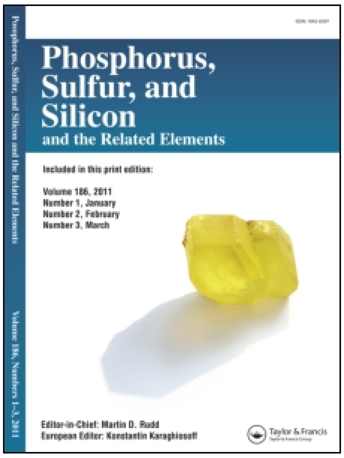

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NEW 2H-1,2,3-DIAZAPHOSPHOLE DERIVATIVES AND RELATED RING-OPENED COMPOUNDS

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To cite this Article Baccolini, Graziano , Todesco, Paolo E. and Bartoli, Giuseppe(1980) 'NEW 2H-1,2,3-DIAZAPHOSPHOLE DERIVATIVES AND RELATED RING-OPENED COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 9: 2, 203 — 207

To link to this Article: DOI: 10.1080/03086648008078241

URL: http://dx.doi.org/10.1080/03086648008078241

Phosphorus and Sulfur, 1980, Vol. 9, pp. 203–208
0308-664X/80/0902-0203$06.50/0

NEW 2H-1,2,3-DIAZAPHOSPHOLE DERIVATIVES AND RELATED RING-OPENED COMPOUNDS

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(*Received January 15, 1980*)

The addition of phosphites to the azoalkene **1** gives mixtures of diazaphosphole derivatives **4** and related ring-opened compounds **3** in different proportions depending on the phosphite used.

The compounds **3** have the Z-configuration, while cyclic compounds **4** are a mixture of isomers in which predominates the isomer bearing the C_4-Ph and OR groups in a trans configuration. When $P(OPh)_3$ is used in dry hexane with rigorous exclusion of moisture the new diazaphosphole derivative **5** is obtained. The results are explained in terms of the relative apicophilicities in the pentacoordinated intermediates.

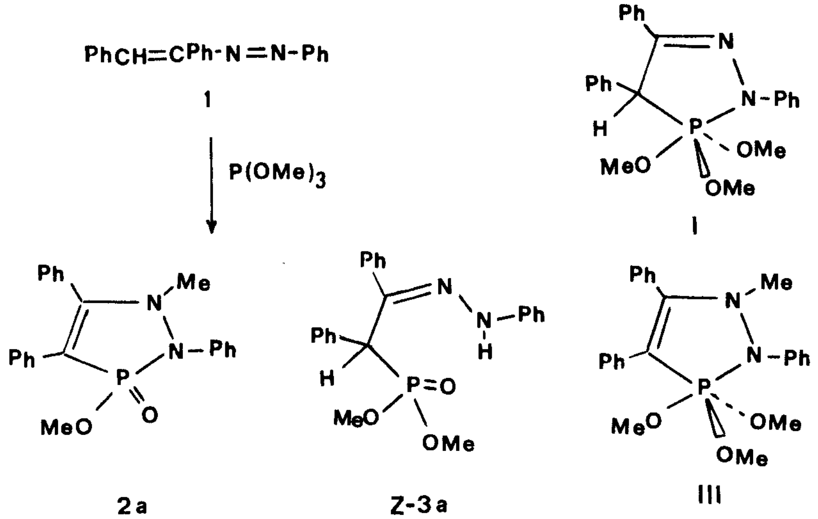
Intensive investigations on diazaphosphole derivatives by numerous research groups have led to many interesting and far-reaching developments, especially in the past few years.[1]

Continuing our studies on phosphorus heterocycles containing the P—N—N linkages we have found that the addition of $P(OR)_3$ (R=Me, Et, Ph) to azoalkene **1** gives new 2H-1,2,3-diazaphosphole derivatives and related ring-opened compounds depending on the nature of phosphite and the experimental conditions.

