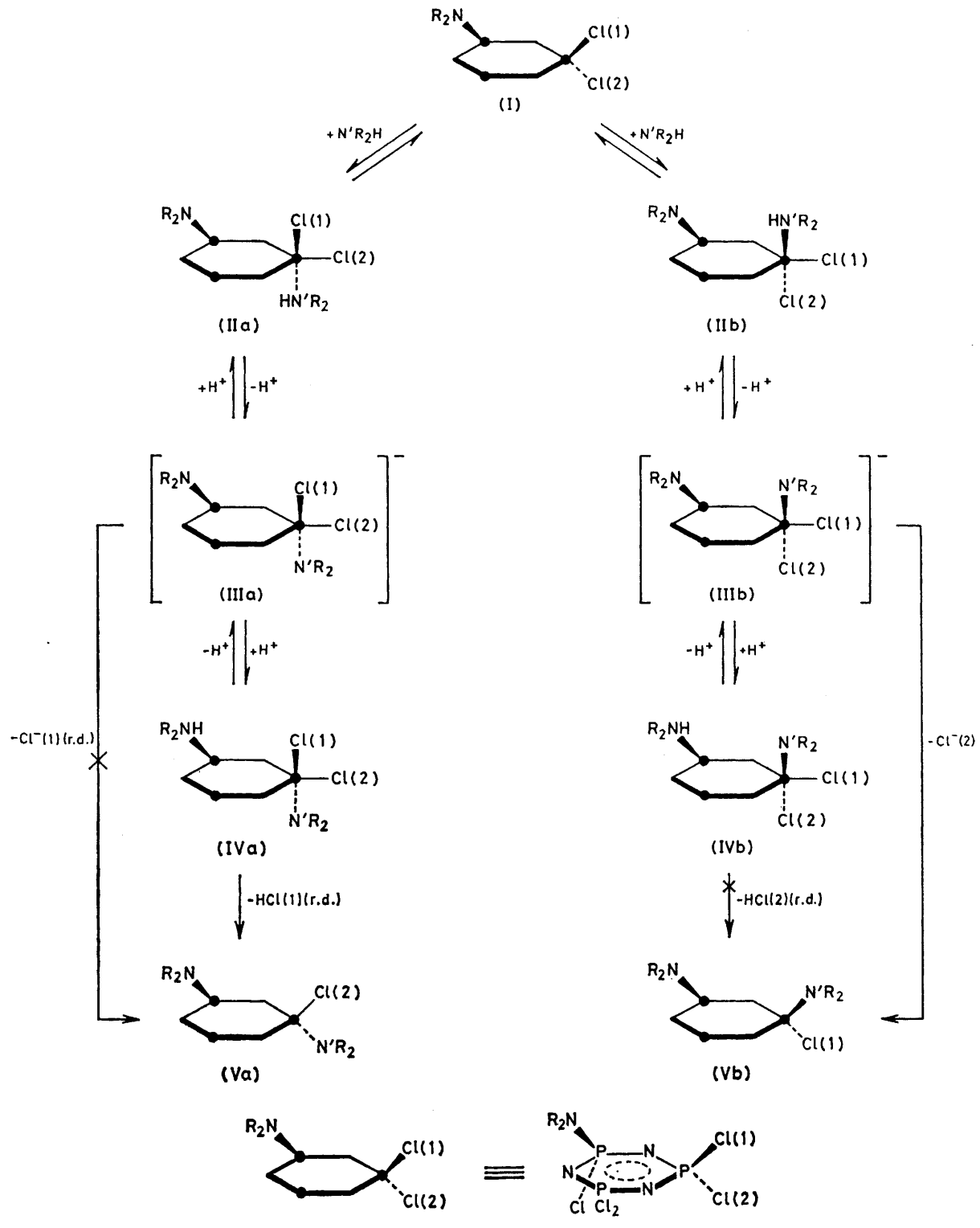
Expt. no.	Initial concentration/ 10^{-4} mol dm^{-3}		Reaction covered/%	θ_c/°C	k_2/dm^3 mol^{-1} s^{-1}	
	$N_3P_3Cl_5(NMe_2)$	NMe_2H			*trans*	*cis*
1	7.21	14.43	81	10	0.39 ± 0.01	0.164 ± 0.009
2	9.45	18.89	80	10	0.40 ± 0.01	0.113 ± 0.004
3	5.75	11.50	82	10	0.41 ± 0.01	0.116 ± 0.006
4	9.23	14.50	82	10	0.41 ± 0.02	0.134 ± 0.005
5	11.70	14.14	85	10	0.41 ± 0.01	0.125 ± 0.003
6	8.69	13.75	92	10	0.41 ± 0.01	0.130 ± 0.005
7	12.30	12.30	96	10	0.37 ± 0.01	0.137 ± 0.006
8	15.60	15.60	97	10	0.42 ± 0.02	0.123 ± 0.007
9	10.77	10.77	91	10	0.41 ± 0.02	0.121 ± 0.008
10	11.29	22.58	84	0	0.24 ± 0.01	0.105 ± 0.003
11	15.12	30.25	82	0	0.24 ± 0.01	0.124 ± 0.005
12	12.98	25.96	81	0	0.25 ± 0.02	0.116 ± 0.003
