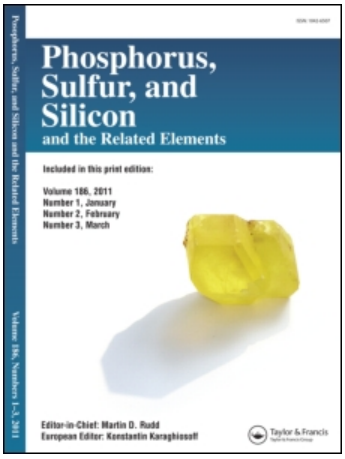

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Graziano Baccolini[a]; Paolo E. Todesco[a]; Giuseppe Bartoli[a]
[a] Istututo di Chimica Organica Universitá, Bologna, Italy

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THE STAUDINGER REACTION BETWEEN 2-H-1,2,3-DIAZAPHOSPHOLENES AND AROMATIC AZIDES

GRAZIANO BACCOLINI, PAOLO E. TODESCO and GIUSEPPE BARTOLI

Istututo di Chimica Organica, Universitá, Risorgimento, 4, 40136 Bologna, Italy

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The title reaction between substituted phenyl azides **2** and diastereomeric diazaphospholenes **1** gives the corresponding cyclic phosphazenes **3** with different stereochemical results. Hydrolysis of some phosphazenes **3** yield the corresponding ring-opened compounds **Z–4l** together with small amounts of diazaphospholene-oxide **5** and anilines **6**. The configuration of the compounds obtained are established by ^{1}H n.m.r. spectroscopy. The results are explained invoking the formation of pentacoordinate phosphorus intermediates.

Most covalent azides react with phosphines to give nitrogen and phosphazenes (Staudinger reaction).[1] In the past few years intensive investigations of this reaction with different tricoordinate phosphorus compounds led to many interesting developments.[2]

We wish to report the different stereochemical products which have been obtained from the reaction between the diastereomeric diazaphospholenes **1** and several aromatic azides **2**. (See Figure).

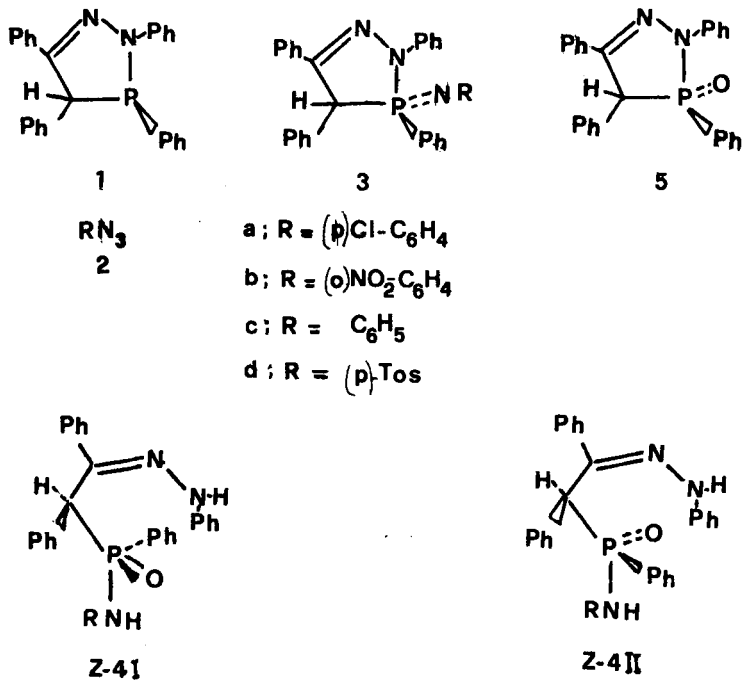
Thus, when equimolar amount of *cis*[3]-**1** and tosylazide (**2d**) were allowed to react in dry benzene at room temperature for about one hour, the corresponding phosphazene *cis*[3]-**3d** was stereospecifically formed in 90% yield. Under the same conditions the isomer *trans*-**1** reacts with **2d** yielding stereospecifically the corresponding phosphazene *trans*-**3d**. The two phosphazenes **3d** are very stable compounds and can be conveniently isolated in pure form by chromatography on silica gel and were identified on the basis of elemental analysis, i.r. and ^{1}H n.m.r. spectra.

