CONCLUSIONS

A chair conformation with an axial orientation of the phosphoryl or thiophosphoryl group is preferable for 2-dimethylamino-2-oxo- and-2-thiono-1,3,2-oxathiaphosphorinanes. The cis isomer of 2-dimethylamino-2-oxo-4-methyl-1,3,2-oxathiaphosphorinane has a similar structure with an equatorial orientation of the 4-methyl group, while the corresponding sulfide is characterized by a trans configuration with a reoriented positioning of the substituents attached to the phosphorus atom.

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REACTION OF 1,3,5-DIAZAPHOSPHORINANES WITH BORANE

A. A. Karasik, O. A. Erastov, and B. A. Arbuzov

UDC 542.91:547.1'127'118:547.89

It has been shown that upon reaction of 1,3-diazacyclopentane with diborane, ring opening occurs to form 1,2-diaminoethane with secondary and tertiary amino groups [1]. In connection with this it was of interest to study reactions of 1,3,5-diazaphosphorinanes with diborane, since for these compounds two directions of ring opening (at the electrophilic carbon atoms in the N–C–N and P–C–N systems) are possible. Realization of one or the other direction will be determined by the nature of the ring substituents. For an intact ring the number of attached borane molecules depends on its conformation. By x-ray analysis, dipole moments, and PMR spectroscopy it was found that 1,3,5-diazaphosphorinane molecules have the chair conformation with equatorial orientation of the phenyl at the P atom and equatorial orientation of the aromatic substituents at the N atoms. For benzyl substituents at the N atom one of them is axial [2, 3]. The pyramidality of the N atoms with aromatic substituents is substantially decreased [3-5].

In this work, in order to obtain all theoretically possible products in reaction with borane, 1,3,5-diazaphosphorinanes with various substituents at the N and P atoms were used. The reaction course was checked by ^{31}P NMR spectra.

Reaction of 1,3,5-triphenyl-1,3,5-diazaphosphorinane with borane in THF resulted in formation of a crystalline product with a chemical shift in the ^{31}P NMR spectrum at 18 ppm (DMF). The IR spectrum had an absorption maximum at 2400 cm^{-1}, characteristic of the B–H bond, and the PMR spectrum in DMF, besides product phenyl and methylene proton signals, showed signals for THF methylene protons. The integral ratios for protons $C_6\underline{H}_5:C\underline{H}_2:C\underline{H}_2$ (THF) was 20:8:8. On the basis of spectral and elemental analysis data the product was assigned the structure of 1,3,5,7-tetraphenyl-3,7-diboran-1,5-diaza-3,7-diphosphacyclooctane (I) which contains one THF molecule

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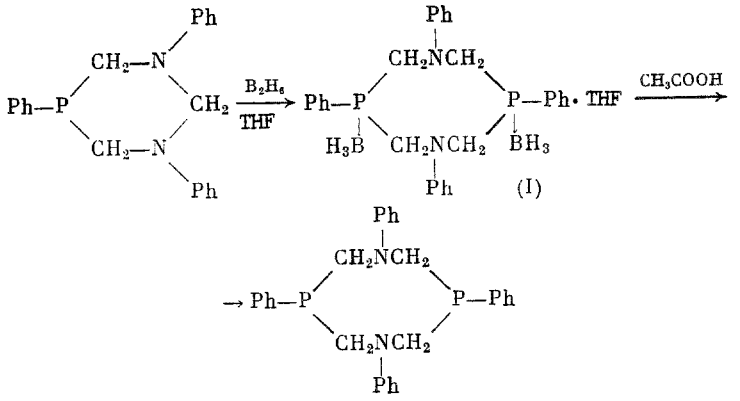
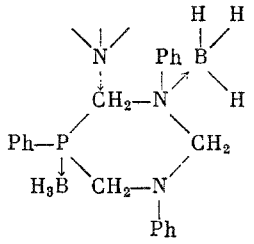
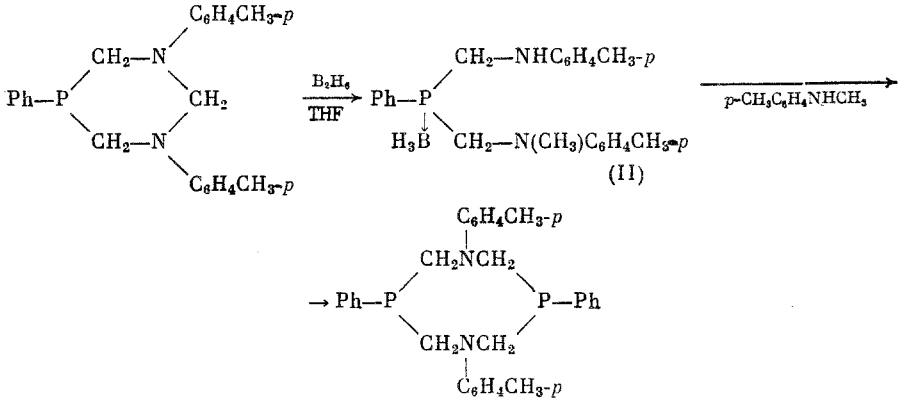


