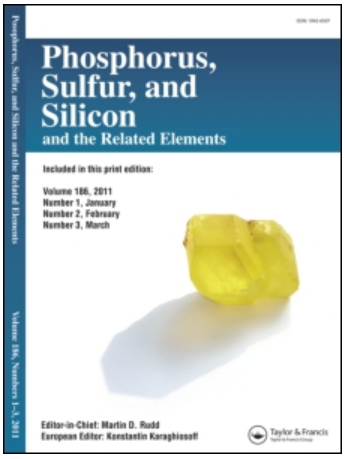

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FACILE STEREOSELECTIVE SYNTHESIS OF 2H-1,2,3-DIAZA-PHOSPHOLE SPIROPHOSPHORANE DERIVATIVES

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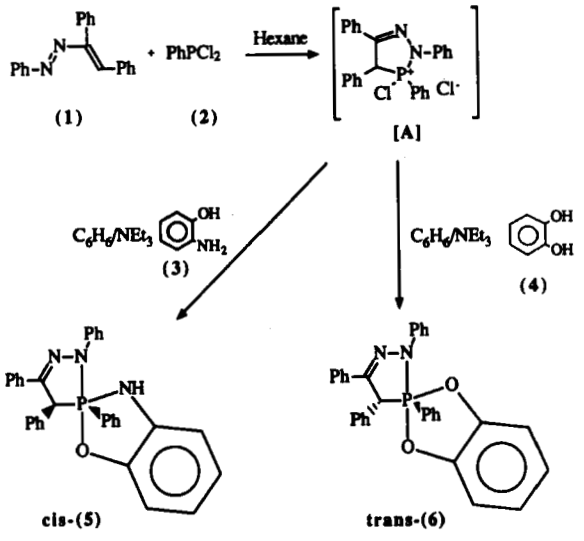
The one-pot reaction of the phenyldichlorophosphine-phenylazostilbene adduct with *ortho*-aminophenol led easily to the almost exclusive stereoselective formation of the *cis*-benzoxazaspirophosphorane. On the contrary, from the reaction with catechol the corresponding *trans*-spirophosphorane was surprisingly obtained.

Key words: benzoxazaspirophosphorane.

2H-1,2,3-Diazaphosphole derivatives are being widely studied by different research groups.[1] In particular, we studied the reactivity of the adducts between azoalkenes and dichlorophosphines[2] or phosphites[3] and recently we have demonstrated that 'in situ' generated diazaphosphole can be intermediates in the facile synthesis of azaheterocycles.[4] Moreover, the chemistry of pentaco-ordinate phosphorus compounds has received increasing attention in recent years, since the understanding of the factors affecting the stability and the chemistry of phosphoranes allows the displacement reactions at tetraco-ordinate phosphorus to be understood.[5] Many attractive stereochemical results have been obtained in the field of spirophosphoranes depending on the constraints of the two-ring system attached to the central atom.[6]

In this paper, we wish to present two opposite stereoselective behaviours in the synthesis of related diazaphosphole spirophosphoranes. The reaction between the phenylazostilbene-phenyldichlorophosphine adduct [**A**] and *ortho*-aminophenol (**3**) was carried out in anhydrous benzene in the presence of triethylamine[7] (Scheme 1).

^{1}H-NMR analysis of the reaction mixture revealed the almost exclusive formation of the *cis* spirophosphorane (**5**)[8] which can be easily separated from the reaction mixture. This compound was recognized by comparison with an authentic sample obtained from the previously reported reaction of *ortho*-azidophenol and *cis*-2,3,4,5-tetraphenyl-3,4-dihydro-2H-1,2,3-diazaphosphole.[9] A trigonal bipyramidal (TBP) structure was tentatively assigned to the phosphoranes (**5**). A subsequent X-ray analysis of the 5′-benzyl derivative of (**5**)[10] (Figure 1) confirmed a nearly perfect TBP geometry with the two rings in an apical-equatorial position in which the oxygen and the nitrogen atoms occupy the apical positions.



SCHEME 1

On the contrary, the reaction between [**A**] and catechol (**4**) led stereoselectively to the spirocycle (**6**) with the *trans* configuration (Scheme 1). The pentaco-ordination of this compound was suggested by $\delta p = -11.0$. The determination of the correct configuration at phosphorus atom is very difficult to be performed without an X-ray analysis. However, notwithstanding the presence of two oxygen atoms, a near TBP geometry seems to be the more probable in