The course of this reaction can be followed by t.l.c. or monitored by ^{1}H n.m.r. spectroscopy when the reaction is carried out in C_6D_6 solution: a gradual disappearance of the methine proton doublet of **1** is observed and replaced by the characteristic doublet of the corresponding phosphazene **3d**. We have also observed that the phosphazenes **3a**, **b** or **c** arising from the reaction between *cis* or *tans*-**1** and the corresponding azides **2a**, **b** and **c** are not stable and are easily hydrolized during the work-up. However, if these reactions are carried out in C_6D_6 and followed by the ^{1}H n.m.r. technique described above, it is possible to observe the formation of the corresponding azides. In particular, when *cis*-**1** was allowed to react with the azide **2a** in a sealed n.m.r. tube at room temperature the stereospecific formation of the phosphazene *cis*-**3a** was observed, as revealed by the appearance of its characteristic methine doublet.

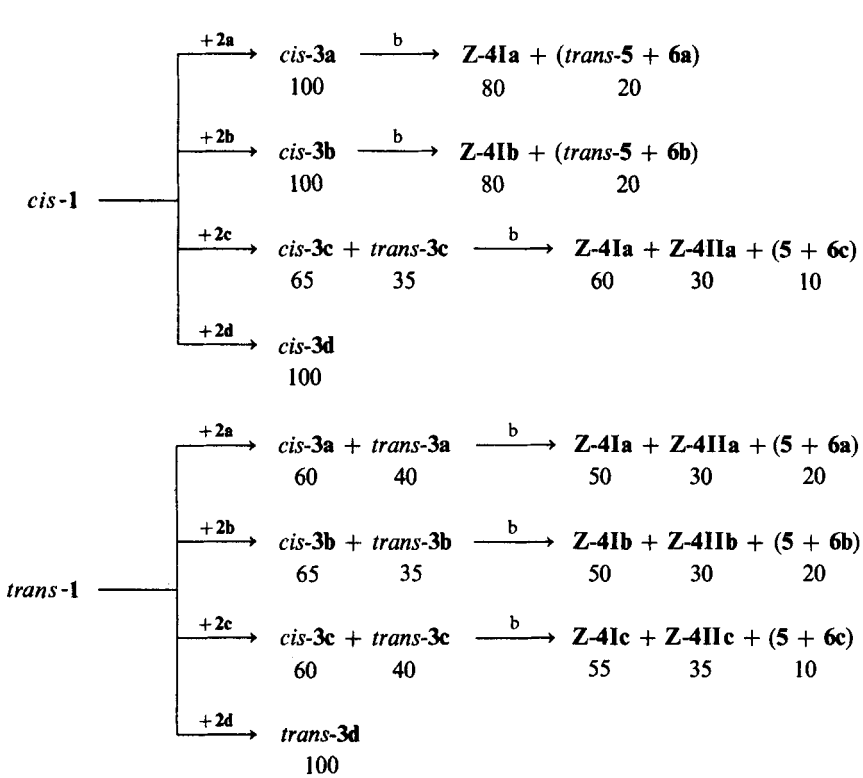
Under the same conditions *cis*-**1** and **2b** gave after one hour the phosphazene *cis*-**3b**. In contrast, when *trans*-**1** was allowed to react under the same conditions with the azides **2a** or **2b**, a mixture of the corresponding *cis* and *trans* **3a** or **3b** in the ratio of about 60:40 was observed as determined by ^{1}H n.m.r. analysis. On the other hand, when the azide **2c** was used with either the *cis*-**1** or the *trans*-**1** isomer a mixture of phosphazenes *cis*-**3c** and *trans*-**3c** in the ratio of about 60:40 was always detected. The reactions with the azides **2a**, **b** and **c** goes to completion after about two hours. The different stereochemical results obtained in these reactions are summarized in Scheme I.

