REACTION OF BIS (HYDROXYMETHYL) PHENYLPHOSPHINE

WITH DIMETHYLFORMAMIDE DIMETHYLACETAL

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The reactions of bis(α -hydroxyalkyl)phenylphosphines with ethyl orthoformate [1] and ketone acetals [2] exclusively give 5-phenyl-1,3,5-dioxaphosphorins, while the reaction with aldehyde acetals [2] leads to a mixture of 5-phenyl-1,3,5-dioxaphosphorinanes and bis(α -alkoxyalkyl)phenylphosphines.

Among the various substituents in aldehyde acetals, special interest is found in the dimethylamino group, which by analogy with the alkoxy group in orthoformate esters, may facilitate the formation of 1,3,5-dioxaphosphorinanes in this reaction. The dimethyl-amino group has also been found to stabilize dicoordinated phosphorus compounds [3].

We have studied the reaction of bis(hydroxymethyl)phenylphosphine (I) with dimethylformamide dimethylacetal (II). In contrast to the reaction with ethyl orthoformate and acetals of furfural, benzaldehyde, acetaldehyde, acetone, cyclohexanone, acetophenone, and 2-butanone, which were carried out at 120-140°C [1, 2] with the elimination of ethanol, this reaction proceeded exothermally. The signal for the starting diol disappeared in the ³¹P NMR spectrum of the reaction mixture 30 min after the onset with the appearance with δ -50, -55, and 68 ppm in 3:10:1 intensity ratio. The signals at -50 and -55 ppm are related to stereoisomers of 2-dimethylamino-5-phenyl-1,3,5-dioxaphosphorinane (III) (the chemical shifts (CS) of the signals for the stereoisomers of 2-ethoxy-5-phenyl-1,3,5-dioxaphosphorinane in the ³¹P NMR spectrum are -48 and -50 ppm [1]), while the signal at 68 ppm is related to dimethylaminomethylenephenylphosphine (IV) (the CS of the signal for (II) in the ³¹P NMR spectrum is 68.4 ppm [3]). Upon vacuum distillation, the first fraction contained a 4:1 mixture of (III) and (IV) and the second fraction contained only (III).

$$\begin{array}{c} PhP(CH_2OH)_2 + (MeO)_2CHNMe_2 \rightarrow Ph-P & CH-NMe_2 + PhP=CHNMe_2 + MeOH \\ (I) & (II) & CH_2-O & (III) & (IV) \end{array}$$

Thus, the reaction of (I) with (II), in contrast to the reactions with other aldehyde acetals, gives a 1,3,5-dioxaphosphorinane as the major product, which suggests a new approach to phosphaalkenes.

The reported method for the preparation of (IV) is based on the reaction of phenylphosphine with (II) at 80°C and gives the product in 70% yield [3]. We have shown that an even more convenient method for the preparation of (IV) is the reaction of phenylphosphine with bis(dimethylamino)methoxymethane, which proceeds with 89% yield.

$$PhPH_2 + (Me_2N)_2CHOMe \rightarrow PhP = CHNMe_2 + Me_2NH + MeOH_{(IV)}$$

³¹P NMR spectroscopy indicates a 1:1 mixture of the monomer and dimer in the reaction product with CS -14 and 68 ppm, respectively.

Heating (IV) in benzene in the presence of excess 2,3-dimethylbutadiene gave a mixture containing 40% cycloaddition product [4]. Markovskii et al. [5] have reported that the $[4 + 2]_n$ cycloaddition involving phosphaalkenes depends on the nature of the diene [5]. Thus, we may expect that the replacement of 2,3-dimethylbutadiene in the reaction with (IV) by a diene with electron-withdrawing substituents would have a signifi-

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2116-2118, September, 1987. Original article submitted November 17, 1986. cant effect on the reaction conditions. In our previous work [6], we carried out the reaction of 2-acetyl-5-methyl-1,2-diaza-3-phosphole with hexachlorocyclopentadiene.

The reaction of (IV) with tetrachlorocyclopentadienone dimethylacetal proceeded quantitatively. The ^{\$1}P NMR spectrum of the reaction mixture taken 1 h after the onset of the reaction lacked the signal for (IV) but displayed a signal at -8 ppm. After chromatography, the PMR spectrum had signals for protons of C_{6H_5} , CH, CH_3O , and $(CH_3)_2N$ groups, indicating that it is 1,4,5,6-tetrachloro-7,7-dimethoxy-3-dimethylamino-2-phenyl-2-phospha-5-norbornene.



Upon distillation in vacuum, (V) dissociates into the starting compounds, which distill together and give product (V) in the receiver.

Experimental

The IR spectra were taken on a UR-20 spectrometer. The PMR spectra were taken on a Varian T-60 spectrometer at 60 MHz and 34.5°C with 10% concentration. The ³¹P NMR spectra were obtained on a YaMR-KGU-4 spectrometer at 10.2 MHz with proton decoupling and 30-50% concentration. The chemical shifts were given relative to 85% $\rm H_3PO_4$ and positive values indicate low field.

2-Dimethylamino-5-phenyl-1,3,5-dioxaphosphorinane (III). A sample of 5.6168 g (0.0472 mole) (II) was added to 4.018 g (0.0236 mole) (I) and the mixture evolved heat and turned bright yellow. After 1 h, the mixture was distilled in vacuum to give 3.085 g (58%) (III), bp 95-96°C (1.5 mm), δ^{31} P: -50 and -55 ppm. Found, %: C 58.71, H 5.24, N 6.13, P 13.72. C₁₁H₁₆PNO₂. Calculated, %: C 58.67, H 4.89, N 6.22, P 13.78.