The structure of (I) was confirmed by its transformation into 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane [6].

Isolation of (I) indicates that opening of the 1,3,5-diazaphosphorinane ring proceeds at the C–N bond of the N–C–P fragment. Interconversion of 1,3,5-diazaphosphorinanes and 1,5-diaza-3,7-diphosphacyclooctanes was realized in [7] and attack of the nitrogen atom of one molecule on the carbon atom of the N–C–P fragment of the other molecule was assumed.



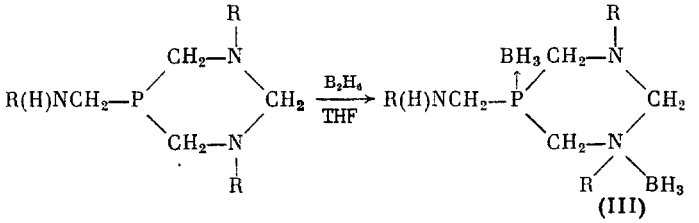
The product, which corresponds to the second possible direction of ring opening (at the C–N bond of the N–C–N fragment) by hydride ion attack on the carbon atom of the N–C–N fragment, was obtained by reaction of borane with 1,3-di-p-tolyl-5-phenyl-1,3,5-diazaphosphorinane. The ^{31}P NMR spectrum of the product had a signal with chemical shift of 14 ppm (DMF). The PMR spectrum in DMF-d_7 and acetone-d_6 revealed signals of phenyl, methylene, methyl tolyl, and N-methyl in an integral ratio ($C_6\underline{H}_5$:$C\underline{H}_2$:Ph–$C\underline{H}_3$:N–$C\underline{H}_3$) of 13:4:6:3, and the IR spectrum had bands at 2410 and 3400 cm^{-1}. On the basis of spectral and elemental analysis data the product was assigned the structure of the borane P-complex with N-methyl-bis-p-toluidinomethylphenylphosphine (II)



Upon boiling in ethanol, compound (II) is transformed into 1,5-di-p-tolyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane [6]. Transformation of bis(diaminomethyl)phenylphosphines into 1,5-diaza-3,7-diphosphacyclooctanes was found in [7].

The change in ring opening direction of 1,3,5-diazaphosphorinanes upon replacement of the phenyl at the N atom by p-tolyl can be associated with electronic effects of the substituents. The stronger donor tolyl increases the mobility of hydride ion.

