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REACTIONS OF TRIVALENT PHOSPHORUS COMPOUNDS WITH AZIDES CONTAINING A MOBILE H-ATOM

A CONCEPTION OF PHOSPHAZO-COMPOUND SPIROCYCLIZATION MECHANISM

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Abstract—Investigation of the reactions of α-azidocarboxylic acids, N-(2-azidoethyl) amides and N-(2-azidoethyl) amines with trivalent P compounds shows that the intramolecular cyclization to spirophosphoranes of the intermediate phosphazo-compounds is typical of the azides of the first and third types but not of the second type. It is concluded that such cyclization is possible only where the functional group of the starting azides contains either a sufficiently mobile hydrogen atom or a highly nucleophilic proton-containing group. A new general process for producing imidazolines and oxazolines has been developed.

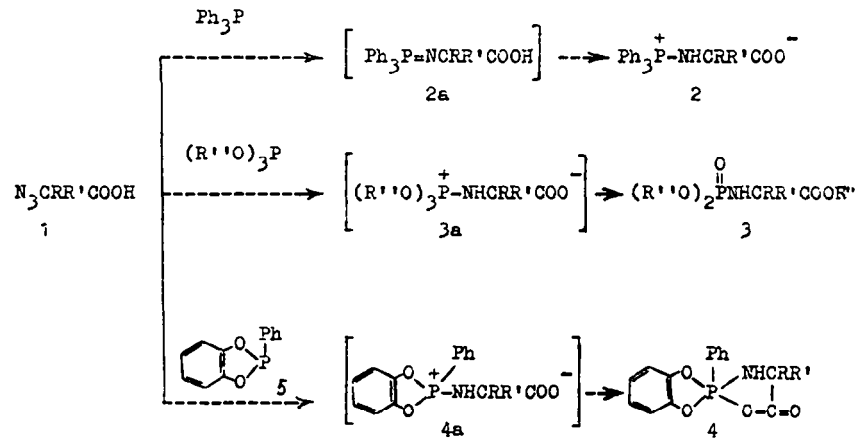
Depending on the nature of the substituents at P and N of phosphazo-compounds the latter exhibit more or less pronounced basic properties and may undergo protonation at the imine N if treated with compounds containing a mobile H-atom. The intramolecular protonation of phosphazo-compounds is of special interest since in this case the products are P betaines capable under appropriate conditions of undergoing various conversions.[1-3]

With a view to study such conversions and seek for new rearrangements, the authors have undertaken a systematic investigation of the Staudinger[4] imination of trivalent P compounds with aliphatic azides containing H-atoms of different mobility in the carboxy, amide or amine groups.

The most acid azides, the derivatives of carboxylic acids **1**, react with trivalent P compounds to form, depending on the nature of the P substituent, betaines **2**, amidophosphates **3** or cyclic phosphoranes **4**.[5-7]

It is quite apparent that **3** and **4** are obtained through the further conversions of the intermediate phosphazo-compounds and betaines (similar to **2a** and **2**). The betaines **3a** formed from trialkyl phosphites are stabilized by a mechanism corresponding to the second step of the Arbuzov reaction, betaines **4a** are cyclized into spirophosphoranes owing, apparently, substantially to the steric factors, since it is known that the 5-member P-containing cycles stabilize the phosphorane structure. The transfer of the proton of the carboxy group to the imine N is, obviously, the key step of the conversions under consideration.

Proton is not abstracted from the amide group even in the most basic phosphazo-compounds **7**



obtained from triamidophosphites and amidoazides 6.[8]

$$N_3CH_2CH_2NHCOR + (Me_2N)_3P$$
6

$$\xrightarrow[-N_2]{} (Me_2N)_3P{=}NCH_2CH_2NHCOR$$
7

R = Me(a), Ph(b), CF_3(c)

Imination of trialkyl phosphites with amidoazides **6** also does not involve amide H atom transition to the imine N, since the phosphazo-compounds **8** formed under these conditions (heated to 150–170°) are converted, on distillation in vacuum, to amidophosphates **9**† with the alkyl group R at the α-rather than the δ-N atom as determined from the spectral data for amine **10** formed by acid hydrolysis of amidophosphate **9**.

$$(R'O)_3P + 6 \xrightarrow[-N_2]{}$$

$$(R'O)_3P{=}NCH_2CH_2NHCOR \xrightarrow{\Delta}$$
8

$$(R'O)_2P(O)NR'CH_2CH_2NHCOR$$
9

$$(EtO)_2P(O)N(Et)CH_2CH_2NHCOPh$$
9

$$\xrightarrow{H^+/H_2O} EtNHCH_2CH_2NHCOPh$$
10

It is interesting to note that imination of trialkyl phosphites with azide **6c**, a derivative of trifluoroacetic acid, yields phosphazo-compounds **8c** which not only rearrange into amides **9c** but also decompose competitively producing trialkyl phosphates and 2-trifluoromethyl imidazoline **11c**. Here, the easier the phosphazo-compound **8c** rearranges to amide **9c**, the smaller the yield of imidazoline **11c**. For example, decomposition of triethoxyphosphazo-compound **8c** (R=Et) yields 1–1.5% of amidazoline, whereas the decomposition of **8c** (R=Bu) yields 27%, conforming to the fact that Bu group has a lower tendency for migrating from O to N in transformations of phosphazo-compounds to isomeric amides.

$$(RO)_3P{=}NCH_2CH_2NHCOCF_3$$
8c

$$\longrightarrow (RO)_2P(O)N(R)CH_2CH_2NHCOCF_3$$
9c

$$\longrightarrow (RO)_3PO + CF_3C(=N{-}CH_2)NHCH_2$$
11c

†See Ref. 16.

