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STRUCTURE AND SOME REACTIONS OF PHOSPHAZIDES

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STRUCTURE AND SOME REACTIONS OF PHOSPHAZIDES

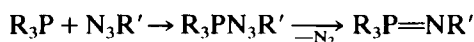
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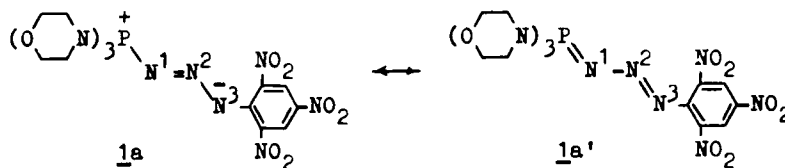
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The molecular structure of phosphazides, R_3PN_3R' , formed in the Staudinger reaction as intermediates was studied by X-ray analysis. The essentially zwitterionic character of these compounds and (E)-arrangement of their charged terminal groups relative to central N—N double bond in PN_3 chain were established. The alkylation of phosphazides by triethyloxonium tetrafluoroborate was found to proceed in regio- and stereospecific manner at the negatively charged nitrogen atom.

Phosphazides, R_3PN_3P' , as a class of organophosphorus compounds are known for a long time. Most of them have been prepared by the Staudinger reaction, i.e. by imination of trivalent phosphorus derivatives with covalent azides wherein the phosphazides are formed as intermediates.¹



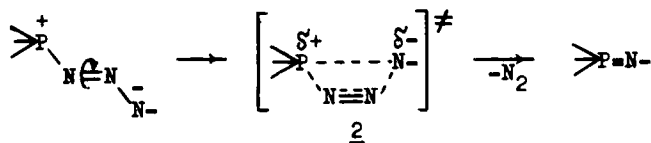
The problem of molecular structure of phosphazides was raised more than once (see Reference 1) but only recently we have succeeded in elucidating its most important features by means of a single crystal X-ray analysis.



In the case of phosphazide **1a** it was found² that atoms in the fragment PN_3 are linked in a consecutive way i.e. the starting picryl azide adds to trimorpholino phosphine with its end nitrogen atom. The chain PN_3C is nearly planar with the phosphorus and arylimino terminal groups being in (E)-position with respect to the central N^1-N^2 bond. The distribution of bond lengths in this compound is indicative² of substantial contribution of a zwitterionic resonance structure **1a'**

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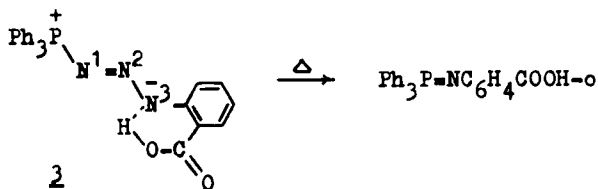
containing a double bond between N^1 and N^2 atoms. Just around this bond the terminal groups should turn for attainment of cyclic transition state **2** required for nitrogen elimination.



The observed shortening of the N^3 —C(Ar) bond reflects the effective delocalization of negative charge from N^3 atom to aromatic ring though the latter is twisted by 32.2° out the PN_3C plane.

The enhanced electronic stabilization and considerable steric hindrances which hamper the intramolecular rotation around the N^1 — N^2 bond result in a high thermal stability of the phosphazide **1a**. It decomposes at 155 – 158°C , however, we have failed to isolate the expected iminophosphorane.

Contrary to the phosphazide **1a**, the more thermally labile 2-(triphenylphosphazido)benzoic acid, **3**, is a typical intermediate of the Staudinger reaction. It is formed on treatment of triphenyl phosphine with 2-azidobenzoic acid and smoothly converts into the corresponding iminophosphorane on heating.^{3,4} Therefore, the molecular structure of **3** is of special interest as a model for clarifying the Staudinger reaction mechanism.



According to the obtained X-ray data⁵ the phosphazide **3** has the same (E)-configuration as in the case of **1a**, however, for the former the contribution of a zwitterionic structure having the $N^1=N^2$ double bond is somewhat lower and the conjugation of the N^3 atom with phenyl group is appreciably weaker though the angle of inclination of the aromatic ring to the PN_3C plane is only 9° . Furthermore, the steric conditions for the N^3 —Ar group rotation around the N^1 — N^2 bond are less rigid than in **1a** and permit a more close approach between the P and N^3 reactive sites in the transition state **2**. These data allow to suppose that the overcoming of the rotation barrier of the N^1 — N^2 bond makes a remarkable contribution to activation energy of the phosphazide cleavage step in the Staudinger reaction.

It is interesting to note that hydroxyl H atom in **3** participates in a strong intramolecular hydrogen bond with the N^3 atom closing the almost planar six-membered cycle. Thus, the H—O bond dissociation supposed in Reference 3 does not occur.