Increase of electron density at the P and N atoms increases ring stability, which leads to formation of 1,3,5-diazaphosphorinane complexes. This takes place upon replacement of the phenyl at the phosphorus atom by the p-toluidinomethyl group. 1,3-Di-p-tolyl-5-p-toluidinomethyl-1,3,5-diazaphosphorinane reacts with borane giving a complex with borane molecules at the phosphorus atom and one of the nitrogen atoms – 1,3-di-p-tolyl-5-(p-toluidinomethyl)-1,5-diborane-1,3,5-diazaphosphorinane (III)



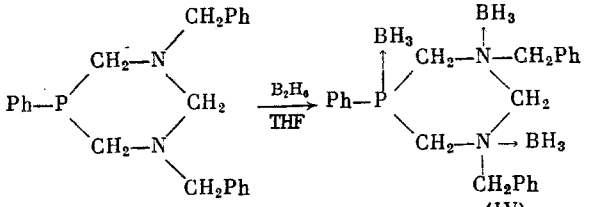
(III)

R = p-$CH_3C_6H_4$.

The IR spectrum of (III) in oil has bands at 2400 and 3290 cm^{-1}. The ^{31}P NMR spectrum has a signal at 4 ppm (DMSO). In the PMR spectrum signals of methyl, methylene, and phenyl protons were found with an integral ratio ($C\underline{H}_3$:$C\underline{H}_2$:$C_6\underline{H}_4$) of 9:8:12, which agrees with the proposed structure.

Electronic effects in compounds with the P–C–N fragment were examined in [8], where transfer of electron density from the nitrogen atom orbitals to the orbitals of the P–C bonds was proposed.

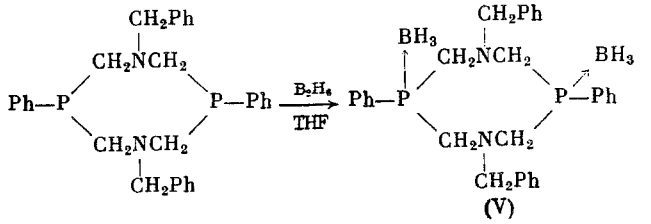
Stabilization of the ring by donating substituents at the phosphorus and nitrogen atoms was confirmed for 1,3-dibenzyl-5-phenyl-1,3,5-diazaphosphorinane. This compound binds to three borane molecules forming 1,3-dibenzyl-5-phenyl-1,3,5-triboran-1,3,5-diazaphosphorinane (IV). The ^{31}P NMR spectrum of (IV) had a signal at –7 ppm (DMSO) and the IR spectrum revealed bands at 2310 and 2410 cm^{-1}, which correspond with the two types of complexes. In the PMR spectrum of (IV), signals of phenyl and methylene protons of two types are found in an integral ratio ($C_6\underline{H}_5P$: $C_6\underline{H}_5CH_2$:$C\underline{H}_2$:$C_6H_5C\underline{H}_2$) of 5:10:6:4. Elemental analysis data agree with those calculated for (IV)



(IV)

Comparison of structures of (III) and (IV) and also the starting 1,3,5-diazaphosphorinanes indicates a definite connection between the number of attaching borane molecules and the conformation of the molecule. In (III) all substituents are oriented equatorially. Addition goes to the axial positions of two of the three atoms. In (IV) one of the benzyls occupies an axial position and two borane molecules are attached to (IV) axially and one molecule equatorially. Apparently, there is steric hindrance to three axial borane molecules.

The structural specifics explain the addition of only two borane molecules to 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane. Formation of 1,5-dibenzyl-3,7-diphenyl-3,7-diborane-1,5-diaza-3,7-diphosphacyclooctane (V) is confirmed by the chemical shifts in the ^{31}P NMR spectrum, the presence of a band at 2450 cm^{-1} in the IR spectrum, and phenyl and methylene proton signals in the PMR spectrum with an integral ratio ($C_6\underline{H}_5$:$C\underline{H}_2$:CH_2Ph) of 20:8:4 (DMF-d_7), and also by elemental analysis



(V)

According to x-ray analysis data, 1,5-dibenzyl-3,7-diphenyl- and 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctanes have the crown conformation [4, 5]. However, 1,3,5,7-tetraphenyl-3,7-dithio-1,5-diaza-3,7-diphosphacyclooctane is in the skew boat–boat conformation due to interaction between the sulfur atoms [9]. Probably similar interactions in the complex hinder addition of another two borane molecules.

