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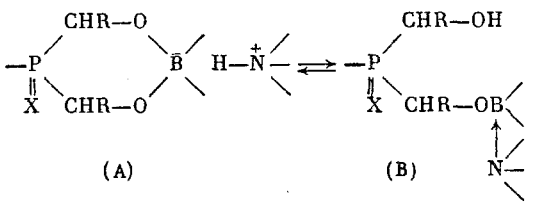
TAUTOMERISM IN 1,3,2,5-DIOXABORATAPHOSPHORINANES AND THEIR ANALOGS

G. N. Nikonov and A. A. Karasik

UDC 541.623:542.91:547.1'127'118

In solutions ammonium 2,2,5-triphenyl-4,6-di-R-1,3,2,5-dioxaborataphosphorinanes are characterized by ion—complex tautomerism. The complex form dissociates reversibly to a secondary phosphine and an aldehyde. The reaction of tris(hydroxymethyl)phosphine with isobutyl diphenylborate in the presence of formaldehyde and a tertiary amine gave 5,5'-spirobi(2,2-diphenyl-1,3,2,5-dioxaborataphosphorinanes).

One of the interesting characteristics of boryloxyalkylphosphines containing a mobile hydrogen atom is their ability to undergo tautomeric transformations. Thus, boryloxyalkylphosphines with electron-withdrawing substituents at the α-carbon atom exhibit ring—chain oxyboryl—borate tautomerism [1]. The oxides, sulfides, and selenides of ammonium 1,3,2,5-dioxaborataphosphorinanes exist in solutions in two tautomeric forms, i.e., salt and complex forms [2-5]:



During the reversible transitions in this process two bond (B—O and H—$\overset{+}{N}$) are broken and two bonds (H—O and B←N) are formed, two particles (a proton and the ammonium group) migrate, the atoms retain their coordination, and only the type of bond changes. The complex (B) and salt (A) forms are present in equilibrium, and (A) is capable of ionic dissociation in solutions. The (A) form has a cyclic fragment, and (B) is an acyclic molecule. Thus, the equilibrium between the two forms (A) and (B) represents ring—chain (depending on the types of structures in the tautomeric forms), double (the number of migrating particles), heptad—diad (the number of atoms between which the proton and the N atom migrate), elemental—protrotropic (the type of migrating particles), and complex—salt or (more precisely) ion—complex (the types of tautomers formed) tautomerism. During examination of this tautomerism we do

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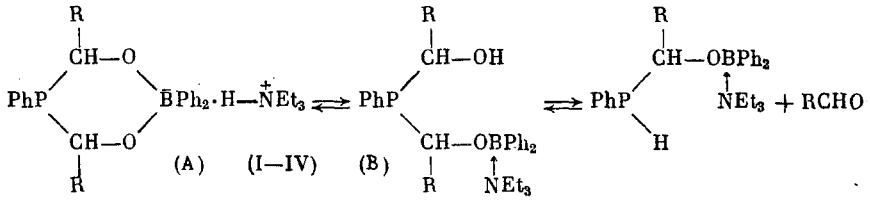
not include the two equivalent acyclic structures (with identical substituents at the α-carbon atom) in the equilibrium, i.e., the so-called degenerate tautomerism [6]. Below we will consider the types of ion—complex tautomerism in ammonium 1,3,2,5-dioxaborataphosphorinanes (P^{III}) and some of its features.

The synthesis of ammonium 1,3,2,5-dioxaborataphosphorinanes with a tricoordinated phosphorus atom was described in [7]. Ion—complex tautomerism should also be observed for them. In this case, however, the tautomeric transformations are accompanied by reversible dissociation of the α-hydroxyalkyl fragment of form (B) by analogy with the dissociation of 1,3,2,5-dioxaborataphosphorinanes to the phosphine and aldehyde [8].



