SYNTHESIS AND STERIC STRUCTURE OF 2,2-DISUBSTITUTED 5-PHENYL-1,3,5-DIOXAPHOSPHORINANES

B. A. Arbuzov, O. A. Erastov, and A. S. Ionkin

UDC 542.91:541.63:547.1'118

A comparison of conformational equilibria of 1-phenylphosphorinane [1, 2] and 5-phenyl-1,3,5-dioxaphosphorinane [3] shows that replacement of the CH_2 group by an oxygen atom stabilizes the form with an axial orientation of phenyl at P atom. This effect may be due interactions in the PCO fragment. Its possible appearance depends on the substituents in the system. The introduction of methyl, isopropyl and phenyl at the 2, 4, and 6-positions of 5-phenyl-1,3,5-dioxaphosphorinane has a different influence on the position of the equilibrium between the stereoisomers [4]. Introduction of ethoxy group at the 2-position shifts the equilibrium in the direction of a form with equatorial orientation of phenyl at the P atom [5]. This can be explained by transfer of electron density from the unshared electron pair (UEP) orbital of the O atom of the ethoxy group to the vacant orbital of an intracyclic C–O bond, subjected to the action of a negative inductive effect on the phosphino group [6]. This, in turn, should lead to suppression of the donor properties of the phosphino group due to the presence of an UEP [7]. The orbital interactions of the $p-\sigma^*$ type depend on the relative disposition of the orbitals [8]. It was therefore interesting to study 2-substituted 5-phenyl-1,3,5-dioxaphosphorinanes with substituents with no UEP.

2-Substituted 5-phenyl-1,3,5-dioxaphosphorinanes can be synthesized by the reaction of phenylbis(hydroxymethyl)phosphine with aldehydes, ketones, and their acetals and ortho-esters. However, acetaldehyde, isobutyraldehyde, and benzaldehyde did not enter the reaction [3]. According to ^{31}P NMR spectral data, substitution products at the P atom are formed with acetaldehyde and benzaldehyde acetals [5]. With orthoformic ester, 5-phenyl-2-ethoxy-1,3,5-dioxaphosphorinane was obtained [5]. In the present work, we carried out reactions of phenylbis(hydroxymethyl)phosphine with ketones and their acetals, and an attempt was made to isolate products in the reaction with aldehyde acetals.

The reactions with ketones were carried out with heating, and they were controlled by ^{31}P NMR spectra. In the spectra of the reaction mixtures there was only a signal of a diol, which indicated that there is no reaction.

The reaction with aldehyde acetals started at 115-145°C, and was carried out up to complete distillation of the alcohol. The ratio of the reagents varied from 1:1.5 to 1:4. In the ^{31}P NMR spectrum of the reaction mixture of phenylbis(hydroxymethyl)phosphine and furfural bis(ethoxy)acetal (1:1.5) there were signals of 2-furyl-5-phenyl-1,3,5-dioxaphosphorinane at −42 ppm, phenylbis(1-ethoxy-1-furylmethyl)phosphine at −6 and −8 ppm, and of phenylbis(1-ethoxy-1-furylmethyl)phosphine oxide at +34 ppm, with a relative intensity of 3:9:6. The first of the products was unstable, and decomposed on distillation. Phenylbis(1-ethoxy-1-furylmethyl)phosphine was distilled. It gave a molecular ion with m/z 358 in the mass spectrum and readily oxidized on standing; it was analyzed in the form of oxide.

The reaction of phenylbis(hydroxymethyl)phosphine with benzaldehyde bis(ethoxy)acetal (1:2) gave a mixture of phenylbis(1-ethoxy-1-phenylmethyl)phosphine and its oxide (8, −10, and 34 ppm, 12:8). The oxide was isolated by distillation. Under the same conditions, phenylbis(hydroxymethyl)phosphine and acetaldehyde bis(ethoxy)acetal at a 1:4 ratio of the reagents form only phenylbis(1-ethoxyethyl)phosphine, which is stable when distilled in vacuo (0, −8 ppm). In the mass spectrum of the product there is a molecular peak with m/z 254. (see next page for scheme)

Reactions with acetals studied proceed in two directions, and with excess acetal gave only phenylbis(1-ethoxyalkyl)phosphines. They are therefore important mainly for the prepara-

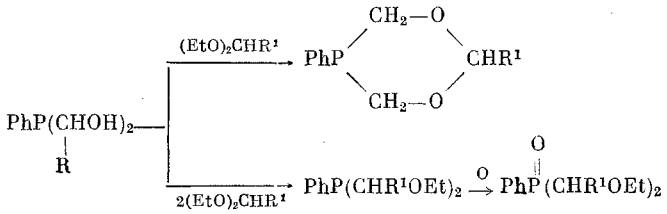
A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2506-2509, November, 1986. Original article submitted May 21, 1985.

