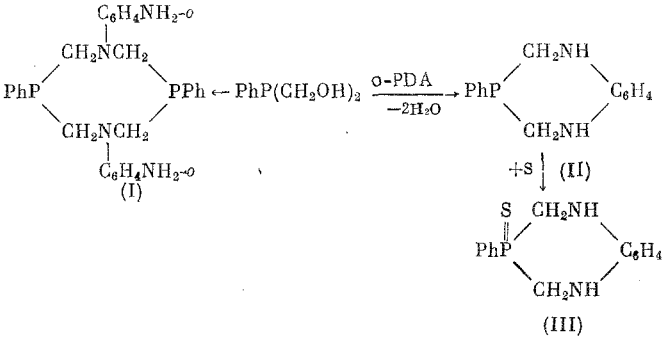
REACTION OF DIHYDROXYMETHYLPHENYLPHOSPHINE WITH o-PHENYLENEDIAMINE

B. A. Arbuzov, O. A. Erastov,
I. P. Romanova, Yu. Ya. Efremov,
and R. Z. Musin

UDC 542.91:547.1'118

As a rule, polymers are obtained when the hydroxymethyl derivatives of phosphine and primary phosphines are reacted with NH_3 and primary amines. The monomeric products were obtained as follows: 1) by reacting trihydroxymethylphosphine with NH_3 in the presence of excess paraform [1]; 2) reaction of phenylphosphine, benzaldehyde, and primary aliphatic amines [2]; 3) reaction of dihydroxymethylalkyl (and phenyl)-phosphines with primary amines [3-5]; 4) reaction of trihydroxymethylphosphine with aniline [6]. Reactions with compounds containing two primary amino groups have not been studied, although cyclic products were obtained in the case of two secondary amino groups [7]. The reaction of o-phenylenediamine with dihydroxymethylphenylphosphine is discussed in the present paper.

o-Phenylenediamine can react simultaneously as either one or two amino groups. In the first case the reaction should proceed the same as the reaction with monofunctional primary amines. A study of such reactions on the example of aniline, p-toluidine, benzylamine, and certain primary aliphatic amines disclosed that 1,5-diaza-3,7-diphosphacyclooctanes are formed instead of the expected 1,3-azaphosphetidines [3, 5]. This was confirmed by the x-ray structure analysis data for the crystalline state [8], PMR spectroscopy for the solutions [3], and mass spectrometry for the gas phase [3]. Only for 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane does the molecular ion (MI) have a mass number that coincides with the molecular mass of 1-phenyl-3-benzyl-1,3-azaphosphetidine [9], which can be due to the thermal dissociation of the substance. In view of these data a product with an eight-membered ring (I) must be expected for o-phenylenediamine when one amino group is used. 6,7-Benzo-1,5-diaza-3-phosphepane (II) can be formed in the case of using both amino groups.



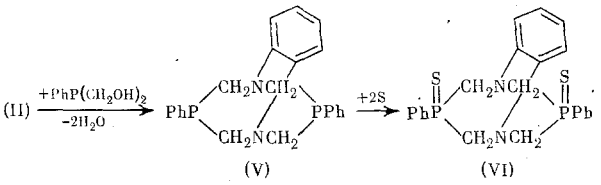
A monomeric product with mp 182°C, whose elemental composition corresponded to structures (I) and (II), was formed when o-phenylenediamine is heated with one mole of dihydroxymethylphenylphosphine. The IR spectrum of the product had bands at 3200 and 3280 cm^{-1}, which belong to the stretching vibrations of the N—H bond and which are retained in the spectrum of the substance in dilute CCl_4 solution. However, since secondary amino groups can take part in symmetric and antisymmetric stretching vibrations, the presence of two bands in the 3100-3600 cm^{-1} region did not permit choosing in favor of either structure. The molecular weight of the product (cryoscopy in naphthalene) proved to be equal to 245, with a theoretical value of 242 for (II) and 484 for (I). In addition, the mass spectrum of the product had an MI with m/z 242. This permitted excluding structure (I) from the discussion and determining the product as being (II). Substituted 6,7-benzo-1,5-diaza-3-phosphepanes were obtained in [7] by reacting dihydroxymethylalkylphosphines with N-substituted ethylenediamines. The reaction of (II) with sulfur and CH_3I gives sulfide (III) and methiodide (IV). Previously it was mentioned that the

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 440-443, February, 1982. Original article submitted June 25, 1981.

0568-5230/82/3102-0399$07.50

chemical shifts of the signals in the ^{31}P NMR spectra of the aminomethyl derivatives of a phenylphosphine with a secondary and tertiary amino group differ sharply [4, 5]. In this connection it is interesting to mention that the chemical shifts of (II) and (III) are equal to the chemical shifts of diaminomethylphenylphosphine (−31 ppm) and diaminomethylphenylphosphine sulfide (40 ppm), respectively.

