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REACTION OF 2-[N,N-BIS(TRIMETHYLSILYL)]AMINO-4,5-BENZO-1,3,2-DIOXAPHOSPHOLANE WITH CARBOXYLIC ACID HALIDES

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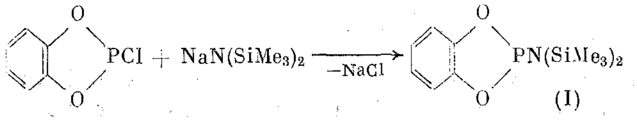
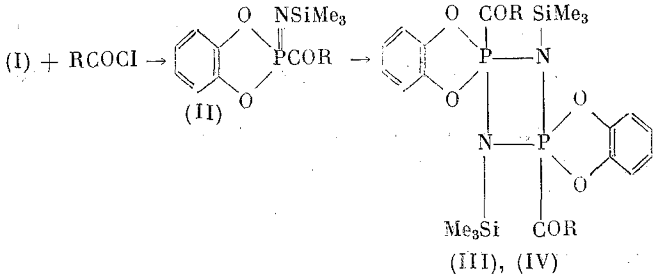
The reaction of N-alkyl and N-aryl-N-trimethylsilylamino-1,3,2-oxazaphospholanes with acetyl chloride proceeds with the participation of the nitrogen atom of the P—N system and leads to N,N-diphosphorylated primary amines. In the case of N,N-disilylated P(III) amido derivatives, the P-acylation products, namely, N-silylated imidophosphonates, are formed. Both reaction pathways proceed concurrently for N-acetyl-N-trimethylsilylaminophosphites [1].

In order to study the effect of the nature of the cyclic fragment on the direction of the acylation, we synthesized 2-[N,N-bis(trimethylsilyl)]-amino-4,5-benzo-1,3,2-dioxaphospholane (I) by the reaction of 2-chloro-4,5-benzo-1,3,2-dioxaphospholane with the sodium salt of hexamethyldisilazane.



Phospholane (I), in contrast to the analogous oxazaphospholanes, reacts with AcCl and PhCOCl to form not P-acetyl-N-trimethylsilylimidophosphonates (II) [1], but rather the products of their dimerization, namely, diazadiphosphetidines (III) and (IV) with $\delta\ ^{32}P = -58$ and -54 ppm, respectively.



The IR spectra have carbonyl bands at 1700 (III) and 1660 cm^{-1} (IV) and trimethylsilyl bands at 1255 cm^{-1} (III) and (IV) but lack absorption at 1300-1350 cm^{-1} characteristic for the $>P{=}N{-}Si$ group [2-4]. Thus, the introduction of a dioxaphenylene fragment at the phosphorus atom, which stabilizes the trigonal bipyramidal structure, results in the first example of the dimerization of the N-trimethylsilylphosphoimide bond [4].

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 spectrometer at 10.2 MHz relative to 85% H_3PO_4. The IR spectra were taken on a UR-20 spectrometer for KBr pellets.

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2-[N,N-Bis(trimethylsilyl)]amino-4,5-benzo-1,3,2-dioxaphospholane (I). A sample of 17.5 g catechol chlorophosphite was added dropwise with stirring to an ethereal solution of 18.3 g of the sodium salt of hexamethyldisilazane cooled to −20°C. The mixture was warmed to ~20°C and maintained for 12 h. After separation of the precipitate and removal of the solvent, distillation gave 16.3 g (55%) (I), bp 78°C (0.05 mm), n_D^{20} 1.5190, d_4^{20} 1.0601, ^{31}P 174 ppm. Found, %: C 48.53; H 7.33; P 10.14; Si 18.32. $C_{12}H_{22}NO_2PSi_2$. Calculated, %: C 48.16; H 7.35; P 10.36; Si 18.69.

1,3-Bis(trimethylsilyl)-2,4,6-bis(dihydroxyphenylene)-2,4-diacetyl-1,3,2λ^5,4λ^5-diazadiphosphetidine (III). A mixture of 3 g (I) and 0.8 g acetyl chloride in 20 ml dry benzene was maintained at 20°C for 24 h to give 1.76 g (65%) (III), mp 132°C. Found, %: C 49.19; H 6.03; N 5.33; P 11.66; Si 10.51. $C_{22}H_{32}N_2O_6P_2Si_2$. Calculated, %: C 49.07; H 6.00; N 5.24; P 11.52; Si 10.41.

1,3-Bis(trimethylsilyl)-2,4,6-bis(dihydroxyphenylene)-2,4-dibenzoyl-1,3,2λ^5,4λ^5-diazadiphosphetidine (IV). A sample of 3 g (I) was mixed with 1.41 g PhCOCl. The mixture crystallized after 12 h. Washing with benzene gave 2.01 g (61%) (IV), mp 157°C. Found, %: H 5.54; N 4.11; P 8.87; Si 8.10. $C_{30}H_{36}N_2O_6P_2Si_2$. Calculated, %: H 5.43; N 4.23; P 9.36; Si 8.45.

CONCLUSION

The reaction of 2-[N,N-bis(trimethylsilyl)]amino-4,5-benzo-1,3,2-dioxaphospholane with acetyl and benzoyl chlorides leads to the formation of silicon-containing diazadiphosphetidines.

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SYNTHESIS OF NEW ORGANOSILICON AND ORGANOGERMANIUM DERIVATIVES OF DIALLYLISOCYANURATE AND CYANURIC ACID

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In a continuation of work on the synthesis and investigation of the properties of heteroorganic symm-triazines [1] and in a search for new biologically active compounds and inhibitors of the nitrification of nitrogen fertilizers, we are the first to report the preparation of a series of derivatives of diallylisocyanurate and cyanuric acid containing disilanyl, disiloxane or carbofunctional organogermanium fragments. Thus, the heterogeneous reactions of the silver salt of diallylisocyanurate with pentamethylchlorodisilane or β-trialylgermylpropionyl chloride in ether or benzene solution in a sealed ampule at ~20°C over 70-80 h with rapid stirring (method A) gave high yields of the corresponding pentamethyldisilanyldiallylisocyanurate (I), β-(triethylgermyl)- (II) and β-(tributylgermyl)propionyldiallylisocyanurates (III).

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