The reaction of 1,3-dibutyl-2-ethoxy-4,5-dimethyl-2-oxo-1,3,2-diazaphosphol-4-ene with tetracyanoethylene

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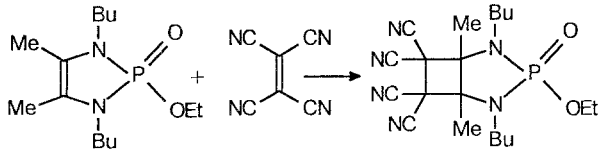
The reaction of 1,3-dibutyl-2-ethoxy-4,5-dimethyl-2-oxo-1,3,2-diazaphosphol-4-ene with tetracyanoethylene gives 6-amino-1,3-dibutyl-5-cyano-2-ethoxy-4-(1-imino-2-cyanoethyl)-2-oxo-1,3,2-diazaphosphindane.

Key words: tetracyanoethylene, cycloaddition.

Previously[1] we demonstrated that the reaction of α-diimines with phosphorous chlorides results in 1,3,2-diazaphospholenes, a new class of cyclic phosphorus- and nitrogen-containing compounds. One of the reaction centers of 1,3,2-diazaphospholene is the C=C bond. It was of interest to study the chemical behavior of these compounds toward tetracyanoethylene, one of the most active reagents in adding to the double bond. It is known that 1,3-diaza(oxaza)-2-E-cyclopent-4-enes (E = Si, Ge, or C) enter [2+2]-cycloaddition reactions.[2–4] In some cases, the cycloaddition products incorporating a four-membered ring have been isolated and characterized. Until now, similar reactions involving phospholenes have not been reported in the literature. The only data available for phosphorus-containing acyclic compounds[5] concern the addition of tetracyanoethylene to dipropyl *N*-butyl-*N*-(2-methyl-2-propenyl)amidophosphite to give a [2+2]-cycloaddition product.

We studied the reaction of 1,3-dibutyl-2-ethoxy-4,5-dimethyl-2-oxo-1,3,2-diazaphosphol-4-ene (**1**) with tetracyanoethylene (**2**). The reaction occurs at room temperature in a benzene solution to give a crystalline compound whose ^{31}P NMR spectrum displays one signal at δ +16 (in $CHCl_3$). The mass spectrum of the reaction product displays a molecular ion peak with *m/z* 416.209 corresponding to the composition $C_{20}H_{29}N_6O_2P$ (calculated: 416.2084), *i.e.*, the 1:1 addition product.

Scheme 1



1 **2** **3**

One could assume that the reaction of compound **1** with **2** occurs by [2+2]-cycloaddition to give bicyclic product **3** (Scheme 1).

However, the ^1H NMR and IR spectral data for the compound obtained do not confirm structure **3**. We performed a detailed analysis of the IR spectra of the starting compounds, the crystalline reaction product, and its $1 \cdot 10^{-3}$ *M* solution in $CHCl_3$. The spectrum of the reaction product did not display any substantial changes in comparison to the starting compounds (an

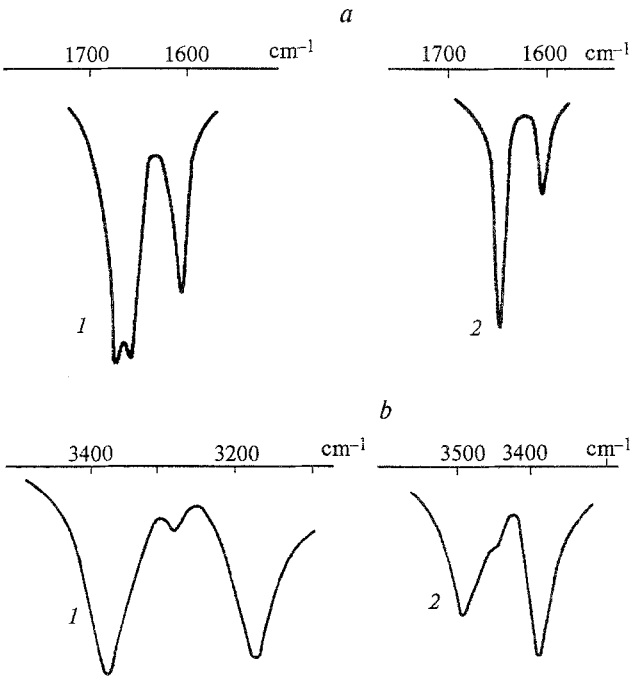


Fig. 1. IR spectra of compound **7** as a crystal (*1*) and as a solution in chloroform (*2*) in the 1600—1700 cm^{-1} (*a*) and 3100—3500 cm^{-1} regions (*b*).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 303—305, February, 1994.