In chemical respect, phosphazides are studied rather inadequately. Only their

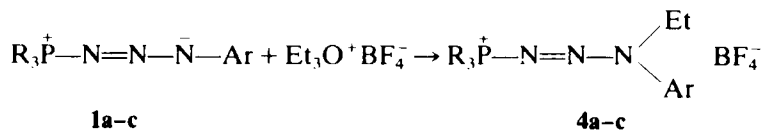
thermolysis producing iminophosphoranes and nitrogen gas, i.e. the second step of the Staudinger reaction, was investigated in detail.⁶⁻⁸ There is some information about relatively high basicity of phosphazides⁹ and their interaction with organic acids.³

The predominant zwitterionic nature of phosphazides implies the possibility of electrophilic addition at the N³ nitrogen atom, in particular, an alkylation reaction. Indeed, the interaction between phosphazide **1a** and triethyloxonium tetrafluoroborate in methylene chloride at room temperature is accompanied by rapid fading of the initially red solution and precipitation of the colourless crystalline product **4a**. Other phosphazides react in a similar manner (see Table I).

TABLE I
Properties of phosphazide derivatives

Compound	Yield, %	M.P., °C (dec.)	Formula	Analyses (%) Calcd. (Found)	³¹ P NMR (MeCN) δ _p , ppm	¹ H NMR δ, PPM ^a
4a	62	173–175 (MeCN)	C ₂₀ H ₃₁ BF ₄ N ₉ O ₉ P	C 36.44 (36.56) H 4.74 (4.82) F 11.53 (11.61) N 19.12 (19.53) P 4.70 (4.46)	33.4	9.15 (s, Ar), 4.32 (q, <u>CH</u> ₂ CH ₃)
4b	79	160–162 (MeCN- ether)	C ₂₀ H ₃₁ BBr ₃ F ₄ N ₆ O ₃ P	C 31.57 (31.31) H 4.11 (4.05) Br 31.50 (31.54) N 11.04 (10.63) P 4.07 (3.82)	30.1 (CH ₂ Cl ₂)	8.35 (s, Ar), 4.52 (q, <u>CH</u> ₂ CH ₃), 1.65 (t, Me)
4c	35	195–196 (MeCN- ether)	C ₂₆ H ₂₂ BF ₄ N ₆ O ₆ P	C 49.39 (48.70) H 3.51 (3.60) F 12.02 (12.04) N 13.29 (13.52) P 4.90 (4.85)	27.5	9.25 (s, Ar), 4.35 (q, <u>CH</u> ₂ CH ₃), 1.48 (t, Me)
1a · 2,4,6- (NO ₂) ₃ C ₆ H ₂ OH	92	133–134 (CH ₂ Cl ₂)	C ₂₄ H ₂₉ N ₁₂ O ₁₆ P	C 37.31 (37.22) H 3.78 (3.79) N 21.76 (21.50) P 4.01 (4.04)	28.9	8.85 (s, Ar), 8.81 (s, Ar')

^a For **4a** and **4b** in CD₂Cl₂, for **4c** and **1a** · 2, 4, 6-(NO₂)₃C₆H₂OH in CD₃CN.



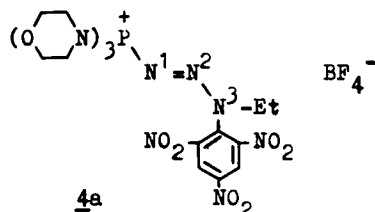
a R = O(CH₂CH₂)₂N—, Ar = 2,4,6-(NO₂)₃C₆H₂;

b R = O(CH₂CH₂)₂N—, Ar = 2,4,6-Br₃C₆H₂;

c R = Ph, Ar = 2,4,6-(NO₂)₃C₆H₂

The X-ray structure determination for **4a** has led to an unambiguous conclusion¹⁰ that the alkylation proceeds at the N³ atom in a regio- and stereospecific manner. It is the first known reaction of phosphazides occurring with retention of nitrogen triad. The initial (E)-geometry of the triad remains also

unchanged, however, the steric demands for ethyl group entering cause the reorientation of the terminal aryl and its rotation by 86.3° out the plane $\text{PN}^1\text{N}^2\text{N}^3\text{C}(\text{Ar})$ resulting in violation of the conjugation chain and discoloration of the product.



