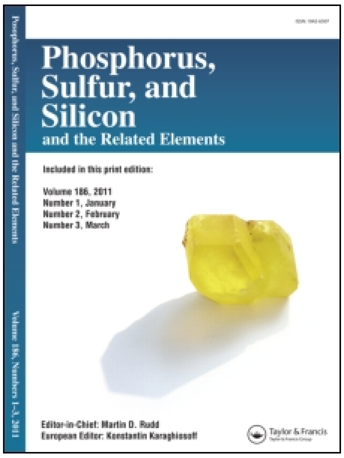

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THE REACTION OF 1,2,3-DIAZAPHOSPHOLE DERIVATIVE WITH PROPYNOL

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Two-coordinated phosphorus compound **1** reacted with propynol to form a tri-coordinated phosphorus compound **2**, which rearranged to tetra-coordinated phosphorus compound **3**. **3** was confirmed by ^{1}H, ^{31}P NMR, IR and MS. The mechanism of the rearrangement was verified by kinetic studies of ^{31}P NMR and FT-IR.

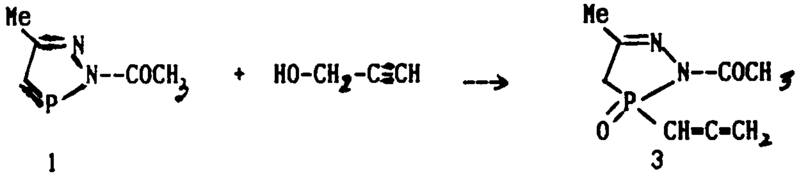
Key words: Diazaphosphole; reaction; kinetics; mechanism

INTRODUCTION

Two-coordinated phosphorus compounds have been developed extensively over the last 20 years and their electronic and structural variants have attracted the interests of numerous synthetic and structural chemists.[1–4] The syntheses of 1,2,3-diazaphospholes have been reported previously.[5] In this paper the reaction of 2-acetyl-5-methyl-1,2,3-diazaphosphole (**1**) with propynol is described.

RESULTS AND DISCUSSION

2-Acetyl-5-methyl-1,2,3-diazaphosphole (**1**) reacted with propynol to yield 2-acetyl-3-allenyl-5-methyl-1,2,3-diazaphosphole 3-oxide (**3**) as shown in Scheme 1.



1 3

Scheme 1

In order to establish the mechanism of this reaction, the progress of the reaction was studied using ^{31}P NMR spectroscopy. When **1** reacted with propynol in 1:1 molar ratio, the ^{31}P NMR spectra were recorded continuously and the repetitive ^{31}P NMR tracings was obtained, shown in Figure 1.

In Figure 1, Pn represents ^{31}P NMR spectra taken at various times and *tn* = [to + (*n* − 1) × 500] Sec.Po is the ^{31}P NMR spectrum of **1** and Pe is the ^{31}P NMR spectrum recorded at the end of the reaction (12h.).

The ^{31}P NMR chemical shifts for **1** and **3** are δ 237 and δ 34 ppm, respectively. When *t* = to, (i.e., P1) there was no signal at δ 237 ppm but a very small peak at

