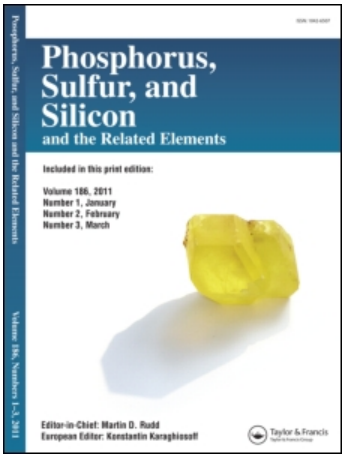

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STEREOSELECTIVE FORMATION OF 3-CHLORO-2,4,5-TRIPHENYL-3,4-DIHYDRO-2H-1,2,3-DIAZAPHOSPHOL-3-OXIDE *VIA* AN "ARBUZOV-LIKE" REACTION AND ITS DECOMPOSITION TO INDOLE

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STEREOSELECTIVE FORMATION OF 3-CHLORO-2,4,5-TRIPHENYL-3,4-DIHYDRO-2H-1,2,3-DIAZAPHOSPHOL-3-OXIDE *VIA* AN "ARBUZOV-LIKE" REACTION AND ITS DECOMPOSITION TO INDOLE

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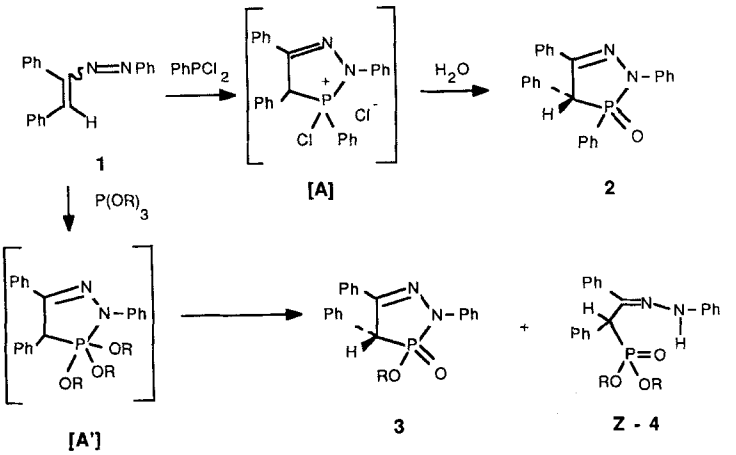
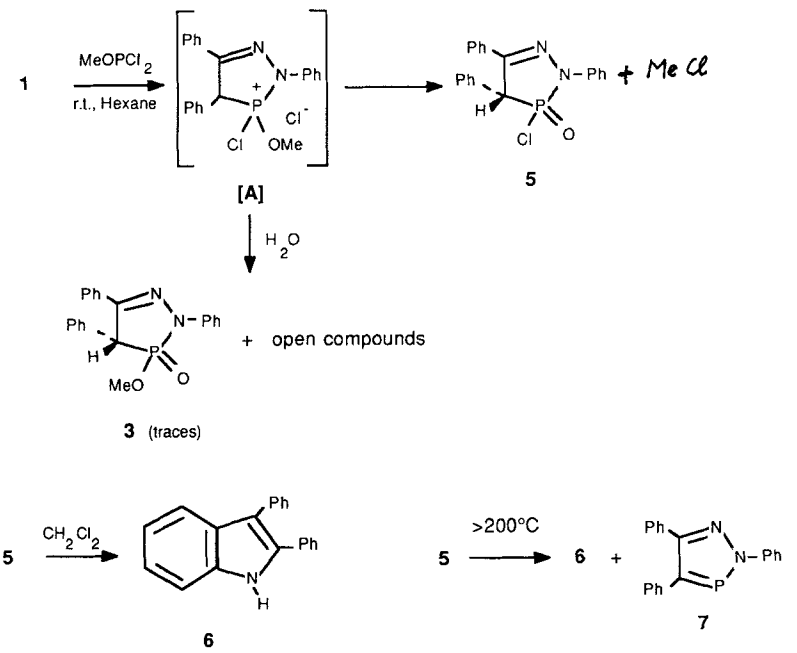
The reaction of phenylazostilbene (**1**) and methoxydichlorophosphine gives the formation of the title compound *via* an intramolecular "Arbuzov-like" reaction. The *trans* isomer is easily isolated in a pure form by simple filtration of the reaction mixture. This compound in dichloromethane solution at room temperature converts into 2,3-diphenylindole. In addition, the reaction of (**1**) with phosphorus trichloride gives a cycloadduct which easily decomposes to the same indole. These results are a further convincing evidence that diazaphosphole system can be an intermediate in the synthesis of aza-heterocycles.