In a previous work[2] we reported that treatment of azoalkene **1** with $P(OMe)_3$ afforded the unexpected N—Me compounds **2** with small amounts of the ring-opened compound Z-**3a** (10% yield). This reaction was carried out in dry hexane at reflux temperature for five days with rigorous exclusion of moisture. The structures of the obtained compounds were established essentially by IR, N.M.R. and mass spectroscopy. This unexpected result was explained by the formation of the phosphoranes **I** which, by reaction of another molecule of **I** or the 1-H tautomer (**II**) at the equatorial MeO-group (SN_2 reaction at C), give Z-**3a** and the *N*-methylphosphoranes **III**.

Loss of MeOH from **III** by attack of **II** at the equatorial MeO group gives **2** and regenerates **III**.

It should be noted that when $P(OEt)_3$ was used in this reaction, compounds with the N-Ethyl group were not observed even after longer reaction times.



SCHEME I

TABLE I

^{1}H N.M.R. data[a] ($CDCl_3$) of compounds **3** and **4**

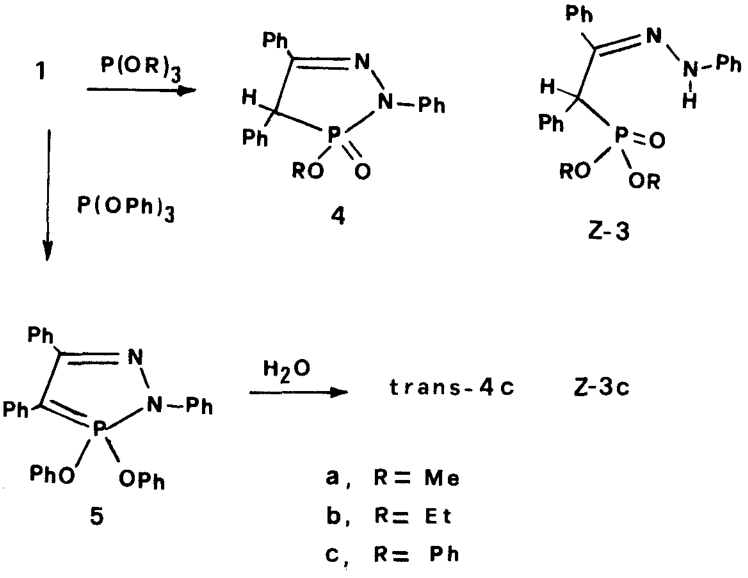
Compd.	δ PCH (J.Hz)	δ POMe (J.Hz) or POEt	δ Arom.	δ NH
Z-**3a**	7.36(d.31)	3.46(d.11) 3.54(d.11)	6.30–7.65(m)	9.90(s)
E-**3a**	4.15(d.23)	3.42(d.11) 3.52(d.11)	6.20–7.65(m)	[b]
Z-**3b**	4.70(d.29)	0.90–1.41(m.6H) 3.50–4.15(m.4H)	6.25–7.70(m)	9.90(s)
E-**3b**	4.10(d.23)	0.90–1.20(m.6H) 3.35–4.05(m.4H)	6.20–7.70(m)	[b]
Z-**3c**	5.10(d.31)		6.12–7.75(m)	9.90(s)
E-**3c**	4.40(d.23)		6.10–7.60(m)	[b]
cis-**4a**	4.72(d.21)	3.30(d.11)	6.90–7.90(m)	
trans-**4a**	4.36(d.20)	3.76(d.12)	6.85–7.92(m)	
cis-**4b**	4.70(d.22)	0.80–1.50(m.3H) 3.50–4.20(m.2H)	6.90–7.92(m)	
trans-**4b**	4.35(d.21)	0.75–1.45(m.3H) 3.70–4.35(m.2H)	6.81–7.90(m)	
cis-**4c**	4.10(d.21)		6.60–8.45(m)	
trans-**4c**	4.76(d.20)		6.61–8.12(m)	
5			6.40–7.51(m)	

[a] Chemical shifts in ppm from Me_4Si.

[b] Masked by aromatic protons.