The attempts to isolate the phosphazene *cis*-**3a**, obtained in the reaction between *cis*-**1** and **2a**, yielded a new product, the β-phenylhydrazonophosphonic amide Z-**4la** (65%). Small amounts (15%) of the diazaphospholene-oxide *trans*-**5** and of the anilino derivate **6a** (15%) were also obtained.

From the reaction between *trans*-**1** and **2a** or **2b**, a mixture of the corresponding distereomeric



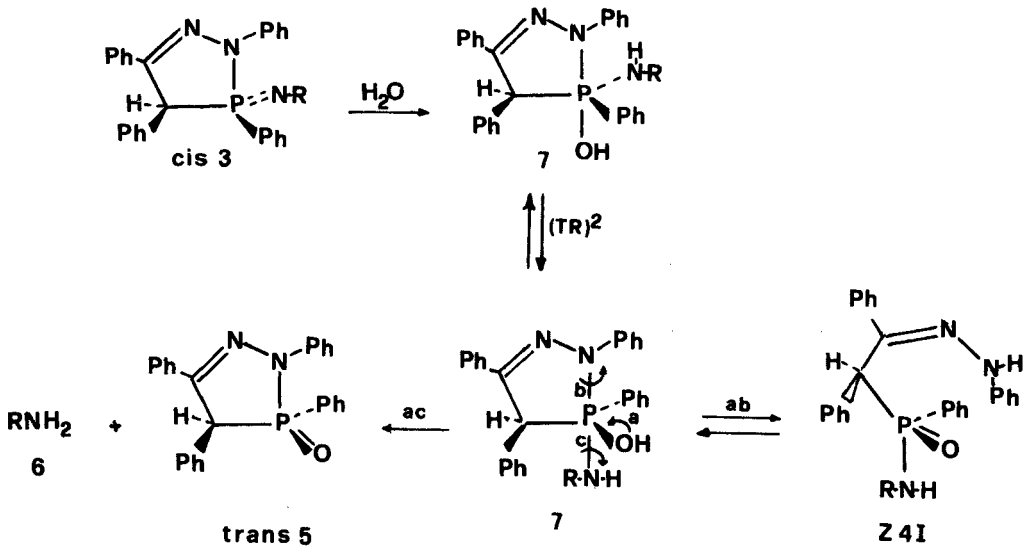
FIGURE



SCHEME I[a]

[a] The numbers found below the compounds represent their ratios (±5%) determined as stated in the text. The ratios are the average of separate runs.

[b] After work-up or hydrolysis.



SCHEME II

ring-opened compounds **Z-4I** and **Z-4II** in the ratio of about 60:40 was obtained together with small amounts of *cis* and *trans*-**5** and the corresponding anilino derivatives **6**. From reaction of both isomers *cis*-**1** and *trans*-**1** with azide **2c** on the other hand, a mixture of the ring-opened compounds **Z-4Ic** and **Z-4IIc** was isolated in the ratio of about 60 :40.

From the above results it is clear that there is intervention by water at some stage of reaction. When the reaction between **2a** and *cis*-**1** was monitored by ^{1}H n.m.r. spectroscopy (as previously described) on completion of the formation of *cis*-**3a** traces of water were deliberately added to the reaction solution and the characteristic methine proton doublet and NH signals of **Z-4Ia** were detected. Similar results were observed with other azides **2b** and **2c**.

ASSIGNMENT OF CONFIGURATION

The *cis* and *trans* stereochemistry of **1** has previously[4] been assigned by means of ^{1}H n.m.r. spectroscopy, the relative configuration of the two chiral center in phosphazene **3** is tentatively assigned on the same basis. The *trans* configuration is assigned to the isomer showing an upfield methine signal since only in this isomer is the aromatic ring capable of shielding the methine proton; this isomer has a much smaller value for J_{PCH} than the *cis* isomer (see Table I).

