SYNTHESIS AND STRUCTURE OF 1,5-DIAZA-3,7-DIPHOSPHACYCLOOCTANES

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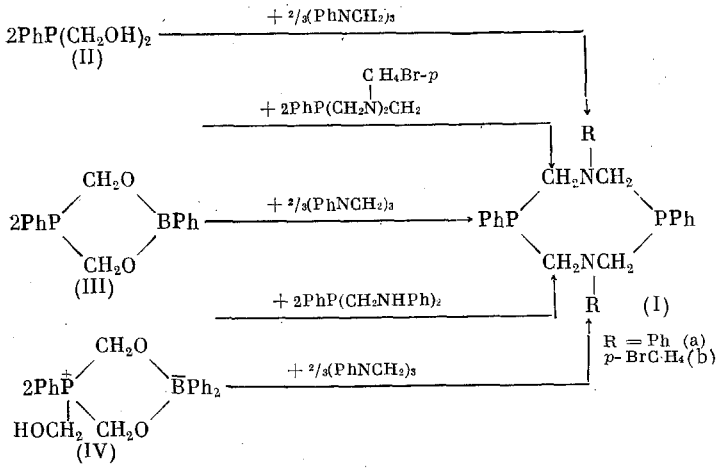
1,5-Diaza-3,7-diphosphacyclooctanes (I) [1, 2] are capable of forming complexes [2] and are suitable molecules for the study of the 1,3-interaction of phosphorus and nitrogen atoms [3]. Studies have been carried out on this question. Syntheses of (I) have been described starting from hydroxy- and aminomethyl derivatives of primary phosphines and phosphonium salts, phosphorus-containing esters of phenyl- and diphenylboric acids and 1,3,5-diazaphosphorinanes by the action of primary, secondary, and tertiary amines with dissociation and disproportionation [1, 2, 4-7]. X-ray diffraction structural analysis has shown the three-dimensional structure in the solid state for 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane [8], 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane [3], and 1,5-di-p-tolyl-3,7-diphenyl-3,7-dithio-1,5-diaza-3,7-diphosphacyclooctane [9]. The ^{1}H and ^{13}C NMR spectra for these compounds indicated the structure of (I) in solution [2]. Mass spectra were taken for 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane [2], 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane and its sulfide derivative [7, 10]. Studies have been carried out on the transformation of (I) to bis(phenylaminomethyl)phosphines and 1,3,5-diazaphosphorinanes [6], the transamination of (I) with amines [11], oxidation [7] and thionylation of (I) [9]. In the present work, the methods for the preparation of (I) are summarized and their structure in solution is studied using the dipole moment method.

Methods have been reported for the preparation of (I) using bis(hydroxymethyl)phenylphosphine (II), 2,5-diphenyl-2-bora-1,3,5-dioxaphosphorinane (III), and 2,2,5-triphenyl-5-hydroxymethyl-2-boranata-5-phosphonia-1,3-dioxane (IV). The possibilities for the synthesis of these compounds may be expanded significantly by using new types of amines and the extension of reactions characteristic for one compound to others. To confirm this hypothesis, we carried out the reaction of (II) with 1,3,5-triphenyl-1,3,5-triazine (III) with bis(phenylaminomethyl)phenylphosphine, 1,3,5-triphenyl-1,3,5-triazine, and 5-phenyl-1,3-di-p-bromophenyl-1,3,5-diazophosphorinane, and (IV) with 1,3,5-triphenyl-1,3,5-triazane. In all cases, good yields of (I) were obtained. Derivatives of (I) may also be obtained under conditions for the intermediate formation of compounds hydroxy- and aminomethyl groups or two aminomethyl groups at the phosphorus atom. For example, phenylphosphine (V) and diphenylboryloxymethyl(acetimidoyl)phosphine (VI) [12] by a reaction



with 1,3,5-triphenyl-1,3,5-triazine gives (I)