The reaction of (II) with dihydroxymethylphenylphosphine gave a new product, whose elemental composition corresponded to 9,10-benzo-3,7-diphenyl-1,5-diaza-3,7-diphosphabicyclo[3.3.2]decane (V):



The mass spectrum of the product had an MI with m/z 376, which coincided with the molecular mass of (V). In addition, the peaks of fragments, formed by the cleavage of the Ph, CH_2-PPh, $(CH_2)_2PPh$, and PPh groups from the MI, were detected in the spectrum. The IR spectrum lacks absorption in the 1600-2800 and 3100-3600 cm^{-1} regions. The presented data proved the structure of (V); (V) with sulfur gives sulfide (VI). An analogous reaction was described in [10] for dihydroxymethylphenylphosphine and hydrazine.

As a result, diamines with primary amino groups, the same as primary monoamines, can react with the hydroxymethyl derivatives of primary phosphines to give monomeric products, but here both of the amino groups react with the hydroxymethyl groups.

EXPERIMENTAL

The IR spectra were obtained on a UR-10 spectrometer, and the ^{31}P NMR spectra were obtained on a KGU-4 NMR spectrometer at a frequency of 10.2 MHz, with noise decoupling from the protons at a frequency of 25.2 MHz. The chemical shifts are given relative to 85% H_3PO_4.

The mass spectra were obtained using electrons with an ionizing energy of 50 eV.

3-Phenyl-6,7-benzo-1,5-diaza-3-phosphepane (II). A mixture of 6.4 g (0.04 mole) of dihydroxymethylphenylphosphine [11] and 7.3 g (0.04 mole) of o-phenylenediamine was heated in benzene for 3 h with azeotropic distillation of the water. The precipitate was filtered and washed with methanol. Yield 8.1 g (89%), mp 182°, $\delta^{31}P$ −32 ppm (DMSO). Found: C 69.26; H 6.20; P 12.24; N 11.50%. $C_{14}H_{15}PN_2$. Calculated: C 69.42; H 6.19; P 12.80; N 11.57%. Infrared spectrum (ν, cm^{-1}): 3200 and 3280 (oil). Mass spectrum of (II): 243(3.5), 242(20), 240(3.5), 134(11), 133(58), 132(19), 131(39), 130(7), 121(16), 120(63), 119(100), 118(18), 110(33), 109(16), 108(33), 107(16), 92(21), 91(11), 83(11), 82(5.3), 81(11), 80(5.3), 79(10), 78(16), 77(27), 57(12), 55(11), 51(11), 45(11). Mol. wt. 233 (cryoscopically in naphthalene), calc. 242.

3-Phenyl-3-thio-6,7-benzo-1,5-diaza-3-phosphepane (III). A solution of 0.5 g (0.002 mole) of (II) and 0.09 g (0.003 mole) of sulfur in 20 ml of MeCN was refluxed, the solvent was evaporated in vacuo, and the residue was washed with benzene. Yield 0.57 g (98%), mp 225-227°, $\delta^{31}P$ 40 ppm (DMSO). Found: C 60.25; H 5.75; P 11.08; N 10.76; S 11.65%. $C_{14}H_{15}PN_2S$. Calculated: C 61.31; H 5.47; P 11.31; N 10.22; S 11.67%. Infrared spectrum (ν, cm^{-1}): 3200 and 3300 (oil).

3-Methyl-3-phenyl-6,7-benzo-1,5-diaza-3-phosphoniepane Iodide (IV). A mixture of 1 g (0.004 mole) of (II) and 1 g (0.007 mole) of MeI was left standing overnight, evaporated in vacuo, and the residue was washed with MeCN. Yield 1.17 g (98%), mp 147°, $\delta^{31}P$ 16 ppm (DMSO). Found: C 46.44; H 4.52; P 8.02; N 7.20%. $C_{15}H_{18}PN_2I$. Calculated: C 46.51; H 4.65; P 8.01; N 7.23%. Infrared spectrum (ν, cm^{-1}): 3210 and 3310 (oil).

9,10-Benzo-3,7-diphenyl-1,5-diaza-3,7-diphosphabicyclo[3.3.2]decane (V). A solution of 1 g (0.004 mole) of (II) and 0.7 g (0.004 mole) of dihydroxymethylphenylphosphine [11] in 50 ml of benzene was refluxed for 3 h with azeotropic distillation of the water, evaporated in vacuo, and the residue was dissolved in pyridine. The addition of MeCN gave a precipitate. Yield 1.53 g (97%), mp 125-127°, $\delta^{31}P$ −40 ppm (DMSO). Found: C 70.41; H 6.03%. $C_{22}H_{22}P_2N_2$. Calculated: C 70.23; H 5.84%. Mass spectrum of (V): 376(100), 299(4), 270(7), 269(2.6), 268(4.8), 267(5.2), 262(4.8), 254(25), 253(13), 230(28), 214(20), 186(17), 185(26), 183(21), 170(31), 160(19), 159(67), 158(43), 156(35), 110(25), 109(20), 108(35), 107(17), 78(95), 77(80).