We wish to report[3] that when the azoalkene **1** is treated with an equimolar amount of $P(OMe)_3$ in the hexane at room temperature for about a month a new 2H-1,2,3-diazaphosphole derivate **4a** is obtained together with the related ring-opened compound **Z-3a** (*Scheme II*). The course of the reaction can be conveniently followed by t.l.c. and the products, separated by chromatography over SiO_2 have been characterized mainly by ^{1}H. N.M.R. spectroscopy (*Table I*). It is noteworthy that under these conditions formation of N—Me compound **2** was not observed. The cyclic compound **4a** is a mixture of isomers (cis[4]- and trans) in which predominates the isomer bearing the C_4—Ph and the OMe group in a trans configuration.

The methynic protons provide a sensitive analytical probe for determining the composition of mixtures by ^{1}H, N.M.R.: the ratio *cis* : *trans* is about 2:3 and the ratio between the cyclic compound **4a** and the ring-opened compound **Z-3a** is about 1:3. Similar results are obtained when $P(OEt)_3$ is used. In this case the ratio between the cyclic compound **4b** and the ring-opened compound **Z-3b** is about



SCHEME II

1:4. Also in the case of cyclic compound **4b** the trans isomer predominates over the cis isomer (cis:trans = 2:3). All the ratios are estimated by ^{1}H. N.M.R. spectroscopy relative integrations of methine peaks. When this reaction is carried out with $P(OPh)_3$ in hexane a mixture of cyclic compound **4c** (only in the trans configuration) and of the corresponding ring-opened compounds Z-**3c** is obtained.

The ratio between the cyclic compound **4c** and the ring-opened product Z-**3c** is about 4:1. In acidic conditions *trans*-**4c** isomerizes into *cis*-**4c**. If this reaction is carried out in dry hexane with rigorous exclusion of moisture a new product is obtained by crystallization from the reaction mixture.

We tentatively propose for this new compound an ylide structure such as **5**, whose formation may be favoured by its possible aromatic character. If traces of water are deliberately added to a solution of **5** in $CDCl_3$ the immediate formation of *trans*-**4c** together with small amounts of **3c** is observed.

It should be noted that all the ring-opened isomers Z-**3** are not interconvertible in several solvent solutions ($CDCl_3$; CH_2Cl_2, C_6D_6) even after many hours at room temperature under neutral conditions, while under acidic conditions an isomerization to the corresponding ring-opened isomers E-**3** was observed.

ASSIGNMENT OF CONFIGURATION

The configurational assignment about the C=N bond of ring-opened products **3** has been made essentially on the basis of ^{1}H. N.M.R. spectra (*see Table I*).

The NH proton resonance of compound Z-**3** is strongly intramolecularly bonded as indicated by its low resonance, and this indicates a Z-configuration about the C=N bond. On the other hand the NH absorption of the E-**3** form cannot give hydrogen bonding and this resonates at a higher magnetic field. We have reported[5] analogous assignments for similar compounds.