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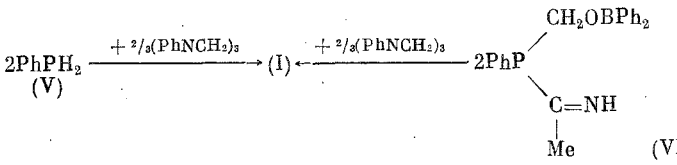
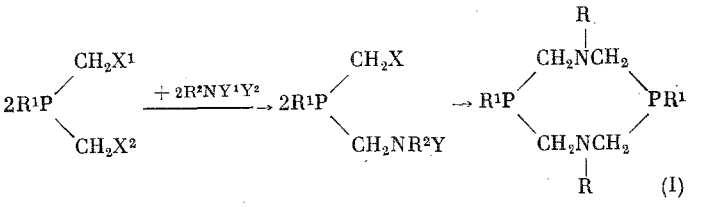
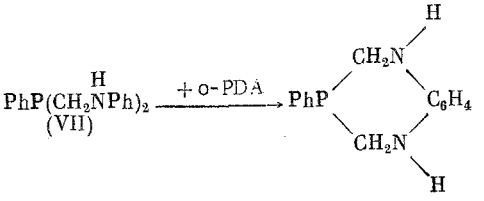


All the methods for the preparation of (I) are based on reactions involving nucleophilic substitution at the carbon atom attached at the phosphorus atom. The nucleophilic reagents are amines, in which the nitrogen atom is bound to two leaving groups. The results of our previous study [6] and of Frank and Drake [13] indicate facile cleavage of the C–N bond in aminomethylphosphines. Hydroxy-, phenylboryloxy-, diphenylboryloxy-, secondary and tertiary amino groups are the leaving groups at the carbon atom bound to the phosphorus atom. The starting compounds have two sites for nucleophilic attack at the carbon atoms attached to the phosphorus atom. In general form



Here X is a leaving group in nucleophilic replacement, Y is a group capable of splitting off from the nitrogen atom in amines, and R is an alkyl or aryl group. Cyclooctanes (I) with aliphatic substituents at the phosphorus and nitrogen atoms were obtained by Markl et al. [2].

This generalization indicates for the development of new methods for the preparation of (I) or the prediction of their formation in the corresponding reactions. An exception is o-phenylenediamine (o-PDA) which reacts with (II) to form 6,7-benzo-3-phenyl-1,5-diaza-3-phosphepane [14]. The reaction of bis(phenylaminomethyl)phenylphosphine (VII) with o-PDA proceeds analogously



The structure of (I) and their sulfide analogs in the crystalline state was found by x-ray diffraction structural analysis. 1,3,5,7-Tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane has a crown conformation with all equatorial (e) substituents [8]. 1,5-Dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane has crown conformation with equatorial substituents at the phosphorus atoms and axial (a) substituents at the nitrogen atom [3] and 1,5-di-p-tolyl-3,7-diphenyl-3,7-dithio-1,5-diaza-3,7-diphosphacyclooctane has a distorted boat conformation [9]. The mass spectra of 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane and its sulfide derivative have molecular ion peaks with m/z 241 and 273 [7, 10] while the mass spectrum of 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane has a molecular ion peak with m/z 454 but lacks the peak with m/z 227 [2]. These findings indicate that (I) and its sulfide analogs may dissociate under mass spectral conditions with the loss of 1,3-aza-phosphetidines and their sulfide analogs, respectively. The structure of (I) in solution was considered by Markl et al. [2] relative to the ^{1}H and ^{13}C NMR spectral parameters for the eight-membered ring which indicated the crown conformation. Attempts to determine the molecular weight of (I) and its sulfide analogs do not give reproducible results due to the poor solubility of these compounds.