Following the reaction course by ^{31}P NMR spectroscopy indicates that at the beginning complexes are formed with two and three borane molecules and then ring opening takes place leading to (I) and (II).

EXPERIMENTAL

1,3,5,7-Tetraphenyl-3,7-diborane-1,5-diaza-3,7-diphosphacyclooctane (I). Into a solution of 4 g (12 mmoles) of 1,3,5-triphenyl-1,3,5-diazaphosphorinane in 60 ml of THF, diborane, which was obtained from 5 g of $LiAlH_4$ and 20 g of $BF_3 \cdot Et_2O$, was passed. Exothermic reaction and formation of an insignificant amount of a fluocculent precipitate of boric acid was observed. The precipitate was crystallized from ether and washed with MeOH. The yield of (I) was 1 g (35%) with mp of 162-165°C. Found, %: C 69.55; H 7.47; N 5.74; P 10.73. $C_{28}H_{34}N_2P_2B_2 \cdot THF$. Calculated, %: C 69.31; H 7.58; N 5.05; P 11.19.

Compound (I) was dissolved in a mixture of acetone and acetic acid (10:1), the solvent was removed under vacuum, and the residue was crystallized from MeOH. The yield of 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane was 97%, mp 191°C (see [6]).

P-Complex of borane with N-methyl-bis(p-toluidinomethyl)phenylphosphine (II) was obtained analogously to (I) from 4 g (10 mmoles) of 1,3-di-p-tolyl-5-phenyl-1,3,5-diazaphosphorinane. The product was crystallized from ether and MeOH yielding 2 g (68%) of (II) with mp of 105-106°C. Found, %: C 73.28; H 8.10; N 7.47; P 7.33. $C_{23}H_{30}N_2PB$. Calculated, %: C 73.40; H 7.97; N 7.45; P 8.24.

Compound (II) in the amount of 0.3 g was boiled in 5 ml of ethanol for 1.5 h. The solvent was removed under vacuum and the residue was crystallized from acetonitrile. The yield of 1,5-di-p-tolyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane was 0.1 g (30%), mp 217°C (lit.: mp 217°C [6]).

1,5-Di-p-tolyl-5-toluidinomethyl-1,5-diborane-1,3,5-diazaphosphorinane (III) was obtained analogously to (I) from 1.65 g (4 mmoles) of 1,3-di-p-tolyl-5-p-toluidinomethyl-1,3,5-diazaphosphorinane. The yield of (III) was 1 g (63%), mp 120-122°C. Found, %: C 69.53; H 8.00; N 9.69; P 6.80. $C_{25}H_{36}N_2PB_2$. Calculated, %: C 69.61; H 8.35; N 9.75; P 7.19.

1,3-Dibenzyl-5-phenyl-1,3,5-triborane-1,3,5-diazaphosphorinane (IV) was obtained analogously to (I) from 2 g (6 mmoles) of 1,3-dibenzyl-5-phenyl-1,3,5-diazaphosphorinane. The yield of (IV) was 1.5 g (70%), mp 135°C. Found, %: C 68.38; H 8.32; N 6.96; P 7.53. $C_{23}H_{34}N_2PB_3$. Calculated, %: C 68.66; H 8.45; N 6.97; P 7.71.

1,5-Dibenzyl-3,7-diphenyl-3,7-diborane-1,5-diaza-3,7-diphosphacyclooctane (V) was obtained analogously to (I) from 2 g (6 mmoles) of 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane. The yield of (V) was 0.5 g (25%), mp 127-130°C, $\delta^{31}P$ 12 ppm (CH_3OH). Found, %: C 69.12; H 8.21; N 4.81; P 9.70. $C_{30}H_{38}N_2P_2B_2 \cdot (C_2H_2)_2O$. Calculated, %: C 69.86; H 8.23; N 4.79; P 10.62.

CONCLUSIONS

1,3,5-Diazaphosphorinanes react with borane yielding, depending on the nature of the substituents at the ring atoms, complexes with two or three borane molecules and the products of ring opening at the C–N bonds of the P–C–N and N–C–N fragments.

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