TABLE I

^{1}H n.m.r. data[a] of compounds **3**

Compd.	δ CH_3	$\delta_{PCH}(J_{PCH})$	δ Arom.
cis-**3a**[b]	—	4.85 (d, 18)	5.95–7.60
trans-**3a**[b]	—	4.25 (d, 11)	5.95–7.60
cis-**3b**[b]	—	5.20 (d, 20)	6.20–8.00
trans-**3b**[b]	—	4.40 (d, 11)	5.80–7.65
cis-**3c**[b]	—	5.28 (d, 21)	6.60–8.15
trans-**3c**[b]	—	4.55 (d, 12)	6.60–8.15
cis-**3d**[c]	2.19	6.17 (d, 21)	6.70–7.80
trans-**3d**[c]	3.32	4.60 (d, 12)	6.60–8.05

[a] Chemical shifts are in ppm from Me_4Si and J in Hz.

[b] The products are not isolable; the data are obtained from reaction mixture in C_6D_6.

[c] In $CDCl_3$.

The ^{1}H n.m.r. data were also useful in determining the ratio of diastereomers **Z-4I** and **Z-4II** in the reaction mixtures. Each of the two diastereomers **Z-4** was isolated in pure form by chromatography on silica gel and the configurational assignment about the C=N bond of the ring-opened products **4** was made essentially on the basis of their ^{1}H n.m.r. spectra (see Table II). The NH proton of the hydrazo group of the ring-opened products **4** gives a broad singlet; it is intramolecularly bonded as indicated by its low resonance and this suggest the Z-configuration about the C=N bond.

We have reported[5] analogous assignments for related ring-opened compounds.

TABLE II

^{1}H n.m.r. data[a] ($CDCl_3$) of compounds Z–4

Compd.	$\delta_{PCH}(J_{PCH})$	$\delta_{PNH}(J_{PNH})$	δ_{NH}	δ Arom.
Z-4Ia	4.75 (d, 18)	5.2 (d, 10)	11.40	6.60–7.95
Z-4IIa	4.76 (d, 17.5)	5.1 (d, 10)	11.70	6.30–7.50
Z-4Ib	5.07 (d, 19)	9.3 (d, 12)	11.05	6.75–8.20
Z-4IIb	5.05 (d, 19)	9.2 (d, 13)	11.20	6.50–8.00
Z-4Ic	4.95 (d, 18)	5.5 (d, 10)	10.80	6.70–7.80
Z-4IIc	4.93 (d, 17.5)	5.2 (d, 10)	11.25	6.40–7.80

[a] Chemical shifts are in ppm from Me_4Si and J in Hz.

The relative configuration of the two chiral centers in **4I** and **4II** is tentatively assumed only on the basis of the proposed mechanism (see Scheme II).

DISCUSSION

The mechanism we propose for the stereospecific hydrolysis of phosphazenes **3** involves the formation of metastable bypiramidal phosphoranes which presumably are sufficiently long-lived to allow stereomutation or positional interchange at pentacoordinated phosphorus by a turnstyle rotation process (TR)[6] or a equivalent Berry pseudorotation (BPR).[7] The transformation of the tetracoordinate phosphazene *cis*-**3** into the pentacoordinate species such as **7** results from an apical attack of water at the tetrahedral phosphorus atom.

Because of steric strain and since the more electronegative atoms tend to prefer the apical positions[6,9] we propose that the favoured attack of water is at the face opposite the P—N bond of *cis*-**3** with formation of **7** which leads to **7I** after a $(TR)^2$ process. The formation of **7I** may be favoured by its stabilization due to ligand subset symmetry,[8] i.e. two identical ligand in the apical subset. Apical cleavage of the endocyclic P—N bond gives, *via ab*, the corresponding ring-opened compound **Z-4I**, while apical cleavage of P—N bond of the anilino group gives *via ac* the diazaphospholene-oxide *trans*-**5** and the corresponding anilino derivatives **6**. Thus the observed preferred formation of the ring-opened compound **Z-4I** rather than that of the compounds **6** and *trans*-**5** can be rationalized on the basis of the different leaving abilities (and hence apicophilicities in the pentacoordinate intermediate) of the R—NH groups compared to the diaza group.