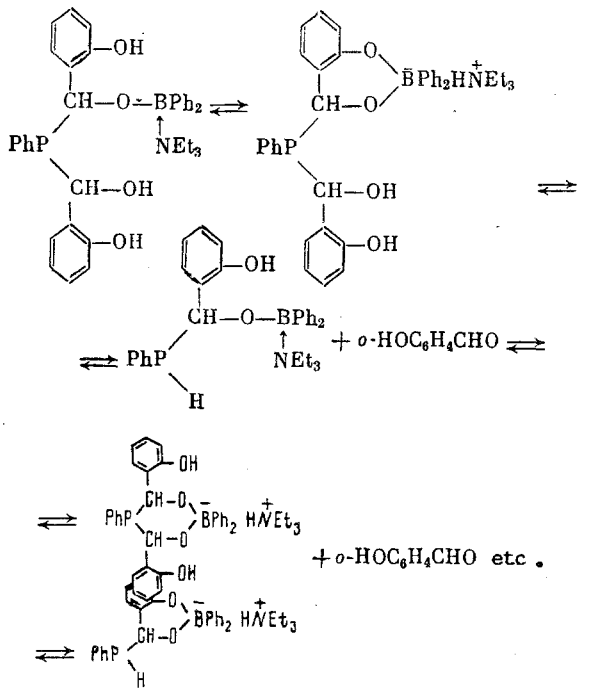
R = Me (I), *i*-Pr (II), Ph (III), C_6H_4OMe-*p* (IV).

In fact, the absorption of the H—$\overset{+}{N}$ group (the ionic form, 2500-2700 cm^{-1}), the O—H group (the complex form, 3200-3400 cm^{-1}), and the P—H (2300 cm^{-1}) and C=O (1720 cm^{-1}) groups [the products from the dissociation of form (B)] are observed in the IR spectra of solutions of (I-IV). It should be noted that dissociation of the hydroxymethyl fragment of form (B) to the secondary phosphine and formaldehyde does not occur in the case of tributylammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane. This is consistent with the fact that displacement of formaldehyde from the hydroxymethyl fragment does not occur in boryloxymethylphosphines under the influence of aldehydes [9, 10].

In contrast to IR spectroscopy it is not possible to detect the individual tautomeric forms in the solutions by NMR at room temperature; an averaged picture of the tautomeric equilibrium is observed in the spectra as a result of the rapid mutual transitions. At the same time the dissociation of the α-hydroxyalkyl fragment is a slower process, and there are signals for the dissociation products in the PMR spectra. Thus, the PMR spectrum of (III) contains a signal for the proton of the CH=O group of benzaldehyde with a chemical shift of 9.5 ppm, while the spectrum of (IV) contains a signal for the proton of the CH=O group and two singlets for the methyl protons of the CH_3O groups of the aldehyde and the undissociated forms. The signals for the protons of the CH_3O groups can be assigned by comparison of the integral intensities of these protons with the signal for the proton of the CH=O group. For the signal at 3.7 ppm this ratio amounts to 1:3, which makes it possible to assign it to the CH_3O group of the aldehyde. The signal at 3.6 ppm corresponds to the CH_3O groups of the undissociated forms. Comparison of the intensities of the signals for the protons of the CH_3O groups makes it possible to estimate the degree of dissociation of (IV), which is dissociated to the extent of ~20% in solution under the conditions under which the spectra were recorded. The PMR spectra were recorded in DMSO-d_6.

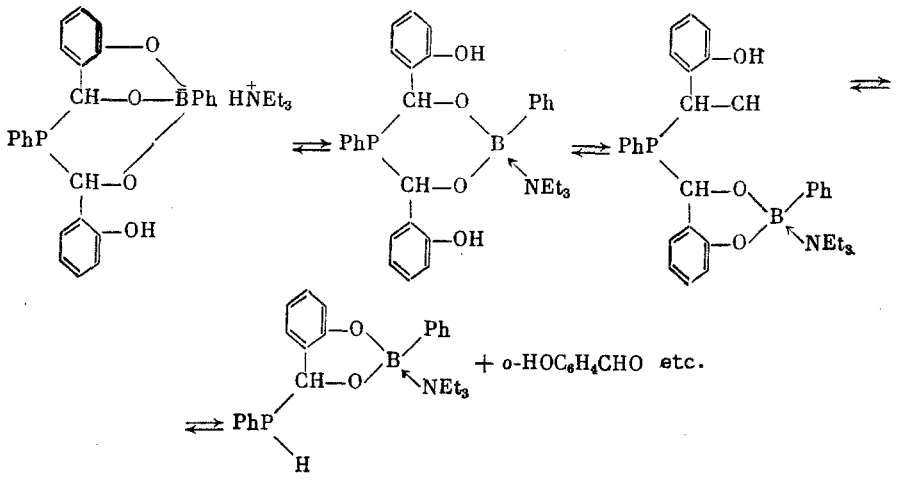
The rapid changes in the substances during dissolution and the absence of changes in the solutions indicate the establishment of an equilibrium. The compounds crystallized from the solutions in form (A) or (B), depending on the radicals R [7].