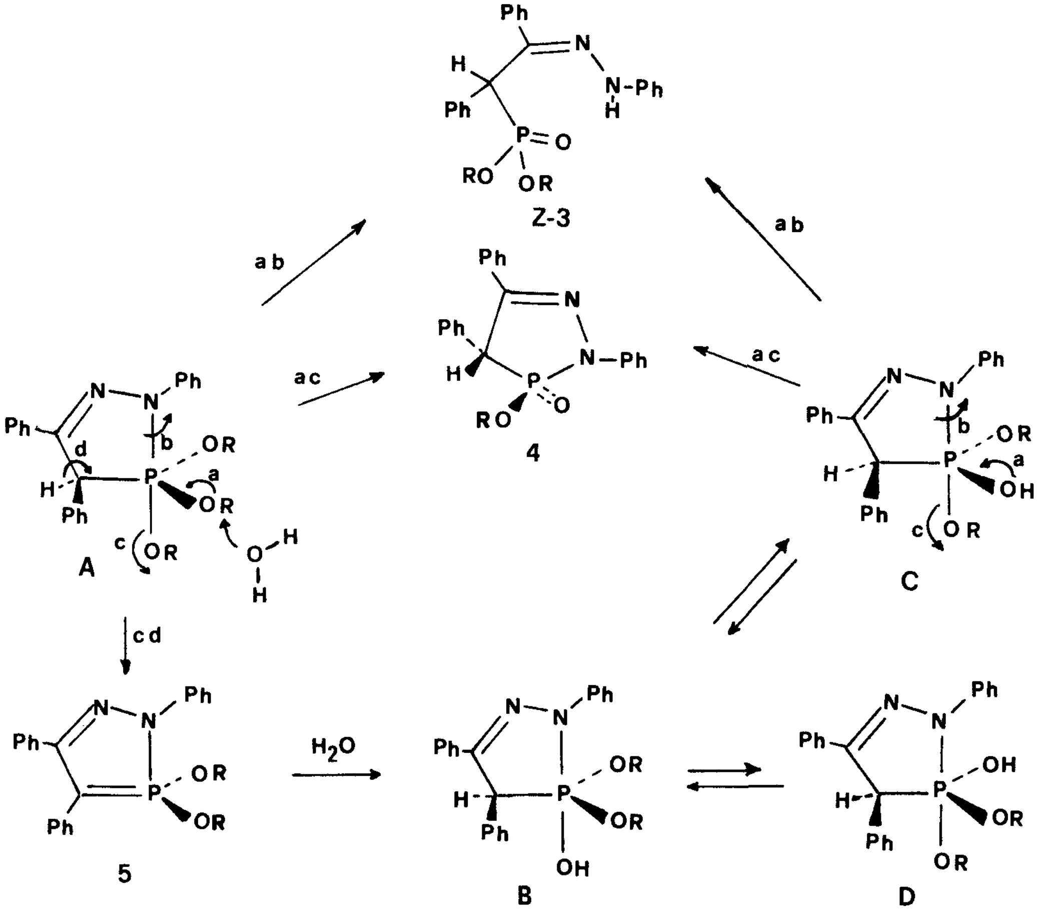
The relative configuration of the two chiral center in the cyclic compounds **4** has been tentatively assigned on the basis of ^{1}H. N.M.R. spectra; in compound **4a** the *cis*-configuration is assigned to the isomer showing an upfield methoxy signal at $\delta 3.70$, since only in this isomer is the aromatic ring capable of shielding the methoxy group. The assignment was further supported by the finding that the methine proton of the isomer *cis*-**4a** is downfield, since in this configuration the P=O group deshields[6] the methine proton. The same deshielding effect is observed in all the isomers *cis*-**4**. This assignment is also consistent with the observation that the methine proton of *cis*-**4** exhibits a smaller coupling with phosphorus than with methine proton of the isomer *trans*-**4**. The ylide structure of compound **5** had been tentatively assigned only on the basis of the ^{1}H and ^{31}P N.M.R. spectra owing to its great instability to moisture. In fact the ^{1}H. N.M.R. spectra of compound **5** showed only aromatic signals, while the ^{31}P chemical shift was found to be downfield from an 85% H_3PO_4 reference very likely excluding a pentacoordinate structure.

DISCUSSION

The large number of relatively stable phosphoranes[7] and the theoretical background that now exists on their structure and dynamic stereochemistry, provide an adequate interpretation of our findings. The mechanism we propose for these reactions here described involves the formation of metastable phosphoranes such as **A** (*Scheme III*).

Since, as a rule, five-membered rings are unable for reasons of strain, to adopt a diequatorial position in the trigonal bipyramid, and since more electronegative atoms tend to prefer the apical positions, only conformers with an apical-equatorial ring in which the nitrogen atom is apical are considered to participate in this mechanism.

