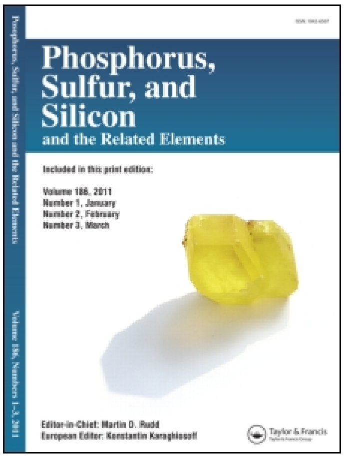

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THE REACTIONS OF 1,2,3-DIAZAPHOSPHOLE DERIVATIVES WITH CATECHOL

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THE REACTIONS OF 1,2,3-DIAZAPHOSPHOLE DERIVATIVES WITH CATECHOL

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Both two-coordinated phosphorus compounds $\overline{P{=}CH{-}C(Me){=}N{-}N}R$ (**1**, R=Ph, C(=O)CH_3) and tri-coordinated phosphorus compounds R-$\underline{P{-}CH_2{-}C(Me){=}N{-}N}{-}C({=}O)CH_3$ (**2**, R=Cl, OEt) reacted with catechol in the presence of triethylamine to yield hexa-coordinated phosphorus compound $R_3P^{\ominus}H^{\oplus}N(Et)_3$ (**3**, R=—O—C_6H_4—O—). **3** were confirmed by elemental analysis, IR, ^{31}P NMR and MS. The mechanism of these reactions was suggested.

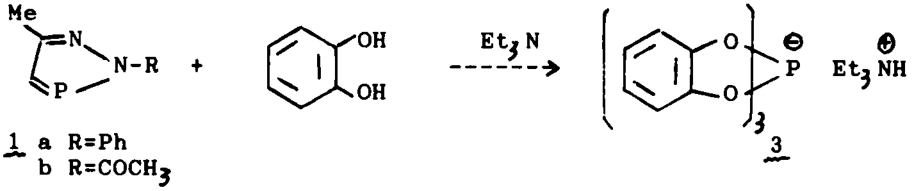
Key words: 1,2,3-diazaphosphole; reaction; catechol; mechanism; cleavage.

INTRODUCTION

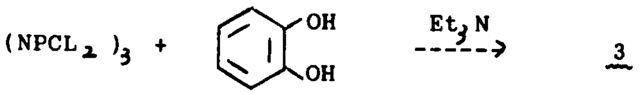
Attention has been given to the study of two-coordinated phosphorus compounds since their appearance 20 years ago. Recently, the reactions of 1,2,4,3-triazaphospholes with bifunctional reagents were reported,[1–5] encouraging us to study the reactions of 1,2,3-diazaphospholes with those reagents. The reactions of 1,2,3-diazaphospholes with catechol are described in this paper.

RESULTS AND DISCUSSION

The substituted 1,2,3-diazaphospholes reacted with catechol in the presence of triethylamine to form a hexa-coordinated phosphorus compound **3**, as shown in Scheme 1. **3** has been first synthesized by Allcock according to the following reaction,[6] see Scheme 2. **1** reacted with catechol in different molar ratios (1:1, 1:2, 1:3) at different temperatures (20°C, 60°C, 80°C), to give **3**. The temperature and



Scheme 1

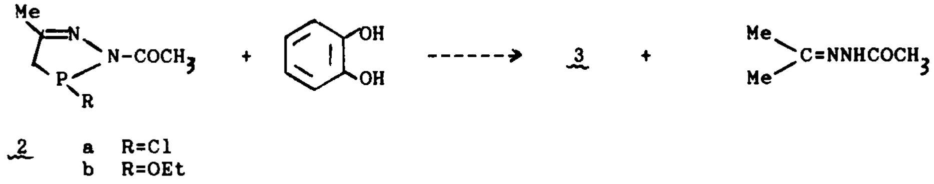


Scheme 2

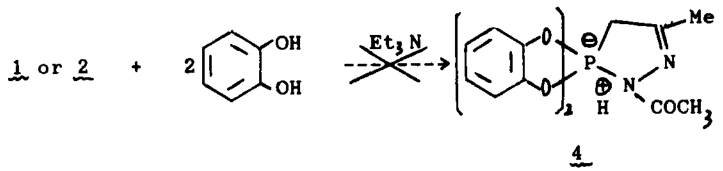
molar ratio affected the yields of **3**. It proved that the phosphorus carbon double bond in **1** was quite active to catechol and the cleavage of the phosphorus carbon bond took place easily. Therefore, raising the temperature increased the tendency of the cleavage of phosphorus carbon bond.

When the corresponding tri-coordinated phosphorus compounds **2** reacted with catechol under the similar conditions, **3** was also formed. For example, **2b** gave **3** and hydrazone as shown in Scheme 3. The reaction of **2b** with catechol in 1:2 molar ratio resulted in two other compounds identified by ^{31}P NMR, with the chemical shifts of 28.8 ppm referred to phosphate and −57.88 ppm referred to phosphorane respectively. Because of the instability of the penta-coordinated phosphorus compound, further identification of these two compounds failed.