We should note the accord in the conformations of (I) in the crystalline state and in solution. This accord for (I) and its sulfide analogs may be checked by the dipole moment method. The dipole moments were determined in benzene at 20°C. The diazadiphosphacyclooctane structure of (I) and their sulfide analogs were supported by comparison of the ^{31}P NMR

TABLE 1. Experimental and Calculated Dipole Moments of (I) and Their Sulfide Analogs (μ, D) [*p*-X-$C_6H_4N(CH_2)_2PPh]_2$, crown

X	Ph-P orientation			Experimental
	ee	*aa*	*ae*	
H	4,61	2,61	4,06	4,73
Br	6,86	4,56	5,86	6,95
Me	4,13	1,83	3,12	3,79

$[PhCH_2N(CH_2)_2PPh]_2$, crown

Bz	*aa*			*ee*			*ae*			Experimental
Ph—P	*ee*	*aa*	*ae*	*ee*	*aa*	*ae*	*ee*	*aa*	*ae*	
μ	2,32	0,96	1,62	3,20	1,83	2,49	2,76	1,40	2,05	2,12

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$[p\text{-X-}C_6H_4N(CH_2)_2PPh]_2$, distorted boat—boat

X	N^1-Ar_a				N^2-Ar_e				Experimental
	ee'	*ea'*	*ae'*	*aa'*	*ee'*	*ea'*	*ae'*	*aa'*	
H	9,68	6,16	6	1,63	9,54	5,86	6,26	1,78	7,45
Br	10,46	6,96	5,71	2,38	9,87	5,77	6,82	1,77	7,73
Me	9,54				9,47	5,89	6,13	1,81	7,17

spectra of melts and solutions. In all cases, the ^{31}P NMR chemical shifts have identical values. The dipole moments were calculated according to the standard method. The geometrical parameters were taken from x-ray diffraction structural analysis data. The bond polarities were taken as in our previous work [15, 16]. The results are given in Table 1 and Fig.1.

The experimental dipole moments of compounds with P(III) correspond to the crown conformation with all equatorial substituents when the substituents on the nitrogen atoms are aromatic and equatorial only on the phosphorus atoms when the nitrogen atom has benzyl substituents. The selection of the preferred conformation is facilitated by the significant difference in the dipole moments of the conformation with different orientation of the substituents at the phosphorus atom, especially in the case of aryl groups at the nitrogen atoms. The conformations obtained from the dipole moments in benzene correspond with those found by x-ray diffraction structural analysis of the crystals, even including the orientation of the substituents at the phosphorus and nitrogen atoms. This result may be seen as evidence for the retention of the conformation of (I) upon entering solution.

In the case of the sulfide analogs of (I), there is no direct agreement of the experimental dipole moments with the calculated values for the distorted boat—boat form established by x-ray structural analysis. In light of the preference of the crown conformation for many phosphorus-containing eight-membered rings, the dipole moment of this form was calculated with different orientations of the substituents at the phosphorus atom. The extent of deviation of the atoms at the crown apices is not known precisely for compounds with P(IV). Thus, the calculations were performed for all the possible variants. The results are given in the form of an Exner plot which gives the dependence of the square of the dipole moment of (Ia) on the square of the dipole moment of (Ib) (see Fig. 1). The dependence of μ^2 of (Ia) on μ^2 of (Ic) (R = p-$CH_3C_6H_4$) is analogous. The experimental points for the compounds are found on the curve corresponding to diequatorial orientation of the phenyl groups at the phosphorus atoms. The same displacement of the compressed nitrogen atoms from the mean plane by 0.1 Å is found for all three compounds. This agreement is strong evidence for the existence of sulfide analogs of (I) in solution in the crown conformation. Hence, the conformation of these compounds is altered upon entering solution.

An attempt was made to compare the experimental dipole moments with the calculated values for N-substituted 3-phenyl-1,3-azaphosphetidines. There was no agreement for all

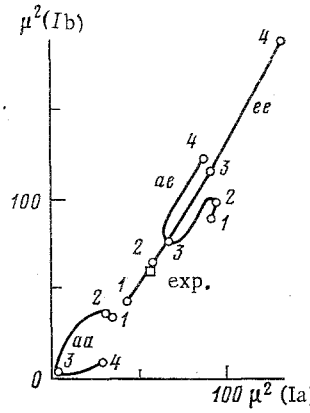

Fig. 1. Dependence of μ^2 of (I) for R = Ph on μ^2 of (I) for R = p-BrC_6H_4: aa) diaxial; ae) axial-equatorial; ee) diequatorial orientation of phenyl groups at the phosphorus atoms. The displacement of the nitrogen atoms from the mean plane: 1) 0.0; 2) 0.1; 3) 0.29; 4) 0.5 Å.

reasonable variants. The calculated dipole moments are significantly less than the experimental values. This result also supports the structure for (I) and its sulfide analogs in solution given above.