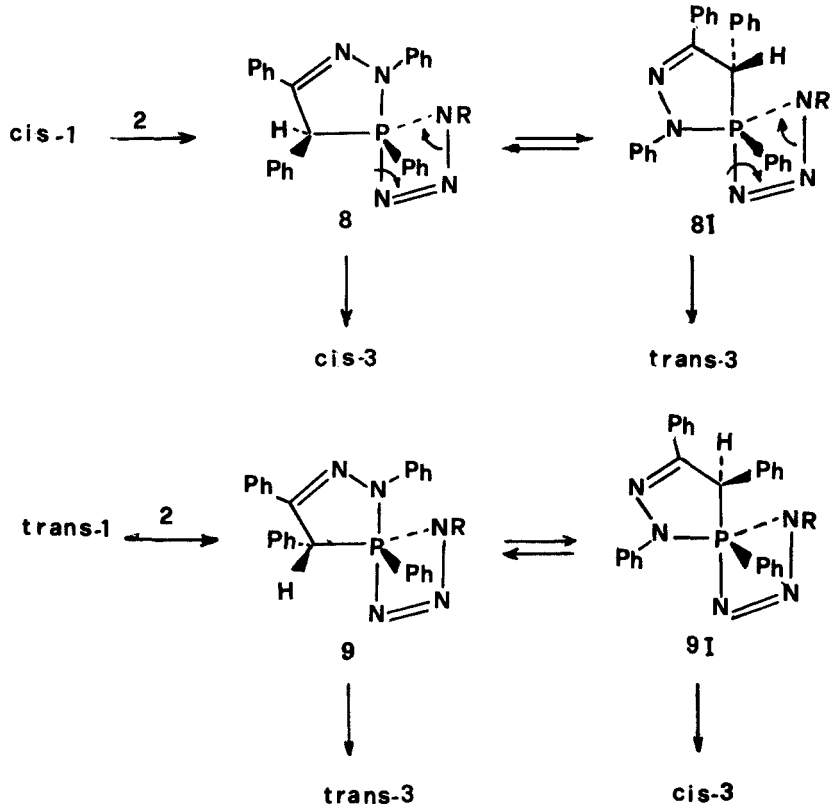
The diaza group is expected to be more apicophilic and a better leaving group than the anilino group and then the route *ab* is favoured over the route *ac*. As a result, the ring-opened compounds **Z-4I** predominates over the corresponding compounds *trans*-**5** and **6**, a mixture of **Z-4I** and **5** or **6** in the ratio of about ca. 80:20 being obtained. This ratio undergoes small variation when different azides are used; probably the different substituents R in the anilino groups play a small role in the relative leaving abilities.

The proposed cyclic phosphorane intermediates such as **7I** are also consistent with the exclusive formation of ring-opened compounds **4I** with the Z-configuration about the C=N bond as well as the exclusive formation of cyclic phosphine-oxide **5** with the *trans*-configuration in the case of hydrolysis of *cis*-3.

On the other hand, preliminary results showed that when the ring-opened product **Z-4Ia** was left in a benzene solution at room temperature, a slow recyclization with formation of the cyclic compound *trans*-**5** and the corresponding aniline derivative **6a** was observed. After three days a mixture of *trans*-**5** and **Z-4Ia** in the ratio of about 20:70 was evident from n.m.r. spectral features. These data are consistent with the proposed mechanism which involves in the recyclization of **Z-4** the same hypothetical intermediate **7I** which is involved in the hydrolysis reaction. We have previously observed[9] an analogous trend in the methanolysis of diazaoxyphospholenes **5**.

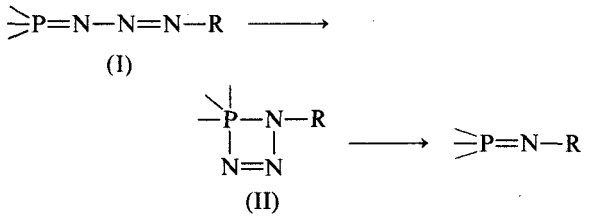
It should be noted, moreover, that phosphazene **3d** does not undergo hydrolysis even when it is left for several hours in neutral, acidic or basic aqueous solution; this stability may be due to the interaction of the SO_2-group with the P=N group.

