MECHANISM OF THE REACTIONS OF DIAZAPHOSPHOLES WITH DIAZO COMPOUNDS

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The cycloaddition of diphenylcarbene at the P=C bond of diazaphosphole proceeds in the reaction of diphenyldiazomethane with 2-acetyl- and 2-phenyl-5-methyl-1,2,3-diazaphospholes [1, 2]. The formation of the bicyclic diazaphospholines may be described both by the direct addition of diphenylcarbene to the P=C bond and by the 1,3-dipolar cycloaddition with the subsequent formation of nitrogen. The catalytic and thermal reactions of diazaphospholes with Ph_2CN_2 were investigated in the present work in order to explain the mechanism of these reactions.

The catalytic reactions of 2-acetyl-5-methyl-1,2,3-diazaphosphole (AMDAP) and 2-phenyl-5-methyl-1,2,3-diazaphosphole (PMDAP) with Ph_2CN_2 were carried out in benzene at 80°C in the presence of $CuSO_4$. No formation of the phosphirane-containing bicycles (I), to confirm the carbene mechanism, was observed.



In the case of PMDAP, the benzophenazine (II) and the initial PMDAP were isolated quantitatively. This indicates that the diphenylcarbene reacts with Ph_2CN_2 , and not with PMDAP, under the given conditions. Diphenylcarbene reacts with AMDAP with the formation of two phosphorus-containing products; this is indicated by the two signals of $\delta^{31}P$ 110 and 218 ppm in the ^{31}P NMR spectrum of the mixture after carrying out the reaction under catalytic conditions. The thermal reactions of AMDAP with Ph_2CN_2 were performed at 75°C. They are accompanied by the instantaneous change of the color of the reaction mixture from dark red to yellow, and the separation of nitrogen. The reactions are very sensitive to insignificant changes in the experimental conditions and are difficult to reproduce. A phosphiranecontaining bicycle is obtained in quantitative yield in some experiments; a derivative of phosphapyrazoline could be isolated in a series of cases. The conditions of the reactions exclude the carbene mechanism, since Ph_2CN_2 is stable at temperatures below 85°C [3]. Therefore, the formation of the bicyclic phosphiranecontaining, compounds under the conditions of the thermal reactions indicates the 1,3-dipolar mechanism of the cycloaddition of diazo compounds to diazaphospholes.

In a series of cases, the intense signal with $\delta^{31}P$ 52 ppm and the weak signal with $\delta^{31}P$ 12 ppm were observed together with $\delta^{31}P - 93$ ppm of the phosphirane-containing bicycle (Ib) in the ³¹P NMR spectrum of the reaction mixture.



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The signal at δ^{31P} 52 ppm appertains to the crystalline product with the mp 89-90°C which is the 1:1 adduct of the addition of Ph_2CN_2 to AMDAP according to the data of the elemental analysis. The intense band of vNH at 3240 cm⁻¹ is present in its IR spectrum; this indicates that the signal with δ^{31P} 52 ppm appertains not to the intermediate Δ' -phosphapyrazoline product (III), but to the product of its isomerization (IV).

Therefore, the first stage of the reaction of AMDAP with Ph_2CN_2 results in the formation of the extremely unstable primary product of the [2 + 3]-cycloaddition (III). This is stabilized in two ways - firstly, by the separation of nitrogen and the formation of the bicycle (I), and secondly, by the migration of a proton from carbon to nitrogen and the formation of the Δ^2 -phosphapyrazoline derivative (IV).

When 2-acetyl-4-methyl-8,8-diphenyl-1-phospha-2,3,6,7-tetraaza[3,3,0]octa-3,5-diene (IV) is treated with solvents at room temperature, it is converted to a powder with the extended mp of 60-74°C. The presence of the absorption band at vPH 2330 cm⁻¹ in its IR spectrum and of the signal with δ^{31} P 11.3 ppm and J_{PH} = 600 Hz in the ³¹P NMR spectrum confirms the structure (V). The product could not be isolated in an analytically pure form, although the percentage of N₂ found corresponds exactly with the theoretical. The Δ^2 -phosphapyrazoline derivative (IV) was also obtained by the reaction of 2-acetyl-5-methyl-3-chloro-1,2,3-diazaphospholine with Ph₂CN₂. The reaction proceeds exothermally with the liberation of N₂, and is accompanied by an instantaneous color change. The presence of several signals in the ³¹P spectrum of the reaction mixture (δ^{31} P 238 very strong, 109 medium, 70 strong, 12 very weak) indicates its complexity. The very intense signal with δ^{31} P 238 ppm for AMDAP is surprising; the formation of AMDAP resulted from the dehydrochlorination of the chlorodiazaphospholine in the presence of Ph₂CN₂.