13	17.37	24.84	88	0	0.24 ± 0.01	0.103 ± 0.003
14	16.78	26.75	93	0	0.23 ± 0.01	0.103 ± 0.006
15	15.58	27.50	88	0	0.23 ± 0.01	0.112 ± 0.003
16	19.01	19.01	91	0	0.24 ± 0.01	0.104 ± 0.006
17	17.37	17.37	98	0	0.23 ± 0.01	0.128 ± 0.009
18	14.85	14.85	97	0	0.26 ± 0.01	0.102 ± 0.005
19	21.21	42.42	75	−10	0.140 ± 0.009	0.099 ± 0.007
20	16.96	33.92	80	−10	0.166 ± 0.009	0.087 ± 0.006
21	17.37	34.74	81	−10	0.140 ± 0.009	0.096 ± 0.005
22	15.38	23.75	87	−10	0.152 ± 0.009	0.093 ± 0.004
23	18.46	25.00	87	−10	0.150 ± 0.009	0.079 ± 0.006
24	21.53	32.35	93	−10	0.150 ± 0.009	0.088 ± 0.006
25	16.79	16.79	95	−10	0.140 ± 0.008	0.086 ± 0.004
26	21.28	21.28	88	−10	0.160 ± 0.009	0.089 ± 0.006
27	12.16	12.16	93	−10	0.143 ± 0.008	0.089 ± 0.007