1066-5285/94/4302-0283 $12.50

intense ν(P=O) band at 1250 cm^{-1}) in the 1300 cm^{-1} region, where the vibrations of the phosphoryl group are clearly observed. Moreover, strong bands are retained at ~980 and ~1030 cm^{-1} due to vibrations of the O—C—C bonds in the P—OEt moiety. The conclusion can be drawn that the reaction actually involves the C=C bond in diazaphospholene **1** and does not involve the phosphorus-containing part of the molecule. On the other hand, the spectra of the reaction product contain three new (in comparison to the original compounds) intense bands for double bonds at ~1610, 1660, and 1680 cm^{-1}. The latter degenerate to a doublet at ~1604 and 1654 cm^{-1} in the $CHCl_3$ solution (Fig. 1, *a*). Probably, the complex nature of the spectrum for the crystalline state is explained by the Davydov splitting of the high-frequency component.[6] The bands mentioned above are located in the region of the C=C, C=N, and C=O type unsaturated bonds.

Another interesting region of the spectrum, where new bands absent in the spectra of the starting compounds **1** and **2** appear, is at 3100—3500 cm^{-1}, where an intense doublet at ~3170 and ~3375 cm^{-1} and a weak peak at 3280 cm^{-1} are observed for the crystalline compound. In the $CHCl_3$ solution, the doublet is displaced to 3389 and 3490 cm^{-1}, and a shoulder at ~3450 cm^{-1} is observed (Fig. 1, *b*). The positions of the bands and their absorbances are in good agreement with empiric correlations derived for the ν_s- and ν_{as}-oscillations of the amino groups directly attached to the aromatic ring.[7] Moreover, the presence of an additional band in the region of the ν(N—H) stretching vibrations makes it possible to assume that the reaction product has at least one more N—H bond along with those in the NH_2 group. On the other hand, the IR spectrum of the considered compound contains an absorption band at ν ~2221 cm^{-1} (crystal) or 2213 cm^{-1} (in $CHCl_3$) of moderate intensity. This band belongs to the stretching vibrations of the C≡N group.

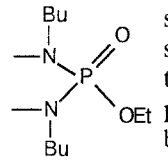
It should be noted that the spectrum of tetracyanoethylene contains a doublet at ~2235 and 2270 cm^{-1} referring to the inphase and antiphase vibrations of the four cyano groups. Thus, it could be assumed that a molecule of the product contains either one cyano group or several cyano groups, which interact with one another in a different manner than in tetracyanoethylene. The number of cyano groups was determined by recording and analyzing the IR spectra of benzonitrile (**4**) and acrylonitrile (**5**) in $CHCl_3$. From the Lambert—Beer law

$$D = \varepsilon \cdot c \cdot l,$$

where D is the optical density, c is the concentration, and l is the cell width, one can easily determine the extinction coefficient of one cyano group, ε_0, according to the equation:

$$D = \varepsilon_0 \cdot n \cdot c \cdot l$$

and then assess the number of cyano groups in the molecule. We calculated ε_0 for compounds **4** and **5** and used its mean value to conclude that a molecule of the compound of interest contains two cyano groups.



6

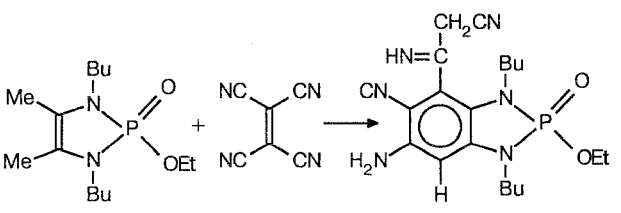
To sum up the results obtained by studying the IR spectra, it may be assumed that the product of the reaction of tetracyanoethylene with 1,3,2-diazaphospholene contains C=C and C=N bonds, an NH_2 group bonded with the aromatic ring, an N—H bond, two cyano groups, and fragment **6**.