2H-1,2,3-Diazaphosphole derivatives were intensively studied by different research groups.[1] We recently proposed that these compounds can be intermediates in the synthesis of indoles[2] and pyrroles[3] from hydrazones and PCl_3. Moreover, we previously studied the addition of aryldichlorophosphine[4] or alkyl phosphites[5] to azoalkenes with the purpose of synthesizing new functionalized diazaphospholes. In the former reaction, it was possible to recover the corresponding diazaphospholene oxide (**2**, Scheme 1) in very good yields, while, in the latter





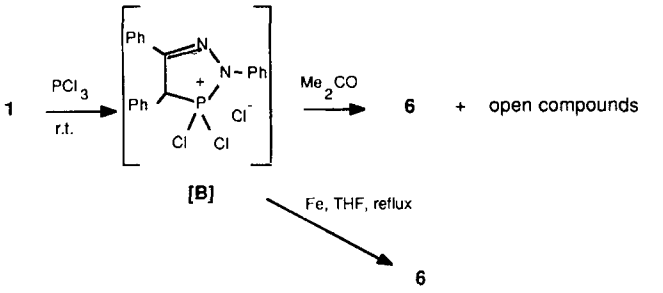
one, the relative proportions of ring-opened compounds (**Z-4**) and oxide (**3**) depended on the phosphite and the reaction conditions with the prevalence in most cases of the open compounds.

These results suggest that in a new synthesis of 2-phenyl-1,2,3-diazaphosphole derivatives the conditions which lead to the corresponding indoles or ring-opened compounds (polar solvent and acidic medium) should be avoided. With this in mind, the reaction of methoxydichlorophosphine and phenylazostilbene (**1**) was carried out in dry hexane at room temperature in order to obtain only diazaphosphole derivatives like (**3**) and/or (**5**) (Scheme 2).

In this reaction the slow disappearance of the red colour of the azoalkene (**1**) and the concomitant formation of a white precipitate was observed. An accurate spectroscopical analysis of this precipitate showed it to be already the chloro derivative (**5**) instead of the expected phosphonium salt [**A**]. Very likely, because of the activation of the methoxy carbon atom towards nucleophilic substitution,[6] intermediate [**A**] immediately underwent an intramolecular "Arbuzov-like"[7] reaction to give (**5**).

^{31}P-NMR analysis of the reaction mixture revealed in the first time of the reaction a small signal at $\delta = 104.1$, which can be attributed to a cycloadduct like [**A**] together with the signals of *cis*(**5**) ($\delta = 44.5$) and *trans* (**5**) ($\delta = 47.0$); while no formation of pentaco-ordinated phosphorus species was observed. Moreover the presence of [**A**] was indirectly demonstrated by formation of small amounts of oxide (**3**) after quenching of the reaction mixture.

It is noteworthy that the reaction is stereoselective leading to a *cis* (**5**): *trans*



(**5**)[8] ratio of about 1:4. The *trans* isomer is sparingly soluble in hexane, precipitates from the reaction mixture in a pure form and can be easily separated by filtration and stored for several days under nitrogen. Finally it is quite easy to handle. On the other hand, *cis* isomer cannot be isolated by chromatographic separation because of its instability on silica gel.

The *trans* structure was assigned to the isomer with the lowest H-P coupling constant and the lowest downfield shift of H-4, according to the previous reported configuration of related compounds.[5,9]

It should be noted that compound (**5**) is the oxidized form of the diazaphosphole key intermediate which we hypothesized in the indolization reaction of arylhydrazones with phosphorus trichloride.[2c] As a consequence, (**5**) should decompose to indole under the experimental conditions employed in the indolization reaction. Actually diazaphospholenoxide (**5**) decomposes slowly to 2,3-diphenylindole, when it was allowed to stand at room temperature in dichloromethane solution. In addition GC-MS analysis of pure (**5**) gave two signals at $m/z = 269$ [2,3-diphenylindole (**6**)] and at $m/z = 314$ [very likely 2,4,5-triphenyldiazaphosphole (7)]. In the same manner, we found that the intermediate of the indolization reaction underwent thermal decomposition to the corresponding indole and diazaphosphole.[2c]

In order to synthesize the oxide (**5**) by an independent route, the reaction of phenylazostilbene with phosphorus trichloride was also carried out. Treatment of the obtained solid cycloadduct [**B**] (Scheme 3) with acetone, according to the synthesis of chlorophospholenoxides,[10] gave compound (**5**) only in traces the indole (**6**) being the major product.

In addition our attempts to convert the cycloadduct [**B**] into diazaphosphole (**7**) by refluxing it over iron powder in THF solution failed and once more indole (**6**) was the only isolable product.

In conclusion these results provide support of adequate strength to the proposed mechanism on our indolization process involving reaction of PCl_3 with arylhydrazones.[2c] Moreover, we think that our mechanism can also better explain the side formation of indoles observed in the synthesis of diazaphosphole sulphides starting from dithiaphospholenedisulphides with aryl hydrazones.[11]

Finally, the formation of the chlorodiazaphospholenoxide (**5**) is peculiar of the reaction between methoxydichlorophosphine and phenylazostilbene and this

compound can be a versatile intermediate for the synthesis of diazaphospholenoxides arising from difficulty available dichlorophosphines. However these reactions must be carried out avoiding as much as possible acidic conditions and polar solvents which leads to indoles or open compounds.