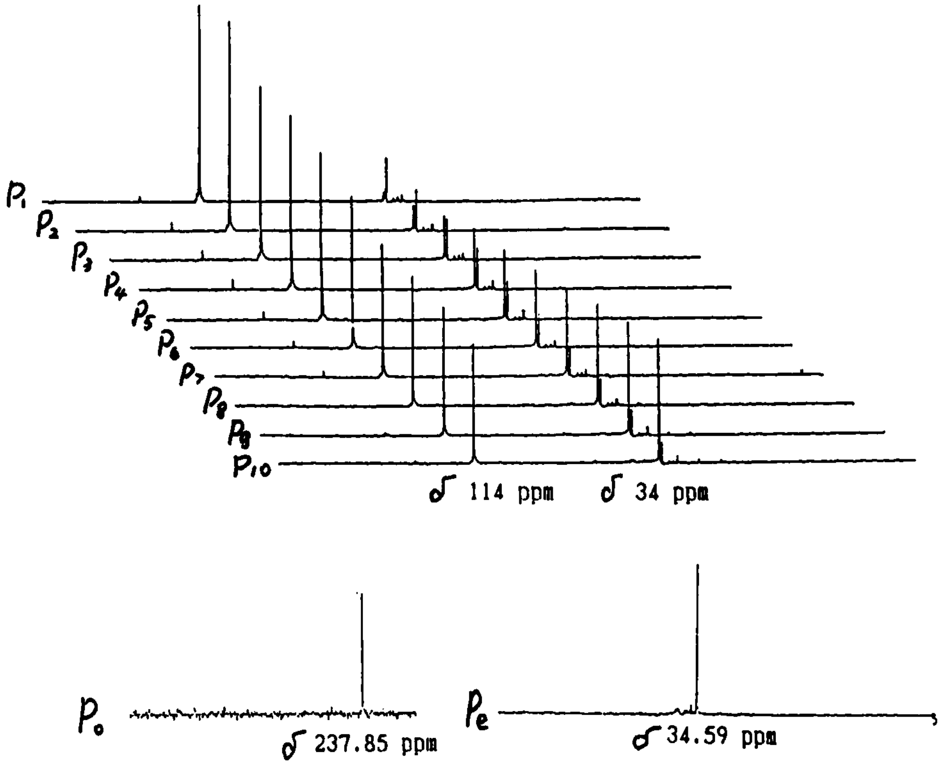
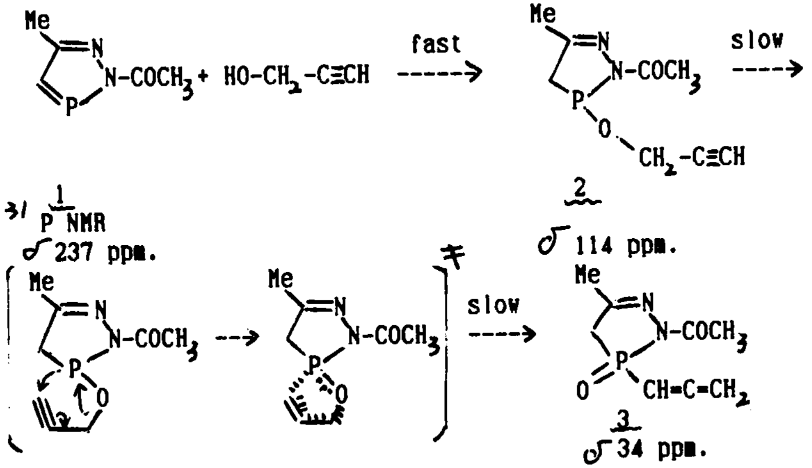


FIGURE 1 ^{31}P NMR Study of the Reaction between Diazaphosphole 1 and Propynol.



Scheme 2

δ 34 ppm and an intense peak at δ 114 ppm. The ^{31}P NMR spectra showed that **1** reacted with propynol spontaneously to form **3** and an intermediate **2** (δ 114 ppm.). From to → *t q* (see P1 to P10) the ^{31}P NMR spectra indicated that the amount of **2** decreased and that of **3** increased. When the reaction was completed, only **3** (δ 34 ppm.) could be detected (see Pe).

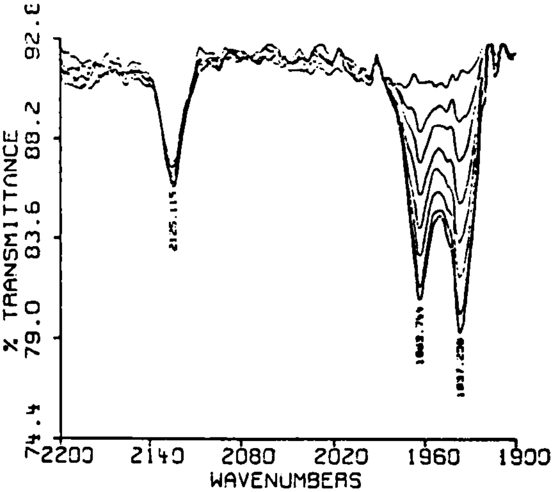


FIGURE 2 FT-IR Study of the Reaction between Diazaphosphole **1** and Propynol.