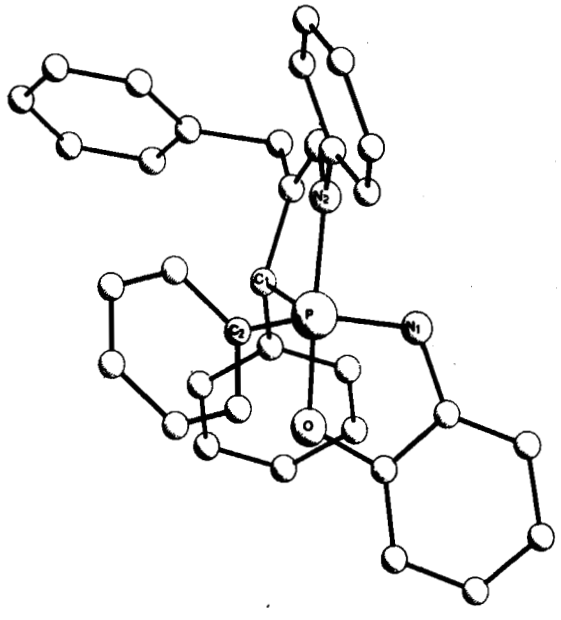
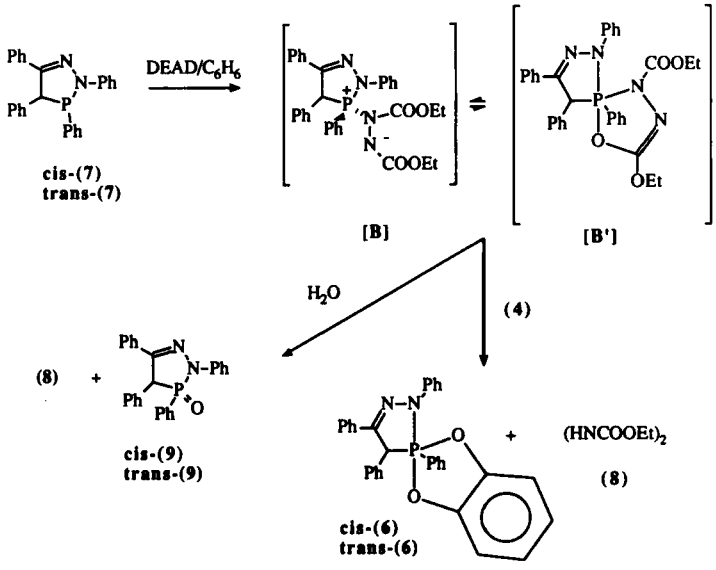


FIGURE 1

analogy with the above reported X-ray structure of compound (**5**)[10]. For a correct determination of the relative positions of the phenyl groups bound to C_4 and P atoms, both (**6**) isomers should be synthesized. In order to obtain them the reaction of 2,3,4,5-tetraphenyl-3,4-dihydro-2H-1,2,3-diazaphosphole (**7**) and diethyl azodicarboxylate (DEAD)[11] was carried out in dry benzene followed by addition of catechol (Scheme 2).

The very broad signal ($\delta p = +17.8$) did not allow us to discriminate between the two possible forms [**B**] or [**B'**] of the diazaphosphole-DEAD adduct formed in the first stage of the reaction, a fast equilibrium between the betainic [**B**] and the pentaco-ordinated form [**B'**][12] being very likely present at room temperature. Isolation of this intermediate can be performed in a completely dry atmosphere and it is stable for few hours before hydrolyzing to the oxide (**9**) and to the hydrazine (**8**). The 'in situ' treatment of [**B**] or [**B'**] with catechol led to the formation of the desired spirophosphoranes (**6**). They are very stable compounds in the solid state, while in solution of polar solvents, such as chloroform or dichloromethane, a slow decomposition to 2,3-diphenylindole and diazaphosphole oxide (**9**) was observed.[7] The isomers (**6**) did not interconvert in dichloromethane solution.

The two isomers were characterized on the basis of their ^{31}P and ^{1}H-NMR spectra. The correct relative configuration of the phenyl groups bound to P and C_4 atoms was assigned on the basis of the ^{1}H-NMR spectra. *Trans* isomers of all 2H-1,2,3-diazaphosphole compounds were found to have the lowest H-P coupling constants and the lowest downfield shifts of H_4^2. This trend was confirmed by several X-ray data[13] performed on these derivatives. Therefore the *trans* configuration was assigned to the product with $\delta_H = 4.70$ and $J_{H\text{-}P} = 6.0$ Hz and the *cis* one to the product with $\delta_H = 5.10$ and $J_{H\text{-}P} = 29.0$ Hz. The pentaco-



SCHEME 2

ordination was demonstrated by the values of $\delta_P = -6.7$ and -11.0 for compounds *cis*-(**6**) and *trans*-(**6**) respectively.

The reaction was found to be completely stereospecific: pure *cis*-(**7**) and *trans*-(**7**) exclusively gave *cis*-(**6**) and *trans*-(**6**) respectively. Very surprisingly the compound synthesized from phenylazostilbene-phenyldichlorophosphine adduct and catechol was identical to the *trans* isomer instead of the *cis* one as expected in analogy with the reaction of *ortho*-aminophenol. These findings show that the stereochemistry at a phosphorus atom is highly dependent on the nature of the substrate. In fact carrying out the same reaction on very similar substrates such as aminophenol and catechol, an opposite final configuration at the phosphorus atom was observed. Therefore the *a priori* determination of a stereochemical trend in a reaction involving phosphorus atoms might result uncorrect.