It remains to consider the different stereochemical results obtained in the reaction of formation of **3**. Some points should be noted: (i) the amounts of *cis*-**3** and or *trans*-**3** are always constant during the course of the reaction and in all cases the isomers **3** are not interconvertible even after longer reaction times; (ii) the isomerization of phosphines **1** is not observed in the reaction condition; (iii) *cis*-**1** and *trans*-**1** give different results attesting that *cis*-**3** and *trans*-**3** compounds do not result from a common intermediate. For these reasons we think that our observations can be rationalised by postulating of intermediates which may be in some cases sufficiently long-lived to undergo isomerization before the elimination of nitrogen.



SCHEME III

It is generally accepted that in the Staudinger reaction an intermediate adduct of the type (I) plays an important role.[2e] However, some studies do not exclude a further possible formation of a cyclic phosphorane of the type (II) as intermediate or transition state.



(I)

(II)

In our particular type of Staudinger reactions the cyclic intermediates (type II) may be the phosphoranes such as **8** and **9** and if their life-time is sufficient to allow pseudorotation, **8** and **9** may isomerize to **8I** and **9I** respectively, thus decomposition of **8** (or **9**) gives *cis*-**3** (or *trans*-**3**) while **8I** (or **9I**) gives *trans*-**3** (or *cis*-3) (see Scheme III). In our cases the phosphorane intermediates may gain in stability because the pentacoordinate phosphorus atom is incorporated into two heterocyclic rings, thus reducing crowding. In addition, the forms **8** and **9** are further stabilized by ligand subset symmetry.[8]

Since we have previously shown that steric interactions influence the stability of such phosphoranes,[9] it is reasonable to suppose that the form **9** should be more stable than **8** which has less steric interference between the P-phenyl and C_4-phenyl groups. Moreover, our findings indicate that the nature of R-group must also influence the course of phosphazene formation, and then it is probable that when R is *p*-Tos the intermediates **8** and **9** are not sufficiently long-lived to permit their isomerization thus giving stereospecifical formation of **3d**; when R is *p*-Cl—C_6H_4 or *o*-$NO_2C_6H_4$, only the intermediate **9** is sufficiently long-lived to give isomerization and finally when R is phenyl both the intermediates **8** and **9** are sufficiently long-lived to permit their isomerization and then formation of both isomer of **3c**.

These explanations of our results are not meant to be definitive but it best serves as a possible directive for future studies; other mechanism could not be ruled out.

EXPERIMENTAL

^{1}H n.m.r. spectra were obtained at 60 MHz for solutions in C_6D_6 or $CDCl_3$. I.r. spectra were carried out in $CHCl_2$ solutions. The microanalyses were performed on pure isomers as well as on mixture of isomers, the results obtained were practically identical. Melting points are uncorrected. The azyl azides were prepared by published procedure[10] and their purities were checked by t.l.c. and ^{1}H n.m.r. examination.

The ^{1}H n.m.r. data of compounds **3** and **4** are summarized in Tables I and II respectively.

Reaction of cis-1 with 2d[10d]

A solution of 0.392 g (1×10^{-3} mol) of *cis*-**1** in 50 ml of benzene was added to a solution of 2d (0.197 g, 1×10^{-3} mol) in 20 ml of benzene at room temperature. The reaction may be followed by observing the evolution of nitrogen or by t.l.c.

The reaction was rapid and gas evolution ceased after 1 hr. The solvent was then removed under vacuum leaving the crude product *cis*-**3d**. Chromatography on a silica gel column (7:3 benzene/ether as eluent) afforded *cis*-**3d** (0.294 g, 75% yield. Rf 0.45) which was crystallized from *n*-pentane and had m.p. 68–70°C, ν_{max} (KBr) 1270 (P=N—SO_2) cm^{-1}.

Anal. Calcd. for $C_{33}H_{28}N_3O_2SP$: C, 70.58; H, 4.99; N. 7.48. Found: C, 71.03; H. 4.75; N, 7.29.