The presence of fragment **6** in the molecule makes it possible to exclude from consideration a C=O bond, which could appear due to any rearrangements changing the oxygen-containing part of the molecule. Hydrolysis of the product, which also could result in a C=O bond, is ruled out on the basis of the mass spectral data for the compound under study; in general, these data confirm the conclusions based on the IR spectra. The high stability of the molecular ion indicates that the product formed is conjugated in character. Deuterium exchange using ethanol labeled with deuterium at the OH group showed the peak of the $[M]^+$ ion with *m/z* 416 shifted by three units towards higher mass. The presence of three active hydrogen atoms in the product is consistent with the fact that it contains one NH_2 and one NH group. On the other hand, the main process during dissociative ionization of the compound studied is the abstraction of the $^{\cdot}CH_2C{\equiv}N$ radical from the molecular ion. This fragmentation of the $[M]^+$ ion is confirmed by analyzing the kinetic energies of the ions and by the elemental composition of the $[M-40]^+$ ion. The ease of fragmentation implies that the CH_2 group in this radical is directly bonded to a conjugated system. Moreover, it should be noted that the fragmentation of phosphates, including 1,3,2-diazaphospholenes,[8] involves the abstraction of a C_2H_4 molecule or a C_2H_3 radical from $[M]^+$. This process is unlikely for the product studied.

Thus, based on the analysis of the IR and mass spectral data, the structure of 6-amino-1,3-dibutyl-5-cyano-2-ethoxy-4-(1-imino-2-cyanoethyl)-2-oxo-1,3,2-diazaphosphindane (**7**) can be assigned to the product of the reaction of compounds **1** and **2** (Scheme 2).

The ^1H NMR spectrum in CD_2Cl_2 confirms the structure of compound **7**. It does not contain signals typical of the methyl protons at the C=C bond[8] in the starting diazaphospholene **1**. In addition to the signals

Scheme 2



1 **2** **7**

corresponding to the butyl and ethoxy groups observed in the spectra of both compounds **1** and **7**, three new singlets appear with chemical shifts 2.84 ppm (NH_2-protons), 4.07 ppm ($-CH_2CN$), and 5.92 ppm (the methine proton in the aromatic ring). The proton of the =N—H imine group could not be identified.

Experimental

IR spectra were recorded on a Bruker IFS-119 Fourier spectrometer with 1 cm^{-1} resolution, using a KBr-based light separator. Cells with KBr windows were used for recording the spectra of liquids. Spectra of solid samples were recorded in KBr pellets. The spectral information obtained was processed using the software supplied with the instrument.

The mass spectrum of compound **7** was recorded on an MX-1310 spectrometer with an energy of ionizing electrons of 30 eV. The compound was introduced directly into the ion source. The precise masses were determined by secondary processing of the mass spectra on an SM-4 computer using reference peaks of perfluorokerosene. The error in determining m/z did not exceed $5 \cdot 10^{-6}$ amu. The deuterio-analog of compound **7** was obtained in an exchange reaction by mixing a sample of the compound with a large excess of C_2H_5OD in an ampule followed by rapid evacuation.

The ^{31}P spectrum was recorded on a nonstandard KGU-4 instrument with 10.2 MHz working frequency using 85 % phosphoric acid as the external standard. The ^1H NMR spectrum was recorded on a Varian T-60 spectrometer (60 MHz) using TMS as the internal standard.

The synthesis was carried out under argon using absolute solvents.

6-Amino-1,3-dibutyl-5-cyano-2-ethoxy-4-(1-imino-2-cyanoethyl)-2-oxo-1,3,2-diazaphosphindane (7). A solution of compound **2** (1.28 g) in benzene (10 mL) was added to a solution of compound **1** (2.88 g) in benzene (10 mL) at ~20 °C. After 3 days, the solvent was removed, and the residue (yield 3.81 g, 91 %) was recrystallized from a dichloromethane—hexane mixture to give 2.25 g of white crystals, m.p. 232—234 °C. Found (%): C, 57.57; H, 7.31; N, 20.05; P, 7.21. $C_{20}H_{29}N_6O_2P$. Calculated (%): C, 57.69; H, 6.97; N, 20.19; P, 7.45.

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Received December 7, 1993