EXPERIMENTAL

^{1}H-NMR spectra were recorded with a Varian EM 360L instrument. Chemical shifts are given from Me_4Si (internal standard) in $CDCl_3$ solutions. ^{31}P-NMR spectra were recorded with a Varian FT 80A instrument. Negative ^{31}P chemical shifts are upfield of external phosphoric acid (85%). Mass spectra were recorded with an HP 59970 workstation formed by an HP 5890 gas-chromatograph equipped with a methyl silicone capillary column and by an HP 5970 mass detector. Melting points are uncorrected and were determined with a Büchi apparatus. Benzene and hexane were dried by distillation over sodium wires. Phenylazostilbene[14] and 2,3,4,5-tetraphenyl-3,4-dihydro-1,2,3-diazaphosphole[2] were synthesized as previously reported. Commercial products were used without purification.

*Synthesis of 2',4'-dihydro-2,2',4',5'-tetraphenylspiro(1,3,2-benzodioxaphosphole-2(3H),3'-[3H,1,2,3]-diazaphosphole) (**6**) from 2,3,4,5-tetraphenyl-3,4-dihydro-1,2,3-diazaphosphole (**7**).* Phosphine (**7**) (0.5 g, 1.27 mmol), diethyl azodicaboxylate (0.2 mL, 1.27 mmol) and catechol (0.14 g, 1.27 mmol) were dissolved in dry benzene. The reaction mixture was allowed to stand at room temperature for 2.5 hours under nitrogen atmosphere. The solvent was removed under reduced pressure. The crude was purified ona silica gel column using light petroleum (bp 40–60°C)-diethyl ether 10:1 as eluant. The spiro derivative (**6**) was crystallized from diethyl ether.

Starting from the *cis*-(**7**), *cis*-(**6**) was recovered: 87% yield, mp 164–166°C, R_f 0.30, δ_H 5.10 (d, PCH, $J_{H\text{-}P}$ 29.0 Hz); 6.75–7.90 (m; 24H ArH); δp-6.7; *m/z* 500 (M^+), 391, 333, 307, 269, 178, 139, 77. Anal. calcd for $C_{32}H_{25}N_2O_2P$ C, 76.80; H, 5.00; N, 5.60. Found C, 76.70; H, 5.02; N, 5.58%. Starting from the *trans*-(**7**), *trans*-(**6**) was recovered: 82% yield, mp 175–177°C, R_f 0.30, δ_H 4.68 (d, PCH, $J_{H\text{-}P}$ 6.0 Hz); 6.33–7.97 (m; 24H ArH); δp-11.0; *m/z* 500 (M^+), 391, 333, 307, 269, 178, 139, 77. Anal calcd for $C_{32}H_{25}N_2O_2P$ C, 76.80; H, 5.00; N, 5.60. Found C, 77.05; H, 5.03; N, 5.58%. Both isomers slowly decomposed to 2,3-diphenylindole and to 2,3,4,5-tetraphenyl-3,4-dihydro-1,2,3-diazaphosphole-3-oxide (**9**), when they were allowed to stand in solution of chloroform or dichloromethane.

*Synthesis of 2',4'-dihydro-2,2',4',5'-tetraphenylspiro(1,3,2-benzoxazaphosphole-2(3H),3'-[3H,1,2,3]-diazaphosphole) (**5**) and 2',4'-dihydro-2,2',4',5'-tetraphenylspiro(1,3,2-benzodioxaphosphole-2(3H),3'-[3H,1,2,3]-diazaphosphole) (**6**) from phenylazostilbene (**1**).* Phenylazostilbene (0.15 g, 1.8 mmol), phenyldichlorophosphine (0.26 mL, 1.8 mmol) and triethylamine (0.26 mL, 3.6 mmol) were dissolved in dry hexane. The mixture was allowed to stand at room temperature under nitrogen atmosphere in a two-necked flask equipped with a septum inlet. After 24 h, the supernatant liquid was removed through the septum by a syringe and 50 mL of a benzene solution of *ortho*-aminophenol (0.2 g, 1.8 mmol) or alternatively of catechol (0.2 g, 1.8 mmol) was added through the septum. After 2 h, the solvent was evaporated under reduced pressure and the crude was purified as above described. The recovered products were identical to the *cis* 2',4'-dihydro-2,2',4',5'-tetraphenylspiro(1,3,2-benzoxazaphosphole-3'-[3H,1,2,3]diazaphosphole)[9] (**5**) and to the *trans* isomer of the spirocyclic phosphorane (**6**). They were obtained in 47 and 51% yield respectively. In both cases ^{1}H-NMR analysis of the crude showed the exclusive formation of one isomer and the presence of the two isomers of the phosphine oxide (**9**) in about 1:1 ratio.

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