EXPERIMENTAL

The dipole moments were determined as in our previous work [15, 16]. The coefficients of the equations used in the calculation are $\alpha = 5.9403$, $\gamma = 0.4246$ for R = Ph, $\alpha = 3.6725$, $\gamma = 0.3423$ for (Ic), $\alpha = 9.1931$, $\gamma = 0.4222$ for (Ib), $\alpha - 1.4773$, $\gamma = 0.4308$ for (Ia), $\alpha =$ $= 12.4080$, $\gamma = 0.4575$ for (Ia) sulfide, $\alpha = 10.9201$, $\gamma = 0.4347$ for (Ic) sulfide, $\alpha = 10.4764$, $\gamma = 0.5990$ for (Ib) sulfide.

Bis(hydroxymethyl)phenylphosphine (II). A sample of 2.7 g (9 mmoles) paraformaldehyde was added to 5 g (4.5 mmoles) phenylphosphine in an argon atmosphere. The mixture was carefully heated until the paraformaldehyde was dissolved. The reaction proceeded with the liberation of heat. A thick, colorless liquid was formed with a yield of 7.7 g (100%), $\delta^{31}P$: −20 ppm [17].

Reaction of (II) with Amines. A sample of 12 g (12.5 mmoles) aniline in 50 ml ethanol was added to 21.6 g (12.5 mmoles) (II). On the following day, the precipitate was filtered off and washed with ethanol. The yield of (Ia) was 27.5 g (97%), mp 190-191°C, $\delta^{31}P$: −52 ppm (C_5H_5N) [1].

The addition of p-toluidine gave (Ic) in 69% yield, mp 216-217°C, $\delta^{31}P$ (C_5H_5N): −52 ppm. The addition of p-bromoaniline gave (Ib) in 98% yield with mp 203-204°C, $\delta^{31}P$ (C_5H_5N): −50 ppm. The addition of benzylamine gave (Ia) in 56% yield with mp 142-143°C and $\delta^{31}P$ (C_5H_5N): −52 ppm [1].

Reaction of (II) with 1,3,5-Triphenyl-1,3,5-triazane (TPTA). A sample of 0.1 g (0.34 mmole) TPTA and 2 ml pyridine was added to 0.18 g (II) (1 mmole). The mixture was heated and 3 ml ethanol was added. The precipitate formed was filtered off and crystallized from acetonitrile to yield 0.05 g (23%) (Ia) with mp 190-191°C, $\delta^{31}P$: −52 ppm.

Reaction of 2,5-Diphenyl-2-bora-1,3,5-dioxaphosphorinane (III) with TPTA. The reaction was carried out by analogy with that for (II). The yield of (Ia) was 30%, mp 190-191°C, $\delta^{31}P$: −52 ppm (C_5H_5N).

Reaction of (III) with Bis(phenylaminomethyl)phenylphosphine (VII). A sample of 0.06 g (2 mmoles) (VIII) was added to 0.5 g (2 mmoles) (III) in 5 ml methanol. The mixture was heated and maintained for 3 h. The precipitate was filtered off and crystallized from acetonitrile to yield 0.6 g (75%) (Ia), mp 190-191°C, $\delta^{31}P$: −52 ppm (C_5H_5N).

Reaction of (III) with 5-Phenyl-1,3-di-p-bromophenyl-1,3,5-diazaphosphorinane (IX). This reaction was carried out by analogy with that for (VII) to yield 30% (Ib), mp 204°C, $\delta^{31}P$: −50 ppm (C_5H_5N).