Triethylamine was previously utilized as a dehydrochlorinating agent in the synthesis of N-substituted 1,2,3-diazaphospholes [4]. The signal of the initial chlorodiazaphospholine at $\delta^{31}P$ 109 ppm disappears with the further addition of Ph₂CN₂; a new signal at $\delta^{31}P$ 52 ppm appears in its place, and the intensity of the AMDAP signal ($\delta^{31}P$ 238 ppm) decreases. The Ph₂CN₂ adds to the P=C bond, which formed in the reaction to AMDAP, and the derivatives (IV) of Δ^2 -phosphapyrazoline was obtained via the intermediate product (III) of the [2 + 3]cycloaddition. The signal at $\delta^{31}P$ 70 ppm in the ³¹P NMR spectrum of the reaction mixture probably appertains to the phosphaimino derivatives (VI), which could not be isolated in a pure form. The product contains chlorine (positive Beilstein test); when it was distilled in a high vacuum, the benzophenazine (II) and a polymer were isolated. Preparative chromatography showed that the substance is changed on silica gel. Therefore, the reaction of 2-acetyl-5-methyl-3-chloro-1,2,3-diazaphospholine with diphenyldiazomethane proceeds in two directions. These are firstly the dehydrochlorination with the formation of AMDAP, and secondly the addition of Ph_2CN_2 to AMDAP. It was established that benzophenazine is formed by the action of HCl on Ph_2CN_2 . However, benzophenazine is not formed in the reaction of chlorodiazaphospholine with Ph_2CN_2 with the 1:1 ratio of the reagents, although the separation of HCl also takes place. The reaction with the chlorodiazaphospholine and AMDAP evidently proceeds more rapidly under these conditions than the decomposition by HCl to diphenylcarbene. The formation of benzophenazine was observed by performing the reaction in an excess of Ph_2CN_2 . The reaction of the chlorodiazaphospholine with Ph_2CN_2 in the presence of Et_3N leads quantitatively to the phosphirane-containing bicycle (Ib). Triethylamine assists the formation of AMDAP, which participates in the 1,3-dipolar cycloaddition with Ph_2CN_2 .



The intermediate Δ^1 -phosphapyrazoline derivative (III) isomerizes to the Δ^2 -phosphapyrazoline derivative (IV) in an acidic medium; the liberation of nitrogen and the formation of the bicycle (Ib) proceed in the presence of Et₃N.

EXPERIMENTAL

The IR spectra were taken on the UR-10 and "Specord UR-75" spectrometers. The ³¹P NMR spectra were taken on the KGU-4 and "Bruker CXP-250" spectrometers. The ¹H NMR spectra were taken on a "Bruker CXP-100" spectrometer. The mass spectra were taken on a MAT-212 mass spectrometer.

Interaction of PMDAP with Ph_2CN_2 . To the mixture of 0.54 g of PMDAP and $CuSO_4$ in 20 ml of C_6H_6 was slowly added, at 80°C, the solution of 0.6 g of Ph_2CN_2 . The benzophenazine (II) (1 g), with the mp 162-163°C, was isolated. A mixing test with the known sample did not give a depression of the mp. Distillation yielded PMDAP [bp 80-83°C (0.06 mm)] which was characterized by the ³¹P NMR spectrum ($\delta^{31}P$ 226 ppm).

Interaction of AMDAP with Ph_2CN_2 . a) To the solution of 0.6 g of AMDAP in 20 ml of C_6H_6 was added the dark red solution of 0.8 g of Ph_2CN_2 in 15 ml of C_6H_6 at 75°C for 1.5 h. A rapid change in the color of the reaction mixture and the liberation of nitrogen occurred. Compound (Ib) was isolated quantitatively; it had the mp 145-146°C (from EtOH), and $\delta^{31}P - 93$ ppm (in CH_2CI_2). The IR spectrum (v, cm⁻¹) was as follows: 710 strong, 725, 770, 1490, 1605 medium, 3025, 3060 weak (Ph), 1575 weak (C=N), 1650, and 1660 strong (C=O). Found: C 70.09, H 5.95, N 9.62, and P. 9.91%. Molecular mass 308 (from the mass spectrum). $C_{18}H_{17}PN_2O$. Calculated: C 70.12, H 5.51, N 9.09, and P 10.06%. Molecular mass 308.3.