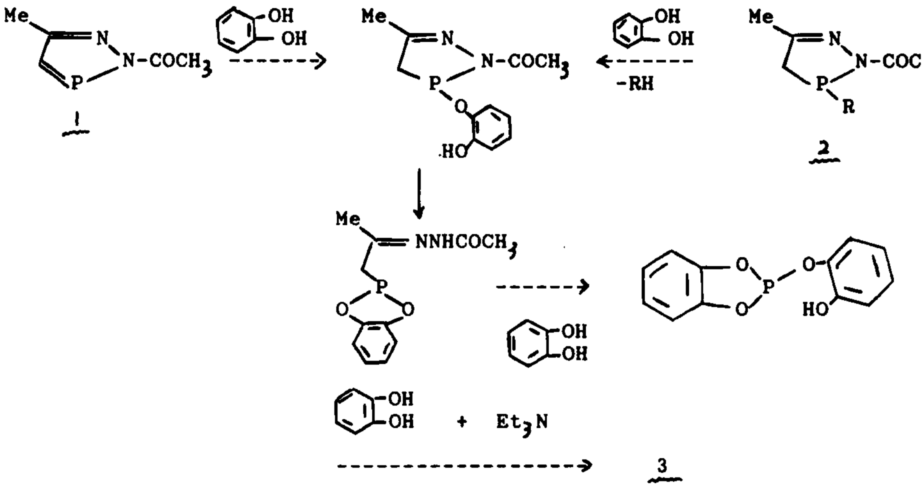
Either **1** or **2** reacted with catechol in 1:1 or 1:2 molar ratio, **4** was never obtained, see Scheme 4. It showed that phosphorus carbon double bond broke easily in the



Scheme 3



Scheme 4



Scheme 5

presence of catechol and triethylamine. Although the mechanism for the reaction of 1,2,3-diazaphosphole with catechol is rather complex, it is suggested that the tri-coordinated phosphorus compound first formed by the addition of catechol to phosphorus carbon double bond in **1** or through the replacement of R in **2** by catechol, then reacted further with catechol to give hexa-coordinated phosphorus compound through the cleavage of phosphorus carbon bond (see Scheme 5).

EXPERIMENTAL

NMR spectra were run on JEOL FX-90Q spectrometer at 90 MHz (^{1}H, TMS, int.) and 36.19 MHz (^{31}P, 85% H_3PO_4 (aq.), ext.). Infrared spectrum was recorded on 170SX instrument. Mass spectrum was obtained at 70 ev on VG.ZAB-HS instrument. Elemental analysis was done with YANACO CHN CORDER MT-3 instrument. The solvent was freshly distilled. Melting points were uncorrected. Compound **1** and **2** were prepared according to literature.[7,8]

Reaction of **1** *with catechol.* 1.1 g (0.01 mol.) catechol is added to 1.42 g (0.01 mol.) **1b** (R=$COCH_3$) in 70 ml benzene in nitrogen atmosphere, then 1.01 g (0.01 mol.) triethylamine is added dropwise and the mixture is stirred for 10 h. at r.t. After filtration, the residue is washed with water and then acetone three times respectively, dried in vacuum, 0.02 g, m.p. > 250°C. ^{31}P NMR −83 ppm (DMSO-d_6), MS m/e 356 ($M^{+\cdot}$ − 101, 1.5%), 247 (100%), IR, Identical to standard spectrum.

Reaction of **2** *with catechol.* 1.76 g (0.016 mol.) catechol is added to 1.40 g (0.008 mol.) **2b** (R=OEt) in 70 ml benzene in nitrogen atmosphere, then 1.01 g (0.01 mol.) triethylamine is added dropwise, and the mixture is heated to reflux and kept at this temperature for 8 h. It is filtered at 40°C, the residue is washed with water and then acetone three times respectively, dried in vacuum, 2.0 g, m.p. > 250°C. Elemental analysis for $C_{24}H_{28}NO_6P$, calcd: C, 63.02, H, 6.13, N, 3.06, found C, 62.96, H, 6.48, N, 3.06. ^{31}P NMR −83.04 ppm (DMSO-d_6), MS, m/e, 356 ($M^{+\cdot}$ − 101, 1.2%), 247 (100%). The filtrate is concentrated in vacuum, the oil obtained is extracted twice with petroleum ether (60–90°C) at 60°C. The colorless solids crystallized from petroleum ether is filtered and dried in vacuum. 0.10 g, m.p. 127–129°C, ^{31}P NMR, no signal. ^{1}H NMR, 1.86 (s, 3H, CH_3—C=N); 1.96 (s, 3H, CH_3—C=N); 2.22 (s, 3H, $COCH_3$), 9.14 (s, 1H, NH), IR, ν max, 3419 cm^{-1} and 3208 cm^{-1} (NH—CO), 1666 cm^{-1} (C=O), 1367 cm^{-1} (C=N). It is confirmed to be hydrazone.

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