Reaction of 2,2,5-Triphenyl-5-hydroxymethyl-2-boronata-5-phosphonia-1,3-dioxane (IV) with TPTA. A sample of 0.1 g (0.34 mmole) TPTA and 2 ml pyridine was added to 0.35 g (1 mmole) (IV). The mixture was heated and 4 ml ethanol was added. The precipitate formed was filtered off after 4 h and crystallized from acetonitrile to yield 0.1 g (33%) (Ia), mp 190-191°C, $\delta^{31}P$: −52 ppm.

Reaction of Phenylphosphine (V) with TPTA. A sample of 1.5 g (0.5 mmole) TPTA was added to 1.6 g (1.4 mmole) (V). On the following day 8 ml acetonitrile was added and the precipitate formed was filtered off and crystallized from acetonitrile to yield 0.4 g (12%) (Ia), mp 190-191°C, $\delta^{31}P$: −52 ppm.

Reaction of Diphenylboryloxymethyl(acetimidoyl)phenylphosphine (VI) with TPTA. A sample of 0.4 g (1.3 mmole) TPTA, a few crystals of p-toluenesulfonic acid and 10 ml pyridine were added to 1.33 g (3.9 mmoles) (IV). The mixture was heated until the TPTA sample dissolved. On the following day, the solvent was removed and the precipitate was filtered and crystallized from acetonitrile to yield 0.2 g (23%) (Ia), mp 190-191°C, $\delta^{31}P$: −52 ppm (C_5H_5N).

Reaction of (VII) with o-Phenylenediamine. A mixture of 2 g (6 mmoles) (VII) and 0.6 g (6 mmoles) o-PDA in 20 ml benzene was heated to reflux. A precipitate formed upon standing which was filtered off and washed with acetonitrile to yield 1.2 g (81%) 6,7-benzo-3-phenyl-1,5-diaza-phosphepane, $\delta^{31}P$: −32 ppm (DMS), mp 182°C [14].

CONCLUSIONS

1. 1,5-Diaza-3,7-diphosphacyclooctanes may be prepared from phosphines having groups which leave upon nucleophilic attack at the two carbon atoms attached to the phosphorus atom and amines with two labile N—R bonds.

2. 1,5-Diaza-3,7-diphosphacyclooctanes have crown conformation in solution.

LITERATURE CITED

1. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 735 (1980); USSR Inventor's Certificate 785,316, Byull. Izobret., No. 45 (1980); USSR Inventor's Certificate 810,715, Byull. Izobret., No. 9 (1981); USSR Inventor's Certificate 854,932, Byull. Izobret., No. 30 (1981).
2. G. Märkl, Jin G. Ju, and C. Schoerner, Tetrahedron Lett., 21, 1409 (1980).
3. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, I. A. Litvinov, D. S. Yufit, and Yu. T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., 2279 (1981).
4. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 952 (1980).
5. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 954 (1980).
6. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 1438 (1980).
7. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 2129 (1980).
8. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, I. A. Litvinov, D. S. Yufit, and Yu. T. Struchkov, Dokl. Akad. Nauk SSSR, 257, 127 (1981).
9. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, D. S. Yufit, and Yu. T. Struchkov, Dokl. Akad. Nauk SSSR, 267, 650 (1982).
10. G. N. Nikonov, in: Abstracts of the Conference on the Synthesis, Structure, and Reactivity of Some Heteroorganic Compounds, Kazan, 1980 [in Russian], Kazan (1980), pp. 45-46.
11. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 2417 (1980).
12. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, T. A. Zyablikova, Yu. Ya. Efremov, and R. Z. Musin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 676 (1982).
13. A. W. Frank and G. L. Drake, J. Org. Chem., 37, 2752 (1972).
14. B. A. Arbuzov, O. A. Erastov, I. P. Romanova, Yu. Ya. Efremov, and R. Z. Musin, Izv. Akad. Nauk SSSR, Ser. Khim., 640 (1982).
15. 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).
16. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, R. P. Arshinova, and R. A. Kadyrov, Izv. Akad. Nauk SSSR, Ser. Khim., 721 (1980).
17. B. A. Arbuzov, O. A. Erastov, and S. Sh. Khetagurova, Izv. Akad. Nauk SSSR, Ser. Khim., 866 (1979).