0568-5230/86/3511-2293$12.50

TABLE 1. Parameters of NMR Spectra of (I)-(IV)

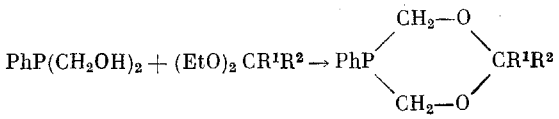
Compound	$\delta^{31}P$	σH_a	σH_e	$^2J_{PH_a}$	$^2J_{PH_e}$	$-^2J_{HH}$	$Me_{a,e}$
(IV)	−50	4.47	4.15	24.5	5.1	14.6	1.33; 1.35
(V)	−48	4.47	4.12	24.0	10.0	14.1	1.23–1.92 (CH_2)
(VI)	−46	4.45	4.14	24.6	5.0	12.6	1.57
(VII)	−48 −49	4.48 4.42	4.17 4.12	24.0 20.7	5.4 7.1	14.5 14.5	1.25 1.25

tion of α-alkoxyalkylphosphines. Methods for synthesizing these compounds have not yet been sufficiently developed [9].



R = H, Me; R^1 = furyl (I), Ph (II), Me (III).

The unexpectedly simple path leading to 2,2-disubstituted 5-phenyl-1,3,5-dioxaphosphorinanes was opened by the reaction of phenylbis(hydroxymethyl)phosphine with ketone acetals. The bis(ethoxy)acetals of acetone, cyclohexanone, acetophenone and methyl ethyl ketone reacted to form only cyclic compounds, even with excess acetal



R^1, R^2 = Me, Me (IV); ⬡ (V); Me, Ph (VI); Me, Et (VII).

The reactions also started at 120-140°C and were carried out up to complete distillation of ethanol. In the ^{31}P NMR spectra of the reaction mixtures, the signal of the initial diol (−20 ppm) completely disappeared and a signal of the product appeared in the −46 to −50 ppm region. In the case of (VII), two signals with chemical shifts (CS) at −48 and −49 ppm, respectively, were observed, which indicated the formation of two stereoisomers. The stereoisomer with CS at −49 ppm predominated. Compounds (IV) and (V) had no stereoisomers. The product with acetophenone is an individual stereoisomer.

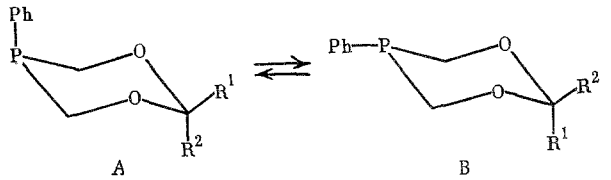
In the IR spectra of all the products obtained, there was no absorption of the OH groups in the 3100-3700 cm^{-1} region. The position and the intensity of signals in the PMR spectra corresponded to the attributed structures.

The difference in the reactivity of the aldehyde and ketone acetals may be due to the number of substituents at the C atom. However, the formation of the cyclic product with orthoformic ester indicates that the nature of the substituent has to be taken into account. The above examples demonstrate the ability of hydroxyalkylphosphines to participate in substitution reactions with electrophilic reagents at both the phosphorus atom and the oxygen atom [10].

The position of the conformational equilibrium of (IV)-(V) and predominating stereoisomers (VI) and (VII) was determined from ^1H NMR spectra. The parameters of the ^1H and ^{31}P NMR spectra are given in Table 1. The spectra of the methylene protons in the ring represent a typical pattern of splitting the $(AB)_2X$ system, where A, B are axial and equatorial protons at the 4, 6-positions, and X is the nucleus of the P atom.

The nonequivalency of the methylene protons indicates that the six-membered rings are present preferentially in a chair conformation, and during inversion the orientation of substituents on the P and C atoms changes. The similarity of the parameters of stereoisomers of (VII) indicates the same orientation of the phenyl at the P atom in them. The stereoisomers differ in the position of substituents at the C atom in the most favorable conformation. The equatorial orientation of phenyl at the C atom in (VI) is proved by the similarity of the

parameters of the spectra of (VI) and (IV), (VII). The last fact, in combination with the similarity of the spectra of all the compounds studied shows that they have one and the same most favorable conformation in a strongly displaced equilibrium.



