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REACTION OF AMMONIUM 1,3,2,5-DIOXABORATAPHOSPHORINANES WITH ELECTROPHILIC REAGENTS

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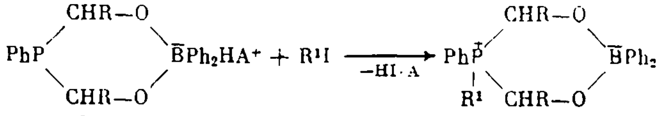
Ammonium 1,3,2,5-dioxaborataphosphorinanes and their derivatives contain a cation having a labile hydrogen atom [1-3], which facilitates reactions with electrophilic reagents involving direct participation of the labile hydrogen atom. In this work alkyl halides, diphenylchlorophosphine, formaldehyde and ethylene oxide were used as electrophilic reagents.

Reaction of N-methylmorpholinium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane (I) and of triethylammonium 2,2,5-triphenyl-4,6-dimethyl-1,3,2,5-dioxaborataphosphorinane (II) with methyl and ethyl iodides proceeds at ~20°C to form 2,2,5-triphenyl-5-methyl- (III) and 2,2,5-triphenyl-5-ethyl-4,6-dimethyl-1,3,2,5-dioxaborataphosphoniarinanes (IV), respectively



(I), (II)

R = H, A = $MeN(CH_2CH_2)_2O$(I)
R = Me, A = Et_3N(II)

(III), (IV)

R = H, R^1 = Me(III)
R = Me, R^1 = Et(IV)

2,2,5,5-Tetraphenyl-4,6-dimethyl-1,3,2,5-dioxaborata-phosphoniarinane (V) was obtained under the same conditions from (II) and diphenylchlorophosphine. Apparently in the first step a bipolar ion is formed which has a diphenylphosphine group as substituent at the phosphorus atom. Subsequent enlargement of the ring, charge transfer to the second phosphorus atom, and contraction of the ring proceed due to the expulsion of $(PhP)_n$

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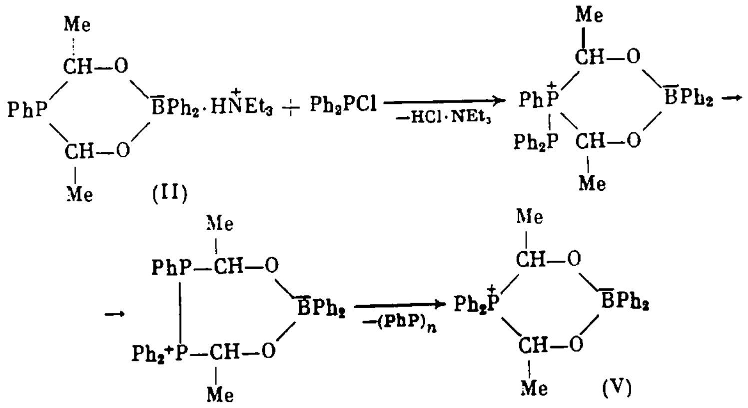
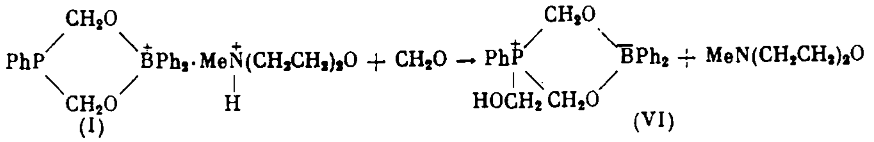
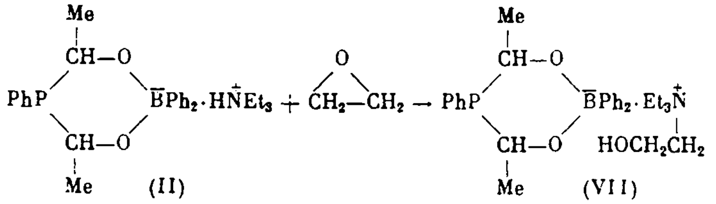