Reaction of trans-1 with 2d

In a similar way the addition of *trans*-**1** in benzene (0.392 g, 1×10^{-3} mol) to a solution of **2d** (0.197 g, 1×10^{-3} mol) in benzene gave after 1 hr *trans*-**2d** (Rf 0.35 with the same eluent) in 72% yield. The pure product, crystallized from *n*-hexane had m.p. 128–130°C; ν_{max} (KBr) 1262 (P=N—SO_2) cm^{-1}.

Anal. Calcd. for $C_{33}H_{28}N_3O_2SP$: C, 70.58; H, 4.49; N, 7.48. Found: C, 70.79; H, 4.78; N. 7.35.

These reactions were also repeated in C_6D_6 and examined periodically by ^{1}H n.m.r. spectroscopy.

Reaction of cis-1 with 2a[10c]

A solution of *cis*-1 (0.392 g, 1×10^{-3} mol) in benzene (50 ml) was added to a solution of 2a (0.153 g, 1×10^{-3} mol) in benzene, the mixture was set aside at room temperature and the reaction may be followed by observing the evolution of nitrogen. After 2 hrs, when the nitrogen evolution ceased, the solvent was removed and the resulting mixture was separated by chromatography on silica gel column (benzene-ether 8:2 as eluent): compound Z-**4Ia** (80% yield) and small amount of *trans*-**5** and **6a** (20% yield) were isolated. The compound Z-**4Ia** (Rf. 0.4) crystallized from *n*-hexane, had m.p. 173–175°C; ν_{max} ($CHCl_3$) 3370 (NH) and 3230 (NH) cm^{-1}. When the reaction was carried out in C_6D_6 and examined periodically by 1H n.m.r., the doublet due to the starting phosphine *cis*-**1** (4.82, J 21 Hz) was replaced by a new doublet at δ 4.85 (J 18 Hz) due to the phosphazene *cis*-**3a**.

No absorptions due to NH groups were observed. When traces of water were deliberately added to the reactions solution the doublet and the signals for the corresponding NH protons of Z-**4Ia** immediately appeared with the concomitant disappearance of the doublet of *cis*-3**a**.

Reaction of trans-1 with 2a

As in the above reaction, the addition of *trans*-**1** (0.392 g, 1×10^{-3} mol) in benzene (50 ml) to a solution of **2a** (0.153 g, 1×10^{-3} mol) in benzene, gave after about 2 hrs at room temperature the ring-opened isomers Z-**4Ia** and *Z*-**4Ia** in the ratio of about 5:3 with small amounts (<20%) of *cis*-**5**, *trans*-**5** and the anilino derivative **6a**.

The products Z-**4Ia** (Rf. 0.4) and Z-**4IIa** (Rf. 0.5) were separated by column chromatography using as eluent benzene-ether 8:2. The isomer Z-**4IIa**, crystallized from *n*-hexane, had m.p. 155–157°C; ν_{max} ($CHCl_3$) at 3360 (NH) and 3220 (NH) cm^{-1}. This reaction was also carried out in C_6D_6 and the course of the reaction followed by ^{1}H n.m.r.: the doublet due to the starting phosphine *trans*-1 (δ 4.51; J 2Hz) was quickly replaced by the two new doublets at δ 4.85 (J 18) and δ 4.25 (J 11) due respectively to *cis*-**3a** and *trans*-**5** in the ratio of about 60:40 (estimated by relative integration in the methine protons). This ratio was always constant during the course of the reaction. When traces of water were added to this reaction solution the doublets and the signals of NH protons of the corresponding Z-**4Ia** and Z-**5IIa** ring-opened compounds immediately appeared as in above reaction.

Anal. Calcd, for $C_{32}H_{27}N_3OPCl$: C, 71.70; H, 5.04; N, 7.84. Found: C, 72.01; H, 5.11; N, 7.79.

Reaction of cis-1 with 2b[10b]

In a similar fashion the addition of *cis*-**1** (0.392 g, 1×10^{-3} mol) in benzene solution (50 ml) to a solution of **2b** (0.164 g, 1×10^{-3} mol) in benzene (20 ml), gave after about **2** hrs at room temperature the product Z-**4Ib** in 80% yield. The compound Z-**4Ib**, crystallized from *n*-hexane-ether, had m.p. 163–165°C, ν_{max} ($CHCl_3$) at 3280 (NH) and 3190 (NH) cm^{-1}.