A B

As a model of the form with axial orientation of phenyl at P atom, we took 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane [11], and as a model of the form with equatorial orientation of phenyl at the P atom, we took 1,3-dibenzyl-5-phenyl-1,3,5-dioxaphosphorinane [12]. The spectra of these models differ appreciably in the value of spin–spin coupling constant $^2J_{PH_a}$, which is equal to +5.5 and −6.3 Hz, respectively. In (IV)-(VII), this constant has a positive value, so that an axial conformation of the phenyl at the P atom can be ascribed to the most favorable conformer.

A study of (IV) by Raman spectroscopy over a wide range of temperatures did not reveal indications of conformational equilibrium.

This result is confirmed by the existence of stabilization of the form with an axial orientation of the phenyl at the P atom in 5-phenyl-1,3,5-dioxaphosphorinanes and the difference in the influence on this effect by substituents at the 2-position in the presence and absence of UEP in them.

EXPERIMENTAL

Phenylbis(1-ethoxy-1-furylmethyl)phosphine Oxide (I). A mixture of 9.42 g of $PhP(CH_2OH)_2$ and 14.13 g of furfural bis(ethoxy)acetal (1:1.5) was heated at 115°C until complete distillation of ethanol. The residue was distilled in vacuo. Yield, 2.36 g (11%), bp 190°C (0.1 mm), $\delta^{31}P$ 34 ppm. Found: C 63.81; H 6.07; P 8.99%. $C_{20}H_{23}O_5P$. Calculated: C 64.17; H 6.15; P 8.29%.

Phenylbis(1-ethoxy-1-phenylmethyl)phosphine Oxide (II). A mixture of 7.11 g of $PhP(CH_2OH)_2$ and 15.05 g of $PhCh(OEt_2)$ (1:2) was heated at 120°C until complete distillation of ethanol. The residue was distilled in vacuo. Yield, 1.2 g (7.3%), bp 110°C (0.1 mm), $\delta^{31}P$ 34 ppm. Found: C 71.14; H 7.04; P 8.28%. $C_{24}H_{27}O_3P$. Calculated: C 73.10; H 6.75; P 7.87%.

Phenylbis(1-ethoxyethyl)phosphine (III). A mixture of 2.7 g of phenylbis(1-hydroxyethyl)phosphine and 6.4 g of $MeCH(OEt)_2$ was heated at 145°C until complete distillation of ethanol. The residue was distilled in vacuo. Yield, 0.7 g (20%), bp 110°C (0.1 mm), $\delta^{21}P$ −8 ppm, m/z 254. Found: C 64.02; H 8.76; P 13.29%. $C_{24}H_{23}O_2P$. Calculated: C 66.14; H 9.06; P 12.20%.

2,2-Dimethyl-5-phenyl-1,3,5-dioxaphosphorinane (IV). A mixture of 4.95 g (0.029 mole) of $PhP(CH_2OH)_2$ and 4.61 g (0.035 mole) of $Me_2C(OEt)_2$ was heated at 110°C until complete distillation of ethanol. The residue was distilled in vacuo. Yield, 2.5 g (41%), bp 120-123°C (0.1 mm), n_D^{20} 1.5630, $\delta^{31}P$ −50 ppm, m/z 210. Found: C 62.70; H 7.38; P 14.79%. $C_{11}H_{15}O_2P$. Calculated: C 62.80; H 7.14; P 14.76%.

3-Phenyl-1,5-dioxa-3-phosphaspiro-[5.5]undecane (V). A mixture of 5.76 g (0.034 mole) of $PhP(CH_2OH)_2$ and 7.04 g (0.041 mole) of cyclohexanone bis(ethoxy)acetal was heated at 120°C until complete distillation of ethanol. The residue was distilled in vacuo. Yield, 2.03 g (24%), bp 160°C (0.1 mm), n_D^{20} 1.5550, $\delta^{31}P$ −48 ppm, m/z 250. Found: C 67.30; H 7.52; P 12.50%. $C_{11}H_{19}O_2P$. Calculated: C 67.20; H 7.68; P 12.40%.

2,5-diphenyl-2-methyl-1,3,5-dioxaphosphorinane (VI). A mixture of 4.87 g (0.029 mole) of $PhP(CH_2OH)_2$ and 5.56 g (0.029 mole) of acetophenone bis(ethoxy)acetal was heated at 140°C until complete distillation of ethanol. The residue was distilled in vacuo. Yield, 1.3 g (17%), bp 160-161°C (0.1 mm), n_D^{20} 1.5941, $\delta^{31}P$ −46 ppm, m/z 272. Found: C 70.60; H 6.29; P 11.67%. $C_{28}H_{27}O_2P$. Calculated: C 70.59; H 6.25; P 11.40%.