In the above reactions of halogen-containing electrophiles with (I) and (II) the ammonium cation binds the halogen anion. Different behavior of the ammonium cation is observed in reactions with (I) and (II) with electrophiles which do not contain a halogen atom. Reaction of (I) with formaldehyde gives 2,2,5-triphenyl-5-hydroxymethyl-1,3,2,5-dioxaboratephosphoniarinane (VI), which promotes dissociation of the ammonium cation with proton transfer to the negative center of electrophile



Reaction of (II) with ethylene oxide gives the addition product at the N—H bond of the ammonium cation, N-β-hydroxyethyl(triethyl)ammonium 2,2,5-triphenyl-4,6-dimethyl-1,3,2,5-dioxaborataphosphorinane (VII)



The structures of the products were established by IR, ^{31}P and ^{1}H NMR spectroscopy. For (VII) x-ray structure analysis was carried out (Fig. 1).

The conformation of the six-membered ring is chair (C_s symmetry). The $O^1O^3C^4C^6$ frame is planar within 0.008 (3) Å. The deviations of atoms P^5 and B^2 from this plane are 0.986(1) and 0.962(5) Å, respectively. The dihedral angles between planes $O^1O^3C^4C^6$ and $C^4P^5C^6$, $O^1O^3C^4C^6$ and $O^1B^2O^3$ are 52.0 and 54.2°. The substituents at atoms C^4, C^6, and P^5 occupy equatorial positions. The deviations of atoms C^{19}, C^{34}, and C^{35} from the $O^1O^3C^4C^6$ plane are 0.339, 0.613, and 0.554 Å, respectively. The plane of the benzene ring C^{29}—C^{24} lies in the plane of symmetry of the heterocycle: the dihedral angles between the planes $O^1O^3C^4C^6$ and C^{29}-C^{24} are 99.0°, $C^4P^5C^6$ and C^{29}-C^{24} are 96.3° (analogous to the 1,3,5-dioxaphosphorinanes [4, 5] and phosphorinan-4-ones [6]).

The endocyclic $C^4P^5C^6$ bond angle, 95.8(2)°, is slightly smaller than the one found in 1-phenylphosphorinanes [7] and the P—C bonds are slightly longer.

The coordination of the B^2 atom is tetrahedral and the planes of the C^7—C^{12} and C^{13}—C^{18} benzene rings are perpendicular to the plane of symmetry of the heterocycle (see Fig. 1). The dihedral angles between the $O^1O^3C^4C^6$ and C^{13}—C^{18} planes and the C^7—C^{12} and C^{13}—C^{13}—C^{18} planes are 100.5 and 93.6°. The lengths of the O^1—B^2 bond (1.507 A) and the O^3—B^2 bond (1.481 Å) are slightly different, which is explained by participation of the O^1 atom in a hydrogen bond with the hydroxyl group of cation $O^1...H$—O^{33} ($O^{33}...O^1$ 2.805(6) Å, $H^{33}...O^1$ 1.441 Å, angle O^{33}—$H...O^1$ 171.4°).

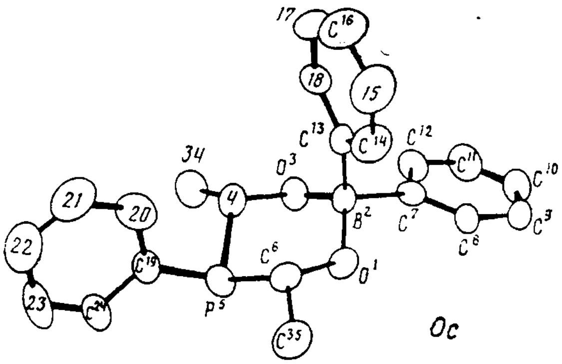
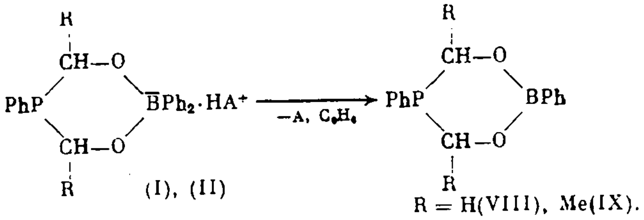


Fig. 1. Geometry of anion of compound (VII) (cation and hydrogen atoms not shown).