9,10-Benzo-3,7-diphenyl-3,7-dithio-1,5-diaza-3,7-diphosphabicyclo[3.3.2]decane (VI). A solution of 0.83 g (0.002 mole) of (V) and 0.18 g (0.005 mole) of sulfur in benzene was refluxed for 2 h, evaporated in vacuo, and

the residue was washed with ether. Yield 0.66 g (69%), mp 140-145°, $\delta^{31}P$ 30 ppm (DMSO). Found: C 59.92; H 5.28%. $C_{22}H_{22}P_2N_2S$. Calculated: C 60.02; H 4.99%.

CONCLUSIONS

The reaction of o-phenylenediamine with either one or two moles of dihydroxymethylphenylphosphine gives respectively either 3-phenyl-6,7-benzo-1,5-diaza-3-phosphepane or 9,10-benzo-3,7-diphenyl-1,5-diaza-3,7-diphosphabicyclo[3.3.2]decane.

LITERATURE CITED

1. H. Harmisch, Angew. Chem., 88, 517 (1976).
2. H. Oehme, I. Issleib, E. Leissrring, and A. Zschunke, Synth. React. Inorg. Met.-Org. Chem., 4, 453 (1974).
3. G. Markl, G. Yu. Jin, and C. Schoerner, Tetrahedron Lett., 1980, 1409.
4. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 2771.
5. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 735.
6. A. W. Frank and G. L. Drake, Jr., J. Org. Chem., 37, 2752 (1972).
7. G. Markl and G. Yu. Jin, Tetrahedron Lett., 1980, 3467.
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, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 2129.
10. G. Markl and G. Yu. Jin, Tetrahedron Lett., 1981, 229.
11. B. A. Arbuzov, O. A. Erastov, and S. Sh. Khetagurova, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 866.

3-MONOHALO DERIVATIVES OF TRIACETONEAMINE, 1-HYDROXY-2,2,6,6-TETRAMETHYL-4-OXOPIPERIDINE, AND 2,2,6,6-TETRAMETHYL-4-OXOPIPERIDIN-1-OXYL

L. A. Krinitskaya and L. B. Volodarskii

UDC 542.91:547.447.5'121:547.824.5

The synthesis of the 3-chloro- and 3-bromo-2,2,6,6-tetramethyl-4-oxopiperidines, and also of their 1-hydroxy derivatives and the corresponding nitroxyl radicals, is described in the present paper.

The α-monohalo ketones, based on 2,2,6,6-tetramethyl-4-oxopiperidine (triacetoneamine), were previously unknown. Data are also lacking on the halogenation of the N-substituted triacetoneamines. The chlorination and bromination of triacetoneamine (Ia) itself in polar media goes either at the N atom to give the N-chloro, N-bromo, and N-perbromo derivatives [1, 2] or it leads to the symmetrical 3,5-dibromo-(Ia) [3, 4]. The 3-bromo ketone cannot be obtained under these conditions [3], probably due to the accumulation of HBr in the reaction mass, which causes the symmetrization of α-bromo ketones to the α,α'-dibromides [5]. The intermediate formation of the 3-iodo-(Ia) was shown recently when (Ia) is treated with hypoiodite [6]. As a result, in order to obtain the 3-monohalo-(Ia) it is necessary to avoid N-halogenation and the formation of 3,5-dibromo-(Ia). Usually in the synthesis of α-halo ketones, containing an amino group, it is first protected by acylation [7]. In the case of (Ia) the acyl protection cannot be removed, evidently due to steric hindrance [4].

We were able to chlorinate and brominate triacetoneamine (Ia) and 1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidine (Ib) as their hydrochlorides. Here the protection of the amino and hydroxylamino groups was achieved by protonation. The halogenation was run in nonpolar solvents, in which the formed hydrogen halide is slightly soluble. The treatment of the (Ia) and (Ib) hydrochlorides with an equimolar amount of either SO_2Cl_2 or Br_2, followed by treatment of the halogenated salts with a base, enables us to obtain the corresponding 3-chloro (IIa, b) and 3-bromo derivatives (IIIa, b) of these ketones. When treated with SO_2Cl_2 the (Ib) hydrochloride

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 443-446, February, 1982. Original article submitted June 25, 1981.