When R=Me a nucleophic attack of water on the equatorial methoxy carbon atom of **A** gives (*via ab*) the corresponding ring-opened compound Z-**3**, while *via ac* it gives the corresponding cyclic compound **4**. The ylide form **5** is obtained from **A** *via cd*. Addition of water onto this ylidic form gives the new phosphorane intermediate **B** which may isomerize to **D** or **C** by a turnstile rotation process[8] or a alternative equivalent Berry pseudorotation.[9] Since there is an intramolecular overcrowding in trigonal-bipyramidal structures, steric factors will have a considerable influence on the stability of such phosphoranes. One consequence of this structural feature is that the form **C** may be favoured over the form **D** because it will avoid the steric interaction of P—OR group with the C_4-pehnyl group. The cyclic compound (*trans*-**4**) is obtained from **C** *via ac*; the ring-opened compound



SCHEME III

Z-**3** is obtained from **C** *via* ab. Thus the observed different ratios between the ring-opened product, Z-**3** and the corresponding cyclic product **4** can be rationalized on the basis of the different leaving abilities (and hence apicophilicities[10] in the pentacoordinate intermediate) of the RO— groups compared to the diaz group.

When R is Me or Et, the route *ab* is favoured over the route *ac*. In fact the diaza group is expected to be more apicophilic and a better leaving group than the methoxy and ethoxy groups; on the contrary when R is Ph, the route *ac* is favoured over the *via ab*: in this case the diaza group is a poorer apicophile and has a smaller leaving ability than phenoxy group. As a result in this case the cyclic compound **4** predominates over the ring-opened compound **3**.

The proposed cyclic phosphorane intermediates such as **A** are also consistent with the exclusive formation of ring-opened compounds **3** with the *Z*-configuration about the C=N bond.

In conclusion, our findings clearly indicate that the stereochemical results are dependent on the steric interaction as well as the relative leaving abilities and apicophilitities of groups when trigonal bipyramidal phosphoranes are involved as reaction intermediates.

EXPERIMENTAL

^{1}H N.M.R. spectra were obtained at 60 MHz for solutions in $CDCl_3$. IR spectra are carried out in $CHCl_3$ 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. Phosphites were redistilled in dry apparatus prior to use. Column chromatography was performed with Merck silica gel of participle size 0.05–0.2 mm.

Reaction of 1 with trimethyl phosphite

To a solution of **1** (2.84 g, 0.01 mol) in 140 ml of n-hexane was added trimethyl phosphite (0.01 mol) and the reaction mixture was set aside at room temperature for about a month until the red colour of the solution disappeared. The course of the reaction was followed by t.l.c. After evaporation of the solvent the mixture was chromatographed on a silica gel column. Elution with 9:1 benzene-ether gave products Z-**3a** in 60% and **4a** in 20% yield. The ratio between *cis*-**4a** and *trans*-**4a** was about 2:3 (estimated by the integration of methine peaks). Pure Z-**3a** (Rf. 0.35) was crystallized from n-pentane and had m.p. 147–149°C; $\nu_{max}(CHCl_3)$ 3240 (NH) cm^{-1}; *trans*-**4a** (Rf. 0.30) and *cis*-**4a** (Rf. 0.25) were separated in mixtures as rich as possible in the *cis* or *trans* isomer: the first collected fractions were richer in *trans* (75%), the final in *cis* (70%).

When a benzene solution of isomer Z-**3a** was saturated with hydrogen chloride and left at room temperature for about 24 hrs a ca. 1:1 mixture of isomers Z-**3a** and E-**3a** was obtained.

Separation of the new isomer E-**3a** was accomplished by chromatography on a silica gel column by elution with 8:2 benzene-ether mixture. Pure E-**3a** (Rf. 0.15), as an oil, showed $\nu_{max}(CHCl_3)$ at 3340 (NH) cm^{-1}.

The ^1H N.M.R. spectra ($CDCl_3$) for compounds **3a** and **4a** are reported in Table I and IR spectra were consistent with the assigned structures.

Anal. Calcd for $C_{22}H_{23}N_2O_3P$: C, 67.01; H, 5.84; N, 7.11. Found: C, 67.10; H, 5.92; N, 7.08. Calcd for $C_{21}H_{19}N_2O_2P$; C, 69.62; H, 5.25; N, 7.73. Found: C, 69.76; H, 5.42; N, 7.84.

Reaction of 1 with triethyl phosphite

In a similar way the addition of triethyl phosphite (0.01 mol) to a solution of **1** (2.84 g, 0.01 mol) in n-hexane gave, after about a month at room temperature, a mixture of Z-**3b** and **4b** (*cis* and *trans*) in a ratio of about 4:1. The isomer ratio between *cis*-**4a** and *trans*-**4b** is about 2:3.