Compounds (I) and (II) decompose upon heating to 120-170°C into amine, benzene, and 2,5-diphenyl-1,3,2,5-dioxaborataphosphorinanes (VIII) and (IX)



In this case the proton formed upon dissociation of the ammonium cation acts as the electrophilic reagent.

EXPERIMENTAL

Synthesis of (I) and (II) are shown in [3].

Reaction of (I) with Methyl Iodide. To 2 g (4 mmoles) of (I) in 20 ml acetone 1.5 ml methyl iodide was added. On the next day the crystalline precipitate was filtered. The yield of N,N-dimethylmorpholinium iodide was 0.15 g (13%). Found: C 29.91; H 5.97; N 5.86%. $C_6H_{14}NOI$. Calculated: C 29.63; H 5.76; N 5.75%. The filtrate was evaporated and the residue crystallized from acetonitrile and washed with ethyl ether. The yield of (III) was 1.3 g (77%), mp 151°C, δ_P 1 ppm (CH_3CN) [8].

Reaction of (II) with Methyl Iodide. To 2.13 g (4.6 mmoles) of (II) in 8 ml dry acetone 1 ml of ethyl iodide was added. After 5 h the precipitate was filtered, washed with acetone, and crystallized from acetonitrile. The yield of (IV) was 1.1 g (61%), mp 102-104°C, δ_P 0, −6 ppm (DMF) [1]. From the filtrate triethylammonium iodide was isolated with a yield of 0.5 g (50%).

Reaction of (II) with Diphenylchlorophosphine. To 2.43 g (5.25 mmoles) of (II) in 6 ml dry acetone 1.16 g (5.25 mmoles) of diphenylchlorophosphine was added at -20°C. On the next day the precipitate was filtered, washed with a mixture of acetone and water (1:1), and crystallized from acetone. The yield of (V) was 1.09 g (47%), mp 80-83°C, δ_P −2, −34 ppm (DMF). Found: C 77.04; H 6.59; P 7.42%. $C_{28}H_{28}PO_2B$. Calculated: C 76.71; H 6.39; P 7.07%.

Reaction of (I) with Paraformaldehyde. To 1.2 g (3 mmoles) of (I) in 1 ml DMF 0.09 g (3 mmoles) of paraformaldehyde was added. The mixture was heated until dissolution of the paraformaldehyde. After 2 h the volatile components were removed under vacuum and the residue was dissolved in acetone. Upon standing crystals precipitated. They were filtered and crystallized from acetonitrile. The yield of (VI) was 0.7 g (60%), mp 134°C, δ_P 4 ppm (DMF) [1].

Reaction of (II) with Ethylene Oxide. To 3 g (6.4 mmoles) of (II) 2 ml triethylamine and 11 ml (0.2 mmole) ethylene oxide were added at 10-15°C, 0.5 h after formation of a homogeneous mixture the volatile components were removed under vacuum and the residue crystallized from acetone. The yield of (VII) was 0.53 g (18%), mp 145°C, δ_P, −32 ppm (DMF). IR