Dimethylaminomethylenephenylphosphine (IV). A sample of 3.66 g (0.0277 mole) bis(dimethylamino)methoxymethane was added to 3.05 g (0.0277 mole) phenylphosphine. Gas evolution was noted and the mixture turned yellow. After 1 h, the mixture was distilled in vacuum to give 3.70 g (89%) (IV), bp 79-80°C (0.01 mm), δ^{31} P: 68 ppm.

 $\frac{1,4,5,6-\text{Tetrachloro-7,7-dimethoxy-3-dimethylamino-2-phenyl-2-phospha-5-norbornene}{\text{A sample of 2.86 g (0.0109 mole) tetrachlorocyclopentadienone dimethylacetal was added to 1.79 g (0.0109 mole) (IV). A black precipitate formed. After 2 h, the mixture was distilled in vacuum to give 4.02 g (86%) (V), bp 120-125°C (0.005 mm), <math>\delta^{31}$ P: -8 ppm. The product was subjected to chromatography on silica gel with elution by 1:1 benzene-ether. Found, %: C 45.67, H 4.20, P 7.96. C₁₆H₁₈O₂PCl₄N. Calculated, %: C 44.76, H 4.20, P 7.23. IR spectrum (ν , cm⁻¹): 1600, 1650 (C=C). PMR spectrum (δ , ppm): 2.67 (CH₃N), 3.66, 3.74 (CH₃O), 3.49 (CH, ²J_{PH} = 3.5 Hz), 7.28-7.47 (C₆H₅).

Conclusions

1. The reaction of bis(hydroxymethyl)phenylphosphine with dimethylformamide dimethylacetal gave 2-dimethylamino-5-phenyl-1,3,5-dioxaphosphorinane as the major product and dimethylaminomethylenephenylphosphine. The reaction of phenylphosphine and bis(dimethylamino)methoxymethane is indicated for the preparation of dimethylaminomethylenephenylphosphine.

2. Dimethylaminomethylenephenylphosphine adds tetrachlorocyclopentadienone dimethylacetal at room temperature to give 1,4,5,6-tetrachloro-7,7-dimethoxy-3-dimethylamino-2phenyl-2-phospha-5-norbornene in quantitative yield.

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SYNTHESIS OF TRIETHYLAMMONIUM 1,4-DIPHENYL-3-o-HYDROXYPHENYL-2,8,9-TRIOXA-1-BORATA-4-PHOSPHA-6,7-BENZENOBICYCLO[3.3.1]NONANE

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The borylation of bis(hydroxyalkyl)phosphines and their derivatives as well as of tris(hydroxyalkyl)phosphines in the presence of tertiary amines is a promising method for the preparation of cyclic and bicyclic compounds containing both phosphorus and boron. Thus, bis(hydroxyalkyl)phenylphosphines, their oxides, sulfides, and selenides, isobutyl diphenylborate, and tertiary amines give ammonium 5-phenyl-1,3,2,5-dioxaborataphosphorinanes, their oxides, sulfides, and selenides, respectively [1-3]. The reaction of tris(α -hydroxy- β , β , β -trichloroethyl)phosphine, phenylboric acid anhydride, and pyridinium gave pyridinium 1-phenyl-3,5,8-tris(trichloromethyl)-1-borata-2,6,7-trioxa-4-phosphabi-cyclo[2.2.2]octane [4]. This reaction in the absence of pyridine gives 5- α -hydroxy- β , β , β -trichloroethyl-4,6-bis(trichloromethyl)-1,3,2,5-dioxaboraphosphorinane [5].

An alcoholic hydroxyl group of the organophosphorus compound underwent borylation in the above examples. Not only alcoholic but also phenolic and carboxylic hydroxyl groups are also borylated in organic compounds [6]. In the present work, we studied the reaction of bis(hydroxy-o-hydroxybenzyl)phenylphosphine with phenylboric acid anhydride in the presence of triethylamine, in which the organophosphorus compound may participate in ring formation by both alcoholic and phenolic hydroxyl groups and the reaction direction cannot be predicted. Since diols are obtained quantitatively from phenylphosphine and aldehydes [7], phenylphosphine and salicyladehyde were used in this reaction.

The reaction of phenylphosphine, salicylaldehyde, phenylboric acid anhydride, and triethylamine began after moderate heating and proceeded exothermally. The IR spectrum of the reaction product displayed bands at 2600, 2500, and 2700 cm⁻¹ characteristic for the N-H bond, which indicated the presence of the triethylammonium cation in this molecule. The spectrum of the benzene solution also displayed a band at 3400 cm⁻¹ due to an OH group. The elemental composition of the product corresponded to the addition of all the reagents in 1:2:1/3:1 with the loss of a water molecule. The PMR spectrum has signals for the methyl and methylene protons of the ethyl group, and the ratio of the integral intensities of these and the phenyl protons was 9:6:18. The chemical shift in the ³¹P NMR spectrum was -13 ppm and corresponded to phosphine phosphorus. Hence, the product was identified as triethylammonium 1,4-diphenyl-3-o-hydroxyphenyl-2,8,9-trioxa-1-borata-4-phospha-6,7-benzenobicyclo[3.3.1]-nonane (I) although isomeric structures could not be eliminated.

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