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# Cyclization of N-Propargylaminophosphines—New Method for Synthesis of 2,5-dihydro-1,2-azaphospholes

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## ABSTRACT

*The reaction of N-methyl-N-propargylamine with dialkoxy-chlorophosphines* **1a–e** *gave N-dialkoxyphosphinyl-N-propargylammonium salts* **2a–e** *which, by heating, undergo cyclization to new five-membered azaphosphole derivatives* **4a–e**.

## *INTRODUCTION*

It is well known that the reaction of dialkoxychlorophosphines with N-methylpropargylamines in the presence of triethylamine leads to stable N-methylpropargylaminophosphines which do not undergo an acetylene-allene rearrangement even at 100°C [1,2], as their O-analogues do [3–5].

## *RESULTS AND DISCUSSION*

In the present article, we describe the results of our studies on the generally familiar reaction of N-methyl-N-propargylamine with dialkoxychlorophosphines **1a–e** but this time in the absence of external base. Here, the base was the amino group of the reagent which therefore led to the formation of the ammonium salts **2a–e** as products. Upon heating of the salts **2a–e**, a heterocyclization reaction took place, leading to the azaphospholes **4a–e**.

The rearrangement of each **2a–e** to the respective **4a–e** conceivably proceeds *via* an intramolecular transfer of a proton from nitrogen to carbon and subsequent addition of the phosphorus to the triple bond to give each cyclic phosphonium intermediate **3a–e**, followed by an Arbuzov reaction (second step) to give each final product.

Each dialkoxychlorophosphine **1a–e** was treated with N-methyl-N-propargylamine in methylene chloride at −5–0°C. After addition of the reagent, a white precipitate of each ammonium salt **2a–e** was observed. During reflux of each reaction mixture, the precipitate disappeared. The NMR spectra of the crude products show that cyclization of **2a–e** to form the respective azapholes took place.

The structures of **4a–e** were confirmed by their $^1H$ and $^{31}P$ NMR and IR spectra as well as by elemental analyses. In the $^1H$ NMR spectra (see Table 1), the signals for $H^3$ and $H^4$ protons appear at low field as two doublets ($H^3$) and two triplets ($H^4$), characteristic of azaphosphole derivatives [6–8]. A multiplet in the range of $\delta$ = 3.74–3.93 for the $H^5$ protons was observed. Furthermore, the doublet for the N-$CH_3$ group and other signals for the alkoxy group on phosphorus were also observed.

The IR spectra of **4a–e** exhibit characteristic absorption bands for the phosphoryl group, $C^3$–$C^4$ double bond and P–N–C moiety.

The new heterocyclization described above is a simple method for synthesis of azaphosphole derivatives. Further work is in progress to examine and extend the synthetic potential of the reaction and uses of the products.

## *EXPERIMENTAL*

### *Analytical Methods*

The $^1H$ and $^{31}P$ NMR spectra were run on a Jeol JNM-PS-10 (100 MHz) spectrometer at the Technical University of Sofia, Bulgaria, and on a Jeol FX-90Q (100 MHz) spectrometer at the University of Copenhagen, Denmark. The IR spectra were re-



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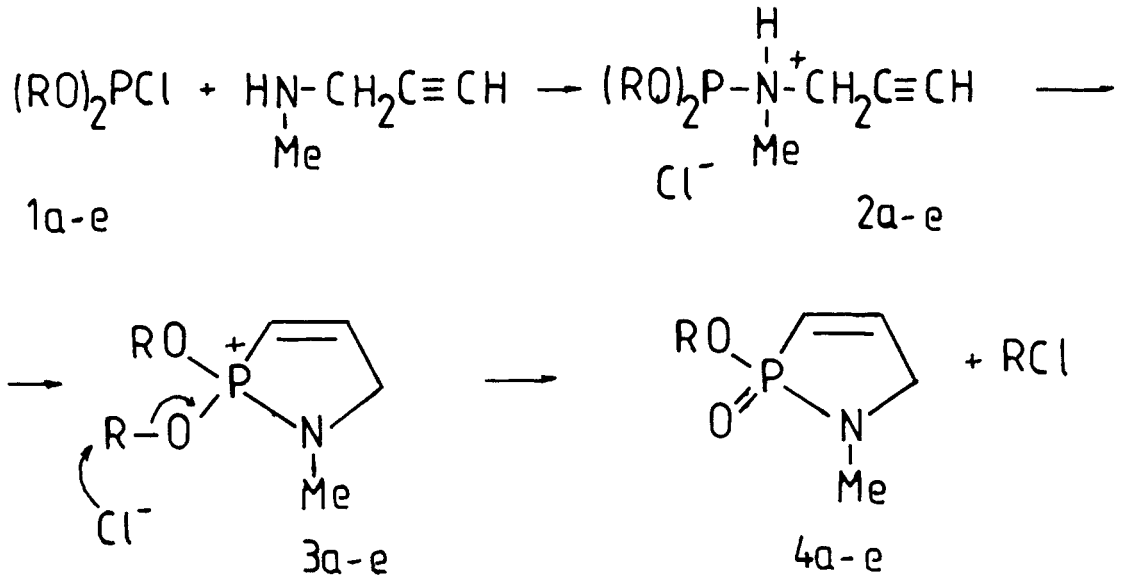