TABLE 1. Coordinates of Nonhydrogen Atoms

Atom	x	Y	z	Atom	X	Y	z
P^5	0,7700(1)	0,10059(8)	0,66739(8)	C^{18}	0,9771(4)	0.3245(3)	0,5909(3)
O^1	0.9240(2)	0,1929(2)	0,7733(2)	C^{19}	0,6196(4)	0.1250(2)	0,6038(3)
O^3	0.9936(2)	0.1505(2)	0,6459(2)	C^{20}	0,5940(4)	0,1955(3)	0.5586(3)
O^{33}	−0,0107(3)	0.0872(2)	0,9075(2)	C^{21}	0.4821(5)	0,2065(3)	0,5083(3)
N	0.1237(3)	−0.0518(2)	0,8259(2)	C^{22}	0.3916(5)	0,1503(4)	0,5037(3)
C^4	0,8753(4)	0.1372(3)	0.5983(3)	C^{23}	0.4128(5)	0.0813(3)	0.5498(3)
C^6	0,7964(4)	0.1870(3)	0,7416(3)	C^{24}	0.5266(4)	0.0682(3)	0.5986(3)
C^7	1,1449(4)	0,2150(2)	0,7573(3)	C^{25}	0,0004(4)	−0,0355(3)	0,7707(3)
C^8	1.1790(4)	0.2433(3)	0.8381(3)	C^{26}	−0,0572(5)	−0.1058(3)	0.7207(4)
C^9	1.3006(4)	0.2423(3)	0.8790(3)	C^{27}	0.1054(4)	−0.1121(3)	0,8912(3)
C^{10}	1,3914(4)	0.2130(3)	0.8390(3)	C^{28}	0,2182(5)	−0,1313(3)	0,9545(3)
C^{11}	1.3608(4)	0.1868(3)	0,7588(3)	C^{29}	0,2149(5)	−0,0867(3)	0,7767(3)
C^{12}	1.2394(4)	0.1885(2)	0.7183(3)	C^{30}	0,2389(5)	−0,0352(3)	0.7053(3)
C^{13}	0.9652(4)	0.3036(2)	0.6716(2)	C^{31}	0.1742(4)	0,0277(3)	0,8639(3)
C^{14}	0.9267(4)	0.3641(3)	0.7186(3)	C^{32}	0.1124(4)	0,0635(3)	0,9313(3)
C^{15}	0,9012(5)	0.4415(3)	0,6878(3)	C^{34}	0,8862(4)	0.0764(3)	0,5304(3)
C^{16}	0,9139(5)	0.4593(3)	0,6075(3)	C^{35}	0,7273(4)	0,1762(3)	0,8117(3)
C^{17}	0,9525(4)	0.4016(3)	0,5599(3)	B^2	1,0017(4)	0.2143(3)	0.7096(3)

spectrum (ν, cm^{-1}): 3170 (oil). Found: C 71.20; H 8.61; P 6.38; N 2.68%. $C_{30}H_{43}PO_3BN$. Calculated: C 71.01; H 8.48; P 6.11; N 2.76%.

Thermal Transformation of (I). Compound (I) (2 g) was heated in an Ar atmosphere to 170°C. After cooling the residue was crystallized from benzene. The yield of (VIII) was 0.8 g (67%), mp 105°C, δ_P −42 ppm (C_6H_6) [9].

Thermal Transformation of (II). Compound (II) (2.4 g) was heated in an argon atmosphere at 120°C for 10 min. The residue was distilled. The yield of (IX) was 1g (48%), bp 140-150°C (0.07 mm), δ_P −26, −27, −33 ppm [9].

Crystals of (VII) $(C_{22}H_{23}O_2BP)^-(C_8H_{20}NO)^+$ are monoclinic. At 20°C a = 16.633(3), b = 11.049(2), c = 16.376(2) Å, β = 100.34(2), Z = 4, d_{calc} = 1.14 g/cm³, spatial group P 2_1/n. The unit cell parameters and intensity of the 1601 independent reflections with $F^2 \geq 3\delta$ were measured on an automatic Enraf–Nonius CAD-4 diffractometer (λMoK_α, graphite monochromator, θ/2θ-scanning $\theta \leq 25°$).