TABLE 3

Summary of average results calculated from data in Table 2

Isomer	k_2/dm^3 mol^{-1} s^{-1}			$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
	−10 °C	0 °C	10 °C		
trans	0.148 ± 0.008	0.240 ± 0.011	0.400 ± 0.010	28.5 ± 1.3	−159 ± 8
cis	0.090 ± 0.002	0.110 ± 0.006	0.129 ± 0.008	8.8 ± 0.5	−239 ± 8
cis + *trans*			0.529 ± 0.010	22.2 ± 1.3	−180 ± 8
Overall [13]			0.508 ± 0.018	21.4 ± 2.5	−159 ± 8

Table 3 is a summary of average values of the rate constants found, and of the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ calculated. For comparison with data obtained for overall rates of disubstitution as measured by a titrimetric method in an earlier study [13] (line 4), this table



SCHEME Mechanism proposed for the reaction: $N_3P_3Cl_5(NR_2) + 2NR_2H \longrightarrow$ *cis*- and *trans*-$N_3P_3Cl_4(NR_2)_2 + [NR_2H_2]Cl$. Partial charges in structures are omitted and the N of the attacking NR_2H is primed for clarity. The route (IIIa) $\longrightarrow$ (Va) accounts for part of the (Va) formed (see text). r.d. = Rate determining

originally proposed, we have modified it to give a better fit to the known facts and data. First, in the original s.s.e., variation of the alkyl groups on the solvating substituents requires changes in the *cis* : *trans* ratio, but all the data available [1] show that this ratio is independent of the alkyl groups. Secondly, no precedent for the s.s.e. was revealed in a wide search of the literature and even Bunnet and Morath's [18] closely related ' built-in solvation ' effect differs from the s.s.e. because the partial charge on the solvating group, an essential component of their argument, is absent in our case. Partially similar prior mechanistic proposals do exist, however, for all steps of the modified version of the s.s.e.

The Scheme presents the proposed sequence of reactions that produce the *cis* and *trans* isomers. In all ' a ' structures attack by $N'Me_2$ (primed for differentiation) is from the side of the phosphazene ring opposite the NMe_2 substituent, whilst in all ' b ' structures the attack is from the other side of the ring. Assuming that displacement proceeds exclusively with inversion,[1,19] ' a ' and ' b ' structures eventually lead to *trans* and *cis* products respectively.

After the common initial fast pre-equilibria which produce (IIa) and (IIb), the following steps of the reactions are their deprotonation giving (IIIa) and (IIIb) respectively. The separation of the deprotonation step from the subsequent dechloridation is a change from our earlier proposal [13] in which these steps were considered concerted because of the observed second-order dependence on amine concentration as found in similar reactions performed in toluene.[20] However, the absence of isotope effects observed in rate studies in toluene employing deuteriated amines [21] leads us to believe that deprotonation and rate-determining chloride-ion departure are separate steps. This interpretation parallels one that is nowadays widely accepted in aromatic nucleophilic substitution, mechanistically a similar reaction.[20,22]

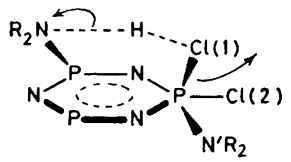
Two pathways for decomposition of the intermediates (IIIa) and (IIIb), the following steps of the reactions, are shown. It is suggested that one of these, a direct dechloridation, produces all the *cis* isomer and presumably part of the *trans* isomer too. The other pathway proceeds *via* reprotonation on the substituent amino-group, followed by rate-determining dehydrochlorination and this leads exclusively to the *trans* isomer. We must compare these two competitive rate-limiting steps which are decisive in determining the *cis* : *trans* isomer ratio.

As direct dechloridation of (IIIb) [and of (IIIa)] by expulsion of Cl^- from this anionic species does not involve any net separation of charge, its transition state can be expected to be associated with relatively low enthalpy. However, the need to solvate the incipient Cl^- being formed in the transition state causes chloride-ion departure to be rate determining, tends to reduce the entropy of the system, and makes $\Delta S^{\ddagger}$ predominant.[13] Since *cis*-isomer formation is thought to proceed virtually entirely by direct chloride elimination from (IIIb) giving (Vb), this description accounts for the relatively low values of $\Delta H^{\ddagger}_{cis}$ and $\Delta S^{\ddagger}_{cis}$ found. However, there will be little difference between reactions (IIIa) ⟶ (Va) and (IIIb) ⟶ (Vb), so that roughly equal quantities of the *cis* and *trans* isomers will be formed by these routes.

In the indirect decomposition of (IIIa) [and of (IIIb)] that proceeds *via* reprotonation on the NMe_2 substituent group two apparently reasonable assumptions are implicit in the equilibrium (IIIa) ⇌ (IVa) [and (IIIb) ⇌ (IVb)] postulated as the next step in this mechanism. The first is that the equilibrium is faster than the following steps, and the second is that the equilibrium constant is large enough to ensure that in the steady state the concentration of (IVa) [and of (IVb)] present is sufficient for the ensuing reactions.