Chromatography of a silica gel column (9:1 benzene-ether as eluent) afforded Z-**3b** in 64% and **4b** in 15% yield. Pure Z-**3b** (Rf. 0.45), was crystallized from n-hexane and had m.p. 80–82°C; $\nu_{max}(CHCl_3)$ 3240 (NH) cm^{-1}; *trans*-**4b** (Rf. 0.30) and *cis*-**4b** (Rf. 0.25 were isolated only in mixtures as rich as possible in the *cis* or *trans* isomer. Isomerization of Z-**3b** into E-**3b** was accomplished under acidic conditions and the new ring-opened compound E-**3b** was separated by chromatography on silica gel column by evolution with an 8:2 benzene-ether mixture. Pure E-**3b** (Rf. 0.15), an oil, showed $\nu_{max}(CHCl_3)$ at 3340 (NH) cm^{-1}. The ^1H N.M.R. data ($CDCl_3$) for compounds **3b** and **4b** are reported in Table I.

Anal. Calcd for: $C_{24}H_{27}N_2O_3P$: C, 68.25: H, 6.40; N, 6.64. Found: C, 68.42; H, 6.45; N, 6.77. Calcd for: $C_{22}H_{21}N_2O_2P$: C, 70.21; H, 5.59; N, 7.45. Found: C, 70.32, H, 5.63, N, 7.51.

Reaction of 1 with triphenyl phosphite

To a solution of **1** (2.84 g, 0.01 mol) in 140 ml of n-hexane was added triphenyl phosphite (0.01 mol) and the mixture was set aside at room temperature for about 20 days. ^1H N.M.R. analysis of a portion of the reaction mixture showed the presence of Z-**3c** and *trans*-**4c** in the ratio 1:4. After evaporation of the solvent, chromatography on a silica gel column (9:1 benzene-ether as eluant) afforded Z-**3c** in 16% and *trans*-**4c** in 63% yield.

Pure Z-**3c**, (Rf. 0.55), was crystallized from n-hexane and had m.p. 130–132°C, ν_{max} ($CHCl_3$) 3245 (NH) cm^{-1}; pure *trans*-**4c** (Ref. 0.35), was crystallized from n-pentane and had m.p. 140–142°C.

Isomerization of Z-**3c** and *trans*-**4c** into E-**3c** and *cis*-**4c** respectively was accomplished under acidic conditions, and the new isomers were separated by chromatography on a silica gel column by elution with an 8:2 benzene-ether mixture. Pure E-**3c** (Rf. 0.20), an oil, showed $\nu_{max}(CHCl_3)$ at 3340 (NH) cm^{-1}; pure *cis*-**4c** (Rf. 0.30) was crystallized from n-pentane and had m.p. 120–123°C.

Anal. Calcd for $C_{32}H_{27}N_2O_3P$: C, 74.13; H, 5.21; N, 5.41. Found: C, 74.21, H, 5.18; N, 5.47, Calcd for: $C_{26}H_{21}N_2O_2P$: C, 73.58; H, 4.95; N, 5.60. Found: C, 73.64; H, 4.81; N, 6.45.

When this reaction was repeated in dry n-hexane with rigorous exclusion of moisture, the new product **5**, as a white precipitate, was formed from the reaction mixture after about a week. This compound was separated from the solution under a purified nitrogen atmosphere. An N.M.R. spectrum taken under nitrogen immediately after separation, showed only aromatic signals (Table I) and ^{31}P ($CDCl_3$) at 43.7 ppm. (downfield from 85% H_3PO_4). When traces of water were deliberately added to the solution ($CDCl_3$) of **5** and the course of the reaction examined periodically by ^1H N.M.R., the corresponding signals of *trans*-**4c** and Z-**4c** immediately appeared. After about an hour the ratio between *trans*-**4c** and Z-**4c** was 4:1.

ACKNOWLEDGEMENTS

We wish to thank the Italian C.N.R. for financial support.

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