The structure was interpreted by a direct method with the MULTAN program and refined by least squares under the isotropic approximation. Using differential synthesis the oxygen atom on one of the ethyl groups of the ammonium fragment and the two carbon atoms C^4 and C^6 of the heterocycle were revealed. After isotropic approximation of the whole structure, more precision was obtained using the anisotropic approximation. Then from a differential series several hydrogen atoms of the end methyl groups were revealed. The remaining hydrogen atoms were placed in the calculated positions. Contribution of all hydrogen atoms to the structural amplitudes was included in the final cycles of more accurate definition with fixed position and isotropic temperature parameters B_{iso} = 5 Å². Final values of the divergence factors were R = 0.035 and R_w = 0.043. Coordinates of nonhydrogen atoms are shown in Table 1, bond lengths, bond angles and torsional angles can be obtained from the authors.

CONCLUSIONS

1. Reactions of ammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinanes with alkyl halides, diphenylchlorophosphine, formaldehyde, and ethylene oxide were carried out.

2. The molecular structure of the N-β-hydroxyethyltriethylammonium salt of 2,2,5-triphenyl-4,6-dimethyl-1,3,2,5-dioxaborataphosphorinane was established.

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REACTION OF α-BORYLOXYALKYL- AND α-HYDROXYALKYLPHOSPHINES AND THEIR DERIVATIVES WITH BASES

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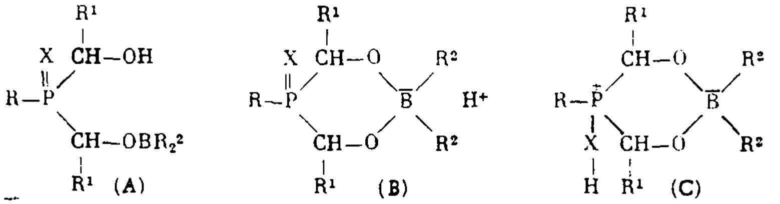
α-Boryloxyalkyl- and α-hydroxyalkylphosphines are formed in the reaction of bis(α-hydroxyalkyl)phosphines with borate esters or anhydrides, and are capable of existing in three tautomeric forms, namely neutral (A), acid (B), and bipolar (C).

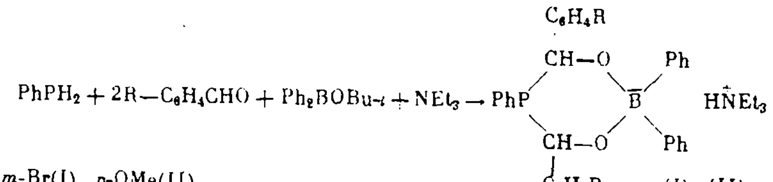


(A) (B) (C)

X = unshared electron pair, O, S, Se.

The presence of the three-coordinated boron atom (a Lewis acid) in form A and a proton in form B makes it possible for these compounds to react with bases to form complexes and salts.

Studies have been reported [1-3] and are described here on the reactions of bis(α-hydroxyalkyl)phosphines and their derivatives with isobutyl diphenylborate (IDB) in the presence of bases. In the case of sufficiently strong bases such as triethylamine and methylmorpholine, reaction occurs with a wide variety of substituents at carbon and phosphorus in the diol. Salts are obtained when IDB and triethylamine or methylmorpholine react with bis(α-hydroxyalkyl)phosphines [1]. Introduction of substituents into the benzene ring of the benzyl group of bis(α-hydroxybenzyl)phosphines has no effect on the structures of the products obtained. For example, triethylammonium 4,6-di-m-bromo- and 4,6-di-p-methoxyphenyl-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinanes (I) and (II) have been isolated. Instead of the diols, phenylphosphine and aldehydes may be used:



R = m-Br(I), p-OMe(II)

(I), (II)

Only the p-nitro group gives rise to the formation of complexes [1].

Oxides, sulfides, and selenides of bis(α-hydroxyalkyl)phenylphosphines with donor and acceptor substituents also give salts on reaction with IDB and triethylamine or methylmorpholine

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