The introduction of functional groups which are capable of forming bonds with the B atom into the substituent at the α-carbon atom to the P atom or into the ammonium cation will lead to the appearance of new tautomeric forms. Thus, in the presence of an OH group at the o position of the benzene ring the existence of tautomers involving the participation of this group becomes possible. There are two such groups in the triethylamine—diphenylboryloxy(o-hydroxybenzyl)oxy(o-hydroxybenzyl)phenylphosphine complex (V). In the crystalline state (V) exists in the complex form [11]. Absorption characteristic of the protonated N atom, the carbonyl group, and the P—H bond and a strong band for the OH group appear in the IR spectra of the solutions. This makes it possible to propose a tautomeric equilibrium involving the cyclic form (A) and also the formation of tautomers with the participation of the phenol groups. In addition, by analogy with (I-IV) it follows from the IR spectra of the solutions that the P—C—OH fragment dissociates to a secondary phosphine and aldehyde. In the light of this (V) exists in solution in several tautomeric forms and dissociation products. In the PMR spectra of (V) there is a signal for the proton of the CH=O group of salicylaldehyde (10.3 ppm).

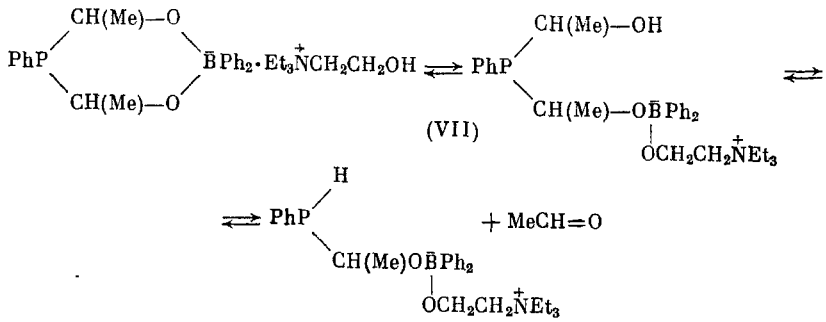


The same conclusion can be reached from examination of the IR spectra of triethylammonium 1,4-diphenyl-3-o-hydroxyphenylene-2,8,9-trioxa-1-borata-4-phospha-6,7-benzenobicyclo[3.3.1]nonane(VI) in the crystalline state [12] and of its solution, where the same set of characteristic absorption bands of the functional groups is present.

The presence of functional groups in the ammonium cation can lead to the appearance of new tautomeric equilibria. Thus, for triethyl(β-hydroxyethyl)ammonium 2,2,5-triphenyl-4,6-dimethyl-1,3,2,5-dioxaborataphosphorinane (VII) the formation of the complex form is impossible. In the crystalline state (VII) exists in the salt form, and this was demonstrated unambiguously by x-ray crystallographic analysis [13].



In the IR spectra of solutions of (VII), however, the absorption of the carbonyl group (1720 cm^{-1}) and P—H bond (2300 cm^{-1}) is observed. This is only possible through dissociation of the α-hydroxyalkyl fragment.

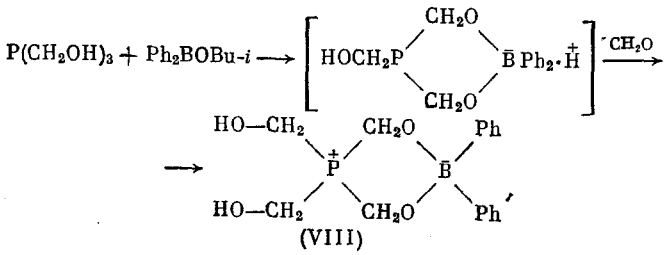


(VII)

In solution (VII) exists in the form of two tautomeric ion pairs, one of which has a free α-hydroxyalkyl fragment. In this case it is possible to speak of element–prototropic tautomerism.

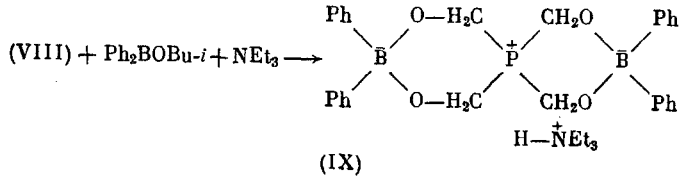
Bicyclo–cyclic ion–complex tautomerism was described in [14] for pyridinium 1-phenyl-3,5,8-tris(trichloromethyl)-1-borata-2,6,7-trioxa-4-phosphabicyclo[2.2.2]octane. The appearance of the bicyclic form is due to the fact that the compound was synthesized from tris(α-hydroxy-β,β,β-trichloroethyl)phosphine.