2-Methyl-2-ethyl-5-phenyl-1,3,5-dioxaphosphorinane (VII). A mixture of 6.8 g (0.04 mole) of $PhP(CH_2OH)_2$ and 7.0 g (0.048 mole) of methyl ethyl ketone bis(ethoxy)acetal was heated at 110°C until complete distillation of ethanol. The residue was distilled in vacuo. Yield,

1.6 g (18%), bp 123-126°C (0.1 mm), n_D^{20} 1.5672, $\delta^{31}P$ −48 ppm, m/z 224. Found: C 63.29; H 7.06; P 14.03%. $C_{12}H_{17}O_2P$. Calculated: C 64.29; H 9.38; P 13.84%.

CONCLUSIONS

Phenylbis(1-ethoxyalkyl)phosphines and 2,2-disubstituted 5-phenyl-1,3,5-dioxaphosphorinanes, with their conformational equilibrium shifted in the direction of the form with an axial orientation of phenyl at the phosphorus atom, were obtained by the reaction of phenylbis(hydroxymethyl)phosphine with aldehyde and ketone acetals, respectively.

LITERATURE CITED

1. S. J. Featherman and L. D. Quin, J. Am. Chem. Soc., 97, 4349 (1975).
2. G. D. Macdonell, K. D. Berlin, J. R. Backer, S. E. Ealick, Dick van der Helm, and K. L. Marsi, J. Am. Chem. Soc., 100, 4535 (1978).
3. B. A. Arbuzov, O. A. Erastov, S. Sh. Khetagurova, T. A. Zyablikova, R. P. Arshinova, and R. A. Kadyrov, Izv. Akad. Nauk SSSR, Ser. Khim., 1626 (1980).
4. B. A. Arbuzov, O. A. Erastov, and S. Sh. Khetagurova, Dokl. Akad. Nauk SSSR, 246, 326 (1979).
5. B. A. Arbuzov, O. A. Erastov, and A. S. Tonkin, Izv. Akad. Nauk SSSR, Ser. Khim., 418 (1986).
6. S. S. C. Chu and C. A. Jeffrew, Acta Crystallogr., 23, 1038 (1967).
7. G. V. Ratovskii, A. M. Panov, and Yu. I. Sukhorukov, Zh. Obshch. Khim., 49, 548 (1979).
8. N. D. Epiotis, W. R. Cherry, and S. Snaik, Structural Theory of Organic Chemistry, Springer-Verlag, Berlin (1977), pp. 1-250.
9. K. A. Petrov, V. A. Chauzov, and S. V. Agagonov, Usp. Khim., 43, 412 (1982).
10. O. A. Erastov and G. N. Nikonov, Usp. Khim., 53, 625 (1984).
11. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, T. A. Zyablikova, R. P. Arshinova, and R. A. Kadyrov, Izv. Akad. Nauk SSSR, Ser. Khim., 2349 (1979).
12. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, T. A. Zyablikova, R. P. Arshinova, and R. A. Kadyrov, Izv. Akad. Nauk SSSR, Ser. Khim., 1571 (1980).

DISPLACEMENT OF ALDEHYDE FRAGMENT IN DIPHENYLBORYLOXY-ALKYLPHOSPHINES

B. A. Arbuzov, G. N. Nikonov,
A. S. Balueva, and O. A. Erastov

UDC 542.91:541.63:547.1'127'118

The reactions of hydroxyalkylphosphines due to the presence of an acidic hydrogen atom are well known. These involve the displacement of the aldehyde fragment by electrophilic reagents, with shifting of the proton to the negative center of the electrophile, substitution of the hydroxyl group by nucleophilic reagents, rearrangement into phosphine oxides, etc. Similar reactions of hydroxyalkylphosphine derivatives in which the hydrogen atom is substituted by a Lewis acid have been studied less [1]. We examined the displacement of the aldehyde fragment in diphenylboryloxyalkylphosphines. For the investigation, we selected diphenylboryloxyalkyl(imidoyl)phosphines and 4,6-disubstituted triethylammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinanes.

Diphenylboryloxymethyl(imidoyl)phenylphosphines were obtained in [2] by the reaction of phenylbis(hydroxymethyl)phosphine with isobutyl diphenyl borate in the presence of MeCN and PhCN. The reaction proceeds via the intermediate formation of diphenylboryloxymethyl(hydroxymethyl)phenylphosphine, in which the hydromethyl group is replaced by the mimdoyl group. It was found that phenylphosphine and different aldehydes can be used in this reaction, instead of phenylbis(hydroxymethyl)phosphine. Diphenylboryloxyalkyl(imidoyl)phenylphosphines are then formed.

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. 11, pp. 2510-2514, November, 1986. Original article submitted May 5, 1985.

0568-5230/86/3511-2296$12.50