From the ^{31}P NMR observations, a reasonable mechanistic rationale can be presented. **1** reacted rapidly with propynol to yield **2** which then rearranged to **3** slowly through a pericyclic transition state as described below, shown in Scheme 2.

The repetitive FT-IR tracings, shown in Figure 2, are consistent with these interpretations.

In Figure 2, the absorption at 2125 cm^{-1} is assigned to —C≡C— group of **2** because **1** reacted with propynol very fast to form **2**, and the absorptions at 1963 and 1937 cm^{-1} are characteristic of the —C=C=C— group in **3**. The intensity of the absorption at 2125 cm^{-1} decreased and the intensity of the absorptions at 1963 cm^{-1} and 1937 cm^{-1} increased gradually. This indicates that **2** rearranges slowly to **3** as discussed previously.

The similar mechanism was suggested for the reaction of phosphorous trichloride with acetylenic alcohols.[6-8]

EXPERIMENTAL

NMR spectra were recorded on the JEOL FX-900 spectrometer at 90 MHz (^{1}H, TMS, int.) and 36.19 MHz [^{31}P, 85%, H_3PO_4 (aq.), ext.]. The kinetic study was manipulated according to the automatic program of the spectrometer itself. Wait 500 seconds.times 100. Infrared spectra were recorded on 170-SX instrument. MS was obtained at 70 ev on VG.ZAB-HS instrument. The solvent was freshly distilled. Melting points were uncorrected. The synthesis of **1** was according to literature.[9]

Synthesis of **3**. 0.38 g (0.0068 mol) propynol is added dropwise to a solution of 0.97 g (0.0068 mol) **1** in 30 ml CH_2Cl_2 under nitrogen atmosphere at room temperature, then the solution is kept stirring for 12 h. The excess solvent is removed in vacuo till the solution turned slightly turbid. The mixture is placed in the refrigerator and **3** crystallizes from the solvent as white crystals which are filtered and dried in vacuo with the yield of 0.50 g, 61%. m.p. 86–8°C. ^{31}P NMR δ 34.59 ppm. ^{1}H NMR δ 2.06 (s, 3H, N=C—CH_3); 2.30 (s, 3H, O=C—CH_3); 2.78–2.98 (*m*, 2H, P—CH_2); 5.10 (d.d, $^{4}J_{H\text{-}H}$, 7.2 Hz, $^{4}J_{P\text{-}H}$, 12.6 Hz, 2H, =CH_2): 5.88 (d.t, $^{2}J_{P\text{-}H}$, 7.2 Hz, $^{4}J_{H\text{-}H}$, 7.2 Hz, 1H, CH=). Mass spectrum, m/z 198 (M^+, 12.6%), 43, (100%). IR Spectrum, ν max, C=O, 1665 cm^{-1}: P=O, 1251 cm^{-1}; C=C=C, 1957 cm^{-1} and 1936 cm^{-1}.

The kinetic study with ^{31}P NMR. 0.0480 g (0.34 mmol) **1** in 0.5 ml $CDCl_3$ is added to 0.0189 g (0.34 mmol) propynol placed in a stoppered NMR sample tube in nitrogen atmosphere, ^{31}P NMR spectra are taken immediately.

The Kinetic study with IR. 0.0224 g (0.4 mmol) propynol is added to 0.0568 g (0.4 mmol) of **1** dissolved in 4 ml CH_2Cl_2 in situ IR cell, IR spectra are taken immediately, and then recorded every 66 seconds.

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