The borylation of tris(hydroxymethyl)phosphine by isobutyl diphenylborate (IDB) led to the formation of 2,2-diphenyl-5,5-di(hydroxymethyl)-1,3,2,5-dioxaborataphosphoniarinane (VIII):



(VIII)

It was not possible to isolate the intermediate product with a P^{III} atom, since a more stable betaine structure is formed through the addition of formaldehyde from the other triol molecule by disproportionation by analogy with [15]. The addition of formaldehyde to the reaction mixture increases the yield of (VIII). The IR spectra of (VIII) in the solid state do not contain the absorption of the $O-B^{III}$ bond in the region of 1300-1350 cm^{-1}. In the PMR spectra the integral intensity ratio of the phenyl and methylene protons amounts to 10:8. The reaction of (VIII) with a second equivalent of IDB in the presence of triethylamine gave the diborylated product triethylammonium 5,5′-spirobi(2,2-diphenyl-1,3,2,5-dioxaborataphosphoniarinane) (IX).



(IX)

The synthesis of (IX) is the first example of the borylation of a phosphonium salt with an α-hydroxyalkyl fragment. In [16] phenyldichloroborane reacted with tris(hydroxymethyl)phenylphosphonium chloride. Here, however, the phosphonium salt was reduced to the phosphine, and the reaction took place under drastic conditions.

Compound (IX) can be obtained in a single stage from tris(hydroxymethyl)phosphine. The reaction in the presence of pyridine takes place similarly, but the pyridine must be added last, since it reduces the reactivity of the IDB.

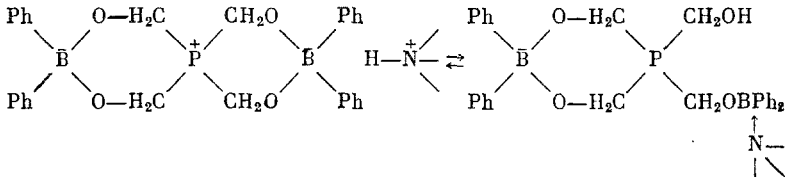
$$P(CH_2OH)_3 + 2Ph_2BOBu\text{-}i + CH_2O + A \rightarrow$$
$$\rightarrow Ph_2\bar{B}(OCH_2)_2\overset{+}{P}(CH_2O)_2\bar{B}Ph_2 + H{-}A^+$$
(IX), (X)

$A = NEt_3$ (IX), NC_5H_5 (X).

Compounds (IX) and (X) are white powdered substances, readily soluble in polar solvents and insoluble in ether and petroleum ether. Compounds (IX, X) crystallize poorly from solvents and are isolated by precipitation with ether or petroleum ether.

The IR spectra of (IX, X) in the solid state in vaseline oil do not contain the absorption of the hydroxyl groups and O—B^{III} bond, but the absorption of the H—$\overset{+}{N}$ (2520, 2730 cm^{-1}), which is strong for (IX) and weak for (X), is observed. The IR spectra of solutions of (IX) and (X) in chloroform contain the absorption of the hydroxyl groups at 3650 cm^{-1} and the H—$\overset{+}{N}$ bonds. In the PMR spectra of (IX) the integral intensity ratios of the protons of the methyl, methylene (CH_2CH_3), methylene (—CH_2O—), and phenyl groups correspond to 9:6:8:20. The protons of the PCH_2O fragment are recorded in the form of a multiplet. In the PMR spectra of (X) the integral intensity ratio for the protons of the phenyl groups, pyridine, and methylene groups amounts to (20 + 5):8.

The ^1H NMR spectra represent an averaged picture of the two tautomeric forms present in equilibrium:



In contrast to the examples of ion—complex tautomerism given above, the equilibrium in this case is established between the spirobicyclic salt and cyclic complex structures, each of which contains a phosphonium fragment.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a "Varian T-60" spectrometer at 60 MHz at 34.5°C with TMS as internal standard. The ^{31}P NMR spectra were obtained on a KGU-4 NMR spectrometer (10.2 MHz with noise proton decoupling at 25.2 MHz). The IR spectra were obtained on a UR-20 spectrometer, and the spectra of the solutions were recorded in KrS-5 cuvettes (0.635 mm) with chloroform and benzene as solvents and at concentrations of 0.5-5%. The reactions were conducted in an atmosphere of argon. The synthesis of (I-IV) was described in [5, 7], and that of (V-VII) in [11-13].