EXPERIMENTAL

^{1}H-NMR spectra were recorded with a Varian EM360L instrument. Chemical shifts are given from Me_4Si (internal standard) in $CDCl_3$ solutions. ^{31}P-NMR spectra were recorded with a Varian XL100 instrument. Chemical shifts are given from H_3PO_4 85% (external standard) in C_6D_6 solutions, positive values indicate downfield shifts. Mass spectra were recorded with an HP 59970 workstation formed by an HP-5890 gaschromatograph equipped with a methyl silicone capillary column and by an HP-5970 mass detector or with a VG 7070 spectrometer. Melting points are uncorrected and were determined with a Buchi apparatus. Hexane and benzene were dried by distillation over sodium wires. Phenylazostilbene was synthesized as previously reported.[12] Commercial products were used without purification. Quantitative GC analyses were run out on a HP-5890 gaschromatograph equipped with a methyl silicone wide bore capillary column using tetradecane as internal standard.

Preparation of 3-chloro-2,4,5-triphenyl-1,2,3-diazaphosphol-5-en-3-oxide (**5**)

Phenylazostilbene (2 g, 7 mmol) was dissolved in 250 mL of dry hexane and methoxydichlorophosphine (0.66 mL, 7 mmol) was added. The reaction was allowed to stand at room temperature under dry atmosphere for two days. The mixture was filtered and the *trans* isomer[8] was recovered in about 60% yield together with small amounts of *cis* isomer. Recrystallization from hexane give the pure *trans* isomer. A sample of the mixture evaporated and dissolved in $CDCl_3$ showed a ratio *trans* : *cis* of about 4:1 by ^{1}H-NMR analysis.

The reaction was carried out in an NMR tube dissolving the reactants in a 1:1 mixture of hexane and deuterated benzene. After an hour, the presence of *cis* and *trans* isomers together with the starting phosphine and a compound at $\delta^{31}p = 104.1$ (intermediate [**A**]) was detected. The starting phosphine disappeared after about five hours, and the intermediate [**A**] after one day.

A sample of pure *trans*-(**5**) was dissolved in CH_2Cl_2 and allowed to stand at room temperature for one day. The GC-MS and TLC analyses of the mixture showed the almost complete conversion of (**5**) into 2,3-diphenylindole (**6**).

A sample of pure *trans*-(**5**) was submitted to GC-MS analysis and two peaks were detected: the first with $m/z = 269$ [indole (**6**)] the second with m/z: 314, 236, 165, 122, 77(2,4,5-triphenyl-1,2,3-diazaphosphole).

trans-(**5**): mp 144–146°C; δ_H ($CDCl_3$) 4.8 (d, PCH, $J_{H\text{-}P} = 18$ Hz); 7.8–8.0 (m, 15H, ArH); δp (C_6D_6) 47.0; m/z:[13] 366 (M^+), 314, 283, 207, 193, 179, 105, 77. Anal calcd for $C_{20}H_{16}N_2ClPO$ C, 65.49, H, 4.40; N, 7.64%. Found: C, 65.15; H, 4.40; N, 7.60%.

cis-(**5**): δ_H ($CDCl_3$) 5.2 (d, PCH, $J_{H\text{-}P} = 19$ Hz); 7.8–8.0 (m, 15H, ArH); δp (C_6D_6) 44.5.

Attempts to synthesize (**5**) *from PCl_3 and acetone*

Phenylazostilbene (1.09 g, 3.5 mmol) was dissolved in 250 mL of dry hexane, phosphorus trichloride (1 mL, 3.5 mmol) and acetone (0.26 mL, 3.5 mmol) were added. The reaction was allowed to stand at room temperature under dry atmosphere for three days. The quantitative GC and ^{1}H-NMR analyses of the mixture showed trace amounts of products (**5**) together with indole (**6**, 30%) and other unidentified products.

Attempts to synthesize 2,4,5-triphenyl-1,2,3-diazaphosphole (**7**)

Phenylazostilbene (1.09 g, 3.5 mmol) was dissolved in 250 mL of dry hexane, phosphorus trichloride (1 mL, 3.5 mmol) was added and the reaction was allowed to stand at room temperature under dry atmosphere for three days. The cycloadduct [**B**] was filtered [^{31}P-NMR (C_6D_6) δ 104.5], then it was dissolved in THF (50 mL). Iron powder (0.4 g, 7 mmol) was added and the slurry was refluxed for several hours. The GC and TLC analyses of the mixture showed indole (**6**) and other unidentified products. After purification of the reaction mixture by silica gel chromatographic separation (**6**) was isolated in 51% yield and identified by comparison with authentic sample.

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