When the reaction was carried out in C_6D_6 and followed by ^{1}H n.m.r. it was observed the rapid disappearance of the doublet of *cis*-**1** with the concomitant appearance of the doublet dus to *cis*-**3b**. When traces of water were added to this solution the typical signals of Z-**4Ib** were immediately observed.

Reaction of trans-1 with 2b

In a similar manner the reaction between *trans*-**1** and **2b** gave, after about 2 hrs, at room temperature, the isomers Z-**4Ib** and Z-**4Ib** in the ratio of about 5:3 and small amounts (<20%) of *cis*-**5**, *trans*-**5** and **6b**. Separation of the isomers Z-**4Ib** and Z-**4IIb** was accomplished by chromatography on a silica gel column by elution with 8:2 benzene-ether mixture. Pure Z-**4Ib** (Rf 0.6) had m.p. 163–165°C, and pure Z-**4IIb** (Rf 0.50) had m.p. 138–140°C, ν_{max} ($CHCl_3$) at 3250 (NH) and 3200 (NH) cm^{-1}.

This reaction was repeated in C_6D_6 and, as above, it was noted the rapid appearance of the two doublets due to *cis*-**3b** and *trans*-**3b** in a ratio of about 60:40. When traces of water were added to this reaction mixture the typical signals of Z-**4Ib** and Z-**4IIb** (ratio 5:3) were observed.

Anal. Calcd. for $C_{32}H_{27}N_4O_3P$: C, 70.32; H, 4.94; N, 10.25. Found: C, 70.52; H, 5.02; N, 10.31.

Reaction of cis-1 with 2c[10a]

In a similar manner the addition of *cis*-**1** (0.392 g, 1×10^{-3} mol) in benzene solution (50 ml) to a solution of **2c** (0.119 g, 1×10^{-3} mol) in benzene (20 ml), gave after about 3 hrs at room temperature the isomers **Z-4Ic** and **Z-4IIc** in the ratio of about 6:3 and small amounts (<10%) of **5** and **6c**. The products **Z-4Ic** (Rf 0.5) and **Z-4IIc** (Rf 0.6) were separated by column chromatography using as eluent benzene-ether 8:2. Pure **Z-4Ic**, crystallized from *n*-pentane, had m.p. 170–172°C, ν_{max} ($CHCl_3$) at 3375 (NH) and 3190 (NH) cm^{-1}; pure **Z-4IIc** had m.p. 158–161°C, ν_{max} ($CHCl_3$) 3370 (NH), 3230 (NH) cm^{-1}.

When this reaction was repeated in C_6D_6 and followed by ^1H n.m.r. the disappearance of the doublet of *cis*-**1** was observed with the concomitant appearance of the two doublets due to *cis*-**3c** and *trans*-**3c** in a ratio of about 65:35. When traces of water were added to this reaction mixture the typical signals of **Z-4Ic** and **Z-4IIc** were observed.

Reaction of trans-1 with 2c

The addition of *trans*-**1** in benzene solution to a solution of **2c** gave after about 3 hrs at room temperature the ring-opened products **Z-4Ic** and **Z-4IIc** in the ratio of about 55:35 and small amounts of **5** and **6c**. These products were separated and characterized as above.

This reaction was repeated in C_6D_6 and as above it was observed the formation of *cis*-**3c** and *trans*-**3c** in a ratio of about 60:40.

Anal. Calcd. for $C_{32}H_{28}N_3OP$: C, 76.64; H, 5.58; N, 8.38. Found: C, 76.95; H, 5.22; N, 8.15.

Preliminary results showed that the ring-opened product **Z-4Ia** left in a benzene solution at room temperature gave small amounts of *trans*-**5** and the aniline derivative **6a**. After 3 days a mixture of *trans*-**5** and **Z-4Ia** in the ratio of about 20:70 was observed by ^1H n.m.r. analysis.

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