b) To the solution of 0.6 g of AMDAP in 20 ml of C_6H_6 was added the solution of 0.8 g of Ph_2CN_2 in 15 ml of C_6H_6 at 75°C for 1.5 h. The change in the color of the reaction mixture and the liberation of nitrogen occurred. The light yellow residue of (Ib) was filtered off; the yield was 20%. The crystalline product (IV) was isolated from the filtrate after 24 h (75%); the mp was 89-90°C. It had $\delta^{31}P$ (C_6H_6) 52 ppm. The IR spectrum (ν , cm⁻¹) was as follows: 600, 700, 760, 790, 1050, 1350, 1360, 1380, 1420, 1650 (CO), and 3240 strong (NH). Found: P 8.65 and N 16.33%. $C_{18}H_{17}OPN_4$. Calculated: P 9.22 and N 16.66%. The product (IV) in pentane, hexane, CCl₄, ether, CH₃CN, CHCl₃, and other solvents transforms quantitatively to the product (V); (V) is a light yellow powder with the mp 60-74°C. It had $\delta^{31}P$ 11.3 ppm, J_{PH} = 600 Hz (C_6H_5 N). The IR spectrum (ν , cm⁻¹) was as follows: 640, 690, 720, 760, 1430, 1480, 1660, and 2330. Found: N 16.60 and P 10.01%. $C_{18}H_{17}OPN_4$. Calculated: N 16.65 and P 9.21%.

Interaction of Chlorodiazaphospholine with Ph_2CN_2 . a) To 2.4 g of chlorodiazaphospholine was added a solution of 2.61 g of Ph_2CN_2 in ether in the course of 40 min. A rapid change in the color of the reaction mixture and the vigorous liberation of nitrogen occurred. We filtered off 2.3 g of the Δ^2 -phosphapyrazoline (IV), which had the mp 89-90°C. The product (VI), with $\delta^{31}P$ 70 ppm, was isolated from the filtrate. The IR spectrum (v, cm⁻¹) was as follows: 610, 680, 730, 1010, 1065, 1420, 1470, 1580, 1655, and 1675.

b) to 1.65 g of chlorodiazaphospholine was added the mixture of 1.8 g of Ph_2CN_2 and 0.93 g of Et_3N in 25 ml of ether for 1 h at -10°C. The color of the reaction mixture changed from dark red to yellow; gas was evolved. Compound (Ib) was isolated quantitatively after filtering the solution and concentrate.

CONCLUSIONS

Diazaphospholes react with diazo compounds by the mechanism of 1,3-dipolar cycloaddition. The reaction of 2-acetyl-5-methyl-1,2,3-diazaphosphole with diphenyldiazomethane proceeds via the intermediate formation of the product of [2 + 3]-cycloaddition.

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PREPARATION AND THERMAL DECOMPOSITION OF 3,3,3-TRIPHENYL-

AND 3,3,3-TRIMETHYL-7,8-DIMETHYLBENZO[e]-2,4,3-DITHIASTIBEPIN

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Organic compounds of antimony containing Sb-S bonds in contrast to their oxygen analogs hardly exist in a combined state, and mercaptides of pentavalent antimony are thermally unstable [1]. Cyclic Sb(V) mercaptides have been little studied up to the present time. Stable cyclic five-membered mercaptides, obtained from dioxides of trimethyl- and triarylantimony with thioglycolic acids, have been described in [2]. A five-membered Sb(V) dimercaptide was obtained by oxidation of 2-chlorostibino-1,3-dithiacyclopentane [3]. There have not previously been any reports about seven-membered Sb(V) dimercaptides.

We have obtained the first examples of dithiastibepins by reaction of 1,2-dimethyl-4,5di(mercaptomethyl)benzene (I) with dichlorides or dialkoxides of triphenyl- and trimethylantimony (Scheme 1)



R = Ph (II), Me (III); R' = Me, Et.

3,3,3-Triphenyl- (II) and 3,3,3-trimethyl-7,8-dimethylbenzo[e]-2,4,3-dithiastibepin (III) were obtained as a result of these reactions. (II) and (III) were obtained in highest yield

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