The final and rate-limiting step, (IVa) ⟶ (Va), is a concerted dehydrochlorination of (IVa) producing an incipient HCl ion pair in the transition state. The *cis*-pseudo-2,4-diaxial proximity of the departing Cl^- and the protonated amino-substituent allows the formation of the six-membered transition-state ring structure, (VI), with the proton acting as the closing link. The *trans* configuration of the relevant groups in the hypothetical parallel reaction (IVb) ⟶ (Vb) precludes the formation of a similar ring structure and consequently this route to the *cis* isomer is blocked as a viable reaction pathway. The indirect catalyzed reaction can thus only lead to the *trans*-isomeric product.

Next we consider the activation parameters for this route. The formation of (IIa) [and of (IIb)] from (I) is the principal step governing the magnitude of $\Delta H^{\ddagger}$ in these reactions.[13,19] An additional factor that is probably the main cause of $\Delta H^{\ddagger}_{trans}$ exceeding $\Delta H^{\ddagger}_{cis}$ is a specific contribution to the enthalpy of activation of this route that arises in transition state (VI) from some



(VI)

puckering of the phosphazene ring to reduce the distance between the protonated exocyclic nitrogen atom and the leaving group.[1]

Considering now the entropy of activation of this route, and employing the same approach developed earlier,[13] the foremost factor that decreases the entropy of the system is the need for the departing chloride ions to undergo solvation in the transition state. Because in (VI) an ion pair of low net charge is being formed in the transition state, this decrease in entropy will be smaller than when a bare Cl^- is being formed as in the pathway that leads to the *cis* isomer. This dominant and decisive factor is at the root of *trans* preference, since it leads to higher (less negative) values of $\Delta S^{\ddagger}$ for the *trans* than for the *cis* reaction.

In summary, this mechanistic analysis accounts for the relative values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both the *cis* and the *trans* reactions and rationalizes *trans* preference sterically.

The simple second-order rate laws observed are consistent with the full rate equations derived for both reaction pathways described above on two conditions. The first is that the solvent, thf, is acting as the base for the deprotonation step (II) ⟶ (III), as has been postulated previously.[13] The second is that the concentration of dimethylamine hydrochloride, the acid for the protonation step (III) ⟶ (IV), rapidly reaches a constant value because its low solubility in thf leads to saturation after only a few moments of reaction.

Independent evidence for the involvement of the postulated critical hydrogen-bonded transition-state structure comes from a recent observation [23] that the *trans* : *cis* ratio of the disubstituted products formed in the reaction of piperidine with hexachlorocyclotriphosphazene in thf is higher than that found using *N*-deuteriated piperidine, although there is no isotope effect in the reactions that give pentachloropiperidinocyclotriphosphazene.[21]

The revised version of the s.s.e. as a new modification of acid-catalyzed neighbouring-group mechanisms is essentially a novel combination of steps, all of which have individually been described and discussed previously as parts of related mechanisms.[18,24-27] However, none of these mechanisms is identical with the s.s.e. if only because none involves the preprotonation equilibrium step as envisaged here.

Finally it should be noted that unless there is incursion by specific extraneous factors, the proposed mechanism predicts *trans* preference to be independent of the identity of the amine, as was indeed found to be the case. This independence expresses itself in two ways. First, *trans* preference has been found in all aminations that proceed non-geminally [28] and secondly the *cis* : *trans* isomer ratio in them was virtually unaffected by the alkyl groups.[1] Only aminations in acetonitrile are anomalous and with most, but not all, amines, *cis* : *trans* isomeric ratios close to equilibrium ratios were observed.[17,29,30] This is an example of the many subtle and little understood solvent effects that have been emphasized by Shaw.[3] In the absence of kinetic data on the *cis* and *trans* reactions in acetonitrile, there is little to be gained by speculating on the origins of the exceptional behaviour in it.

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