**SCHEME**

**TABLE 1** $^{1}H$ and $^{31}P$ NMR and IR spectral data for **4a–e**

| No. R | Chemical Shift, δ | | | $^{31}P$ | Coupling Constant, Hz | | IR, $cm^{-1}$ P = O (C = C) |
|---|---|---|---|---|---|---|---|
| | $H^3$ ($H^4$) | $H^5$ (N–Me) | R | | $H^3$–P ($H^4$–P) | $H^3$–$H^4$ ($H^4$–$H^5$) | |
| **4a** Me | 6.06 | 3.70 | $CH_3$-2.88 | 38.6 | 28.6 | 9.0 | 1225 |
| | (7.0) | (2.79) | | | (42.1) | (2.1) | (1587) |
| **4b** Et | 6.05 | 3.74 | $CH_3$-2.88 | 38.9 | 29.0 | 9.0 | 1230 |
| | (7.0) | (2.79) | $CH_2$-3.93 | | (42.2) | (2.1) | (1589) |
| **4c** Pr | 6.06 | 3.72 | $CH_3$-2.87 | 38.7 | 29.0 | 9.0 | 1230 |
| | (7.0) | (2.79) | $CH_2$-3.92 | | (42.0) | (2.2) | (1591) |
| **4d** Pr$^i$ | 6.06 | 3.74 | $CH_3$-1.18 | 38.9 | 28.7 | 9.0 | 1225 |
| | (7.0) | (2.78) | CH-3.27 | | (42.1) | (2.1) | (1586) |
| **4e** Bu$^i$ | 6.05 | 3.72 | $CH_3$-1.22 | 38.8 | 28.8 | 9.0 | 1223 |
| | (7.1) | (2.79) | | | (42.2) | (2.2) | (1590) |

corded on an IR-75 spectrophotometer, Karl-Zeis, Jena.

### *Starting Materials*

The dialkoxychlorophosphines **1a–e** were synthesized by following the procedure described earlier (9). The N-methyl-N-propargylamine was supplied by [Ventron GmbH, Karlsruhe] Germany.

### *Synthesis of 1-methyl-2-alkoxy-2-oxo-2,5-dihydro-1,2-azaphospholes* **4a–e**

*General Method.* To a solution of 5 mmol of each dialkoxychlorophosphine **1a–e** in 20 mL methylene chloride was added dropwise a solution of 5 mmol N-methyl-N-propargylamine in the same solvent at −5–0°C. After 1 hour, the reaction mixture was heated to boiling until the precipitate dissolved. The solvent was removed (water pump), and the residue was distilled. After distillation, the products crystallized.

All operations were carried out under argon. **4a** $C_5H_{10}NO_2P$, bp °C/1 mm Hg 70–2. Calc.: P, 21.05; N, 9.51. Found: P, 21.00; N, 9.49. Yield: 3.67 g (50%). **4b** $C_6H_{12}NO_2P$, bp °C/1 mm Hg 73–4. Calc.: P, 19.22; N, 8.68. Found: P, 19.13; N, 8.60. Yield: 3.57 g (45%). **4c** $C_7H_{14}NO_2P$, bp °C/1 mm Hg 75–6. Calc.: P, 17.67; N, 7.99. Found: P, 17.59; N, 7.91. Yield: 3.62 g (44%). **4d** $C_7H_{14}NO_2P$, bp °C/1 mm Hg 77–9. Calc.: P, 17.67; N, 7.99. Found: P, 17.60; N, 7.93. Yield: 4.53 g (55%). **4e** $C_8H_{16}NO_2P$, bp °C/1 mm Hg 78–9. Calc.: P, 16.37; N, 7.40. Found: P, 16.31; N, 7.22. Yield: 4.53 g (48%).

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