An increased electron density at the N^3 atom in phosphazides is reflected in their attitude towards acidic reagents. It has been found³ that picric or carboxylic acids stabilize phosphazides in solutions by salt formation and, as a result, inhibit the Staudinger reaction. This observation prompted us to isolate such a salt. Treatment of **1a** with picric acid in methylene chloride leads to rapid disappearance of red colour and precipitation of a stable crystalline product of 1:1 composition (see Table I). The components of this coplex seem to be linked by a strong $\text{O}-\text{H} \cdots \text{N}^3$ hydrogen bond. At least, in IR spectra of its solution in CH_2Cl_2 the absorption bands attributed to valence vibrations of NH and free OH groups are absent. On the other hand, there is a broad band at $3360\text{--}3200\text{ cm}^{-1}$ characteristic of associated HO groups.

EXPERIMENTAL

^1H and ^{31}P NMR spectra were recorded on a Bruker WP200 or Tesla spectrometer using tetramethylsilane (for ^1H) or 85% H_3PO_4 (for ^{31}P) as external standard. UV and IR spectra were obtained on Specord UV-vis and UR-20 spectrophotometers respectively.

General procedure for ethylation of 1a–c with triethyloxonium tetrafluoroborate. A solution of triethyloxonium tetrafluoroborate (0.65 mmol) in freshly distilled methylene chloride (5 mL) was added dropwise to a stirred solution of an appropriate phosphazide **1** (0.64 mmol) in the same solvent (5 mL) under argon at room temperature. After 15 min the decolorized solution was partially evaporated under reduced pressure and diethyl ether was added to the residue. The white crystalline product **4** was removed by filtration and purified by crystallization (see Table I). UV (MeCN) for **1a**: λ_{max} 400 ($\epsilon 2.7 \cdot 10^4$) nm.

Complex of 1-trimorpholinophosphazido-2,4,6-trinitrobenzene with picric acid. To a solution of phosphazide **1a** (0.75 mmol) in methylene chloride (3 ml) was added slowly 1 equiv. of picric acid in the same solvent (2 ml). The yellow product which precipitated from solution was filtered off and recrystallized from methylene chloride (see Table I).

REFERENCES AND NOTES

1. Yu. G. Gololobov, I. N. Zhmurova and L. F. Kasukhin, *Tetrahedron*, **37**, 437 (1981).
2. A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, I. E. Boldeskul, M. P. Ponomarchuk, L. F. Kasukhin and V. P. Kukhar, *Zh. Obshch. Khim.*, **54**, 1979 (1984). Selected bond lengths (\AA) and angles (deg) for **1a**: PN^1 1.638(5), N^1N^2 1.298(7), N^2N^3 1.316(7), $\text{N}^3\text{C}(\text{Ar})$ 1.367(8) \AA ; PN^1N^2 119.1(4), $\text{N}^1\text{N}^2\text{N}^3$ 111.9(5), $\text{N}^2\text{N}^3\text{C}(\text{Ar})$ 112.1(5)°.
3. J. E. Leffler and R. D. Temple, *J. Am. Chem. Soc.*, **89**, 5235 (1967).
4. L. Horner and A. Gross, *Lieb. Ann.*, **591**, 117 (1955).

5. Selected bond lengths (Å) and angles (deg) for **3**: PN^1 1.651(1), N^1N^2 1.328(1), N^2N^3 1.279(1), $\text{N}^3\text{C}(\text{Ar})$ 1.413(1) Å; PN^1N^2 109.51(7), $\text{N}^1\text{N}^2\text{N}^3$ 112.96(9), $\text{N}^2\text{N}^3\text{C}(\text{Ar})$ 114.79(9)°. The details of the single crystal X-ray study will be published elsewhere.
6. H. Bock and M. Schnöller, *Angew. Chem.*, **80**, 667 (1968); *Chem. Ber.*, **102**, 38 (1969).
7. H. Goldwhite, P. Gysegem, S. Schow and C. Swyke, *J. Chem. Soc. Dalton Trans.*, 16 (1975).
8. L. F. Kasukhin, M. P. Ponomarchuk, L. S. Sologub, A. A. Kisilenko and V. P. Kukhar, *Zh. Obshch. Khim.*, **53**, 568 (1983).
9. V. P. Prokopenko, N. V. Proklina and P. P. Onys'ko, *Zh. Obshch. Khim.*, **54**, 812 (1984).
10. Selected bond lengths (Å) and angles (deg) for **4a**: PN^1 1.684(1), N^1N^2 1.272(2), N^2N^3 1.312(2), $\text{N}^3\text{C}(\text{Ar})$ 1.427(2), $\text{N}^3\text{C}(\text{Alk})$ 1.475(3) Å; PN^1N^2 112.2(1), $\text{N}^1\text{N}^2\text{N}^3$ 113.5(2), $\text{N}^2\text{N}^3\text{C}(\text{Ar})$ 121.0(2), $\text{N}^2\text{N}^3\text{C}(\text{Alk})$ 118.1(2)°. Full data will be published elsewhere.