2,2-Diphenyl-5,5-di(hydroxymethyl)-1,3,2,5-dioxaborataphosphoniarinane (VIII). a. To 1.06 g (8.6 mmoles) of tris(hydroxymethyl)phosphine in 20 ml of acetone we added 2 g (8.6 mmoles) of IDB. After 30 min the mixture was evacuated at 40-50°C (0.1 mm Hg) for 1 h. The residue was dissolved in 10 ml of acetone and gradually added to 100 ml of ether with stirring. The mixture was stirred for 2 h, and the precipitate was filtered off. The yield of (VIII) was 1.2 g (44%); mp 88-92°C, δ ^{31}P 17 ppm (DMF).

b. To 5 g (40 mmoles) of tris(hydroxymethyl)phosphine we added 1.2 g of paraform. The mixture was carefully heated to 120-150°C until the paraform had completely dissolved. The reaction was then conducted as described above. The yield of (VIII) was 10.9 g (85%); mp 89-92°C, δ ^{31}P 17 ppm (DMF). IR spectrum (ν, cm^{-1}): 3100-3300 (O—H). Found %: C 60.37; H 6.57; P 9.21%. $C_{16}H_{20}BO_4P$. Calculated %: C 60.38; H 6.29; P 9.75%.

Triethylammonium 5,5′-Spirobi(2,2-diphenyl-1,3,2,5-dioxaborataphosphoniarinane) (IX). a. To a solution of 1.39 g (4.4 mmoles) of (VIII) in 10 ml of acetone we added 1.04 g (4.4 mmoles) of IDB and I ml of triethylamine. After 3 h the mixture was evacuated at 40-45°C at 0.1 mm Hg until a frothy solid was obtained. After the addition of petroleum ether (40-70°C) it changed into the powder state. An analytically pure sample was obtained by precipitation from acetone with ether. The yield of (IX) was 2.1 g (83%); mp 76-78°C. Found %: C 69.87; H 7.60; N 2.77; P 4.98%. $C_{34}H_{43}B_2NO_4P$. Calculated %: 70.10; H 7.39; N 2.41; P 5.33%.

b. To 3.21 g (26 mmoles) of tris(hydroxymethyl)phosphine we added 0.77 g (26 mmoles) of paraform. The mixture was heated until the paraform had dissolved, and 30 ml of acetone, 12.3 g (52 mmoles) of IDB, and 4 ml of triethylamine were then added. After 3 h the mixture was evacuated at 40°C (0.1 mm Hg) until a frothy solid mass had formed. The product was rubbed in diethyl ether to a powder. The yield of (IX) was 9 g (61%); mp 78°C. The IR and PMR spectra correspond to the (IX) obtained from (VIII); δ ^{31}P 5 ppm (DMF).

Pyridinium 5,5′-Spirobi(2,2-diphenyl-1,3,2,5-dioxaborataphosphoniarinane) (X). The compound was obtained by analogy with (IX) from tris(hydroxymethyl)phosphine. Pyridine was added to the reaction mixture 1 h after the other components were mixed. The yield of (X) was 70%; mp 80-81°C. Found %: C 70.31; H 5.86; N 2.31; P 5.72%. $C_{33}H_{34}B_2O_4NP$. Calculated %: C 70.59; H 6.06; N 2.50; P 5.53%. δ ^{31}P 16.8 ppm (DMF).

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SYNTHESIS OF NITROXYLCARBAMIDOPHOSPHORIC ACID AMIDES

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A method for obtaining new organophosphorus nitroxyls was developed based on Kirsanov's phosphazo reaction.

Spin-labeling plays an important role in elucidating the mechanism of action of therapeutic agents and pesticides and in studying their localization and distribution in insects, warm-blooded animals, and plants.

In [1, 2] it was shown that spin-labeled phosphoric acid ethylenimides have a high biological activity, probably due to the presence of a radical fragment. Phosphoric acid hexamethyltriamide is known as a chemosterilizing agent [3], and antitumor agents have been found among aroylamidophosphoric acids [4].

In view of this, we attempted to synthesize spin-labeled pyrrolinecarbamidophosphoric acid tetraalkyldiamides, analogs of aroylamidophosphoric acids, which could be useful in studying the mechanisms of action of these types of compounds.

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