The formation of imidazoline **11c** by decay of phosphazo-compounds **8c** is a new version of the intramolecular Staudinger reaction,[9] since amides have not been observed to undergo such transformations earlier. For this reason, this type of reaction has been studied more thoroughly in this work.

Using phosphazo-compounds which do not contain alkoxy groups at P it is possible to obtain imidazolines containing alkyl and aryl radicals in the second position with high yields. For example, triphenylphosphazo-compounds **12a,b** derivatives of acetic and benzoic acid amides **6a,b** are converted to triphenyl phosphine oxide and the corresponding imidazolines **11a,b** at 180° and trifluoroacetic acid amide compound **12c** at 120°.[10]

$$Ph_3P + \mathbf{6(a–c)} \dashrightarrow Ph_3P{=}NCH_2CH_2NHCOR$$
12

$$\dashrightarrow R{-}C(=N{-}CH_2)NHCH_2 + Ph_3PO$$
11

R = Me(a), Ph(b), CF_3(c)

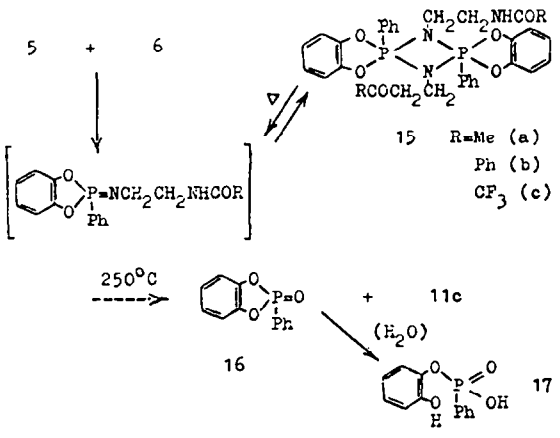
The formation of substituted imidazolines from phosphazo-compounds that are derivatives of azides with substituents in the α- and β-positions is the easiest one. Thus no phosphazo-compound can be isolated during reaction of triphenylphosphine with azide **13** obtained from racemic pseudo-ephedrine, and already at room temperature one observes formation of triphenyl phosphine oxide and imidazoline **14** substituted in the 4- and 5-positions.

$$Ph_3P + N_3CH(Ph){-}CH(Me){-}N(Me)COCF_3$$
13

$$\dashrightarrow Ph_3PO + CF_3C(=N{-}CH(Ph))N{-}CH(Me)$$
14

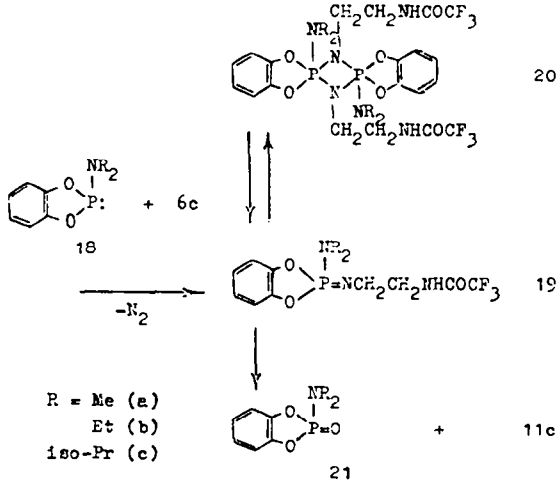
In view of these results it was interesting to investigate such conversions with participation of 5-membered cyclic phosphorus acid esters, e.g. pyrocatechol esters. One would expect in this case the formation of imidazolines from phosphazo dimers—diazadiphosphetidines, as well, owing to the previous thermal monomerization of the latter.

With cyclic phenyl phosphonite **5** azides **6** are converted only to the dimers of the phosphazo-compounds **15**, crystalline high-melting compounds. However, heating of the dimer **15c** to 250° does yield 2-trifluoromethylimidazoline **11c** and phenyl phosphonate **16** identified as 2-hydroxyphenyl-phenyl phosphonate **17**.[11]

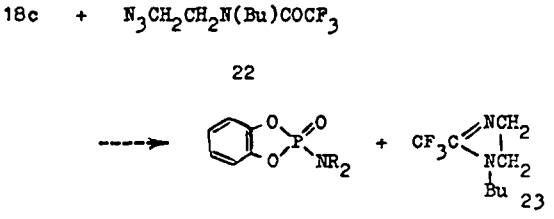


The mechanism by which imidazoline **11c** is formed from the dimer **15c** has not been investigated so far, but one can presume that initially the heating monomerizes **15c** and the monomeric phosphazo-compound that is formed undergoes intramolecular decay via the above scheme.

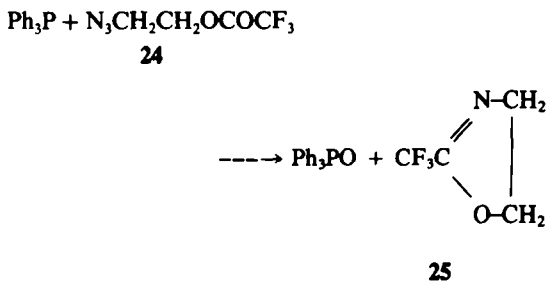
In imination of the more sterically hindered dialkyl amidopyrocatechol phosphites **18** with azide **6c**, the compounds interact via two routes with dominant formation of either the dimeric phosphazo-compounds **20** or imidazoline **11c** plus the corresponding phosphate **21**, depending on the structure of the dialkylamino group at P and reaction condition. The latter route is favored by the bulky dialkylamino groups and the high temperature. Both the factors bias the reaction towards formation of imidazoline, apparently, for the reason that they shift the diazadiphosphetidine **20** ⇄ phosphazo-compound **19** equilibrium towards the latter.



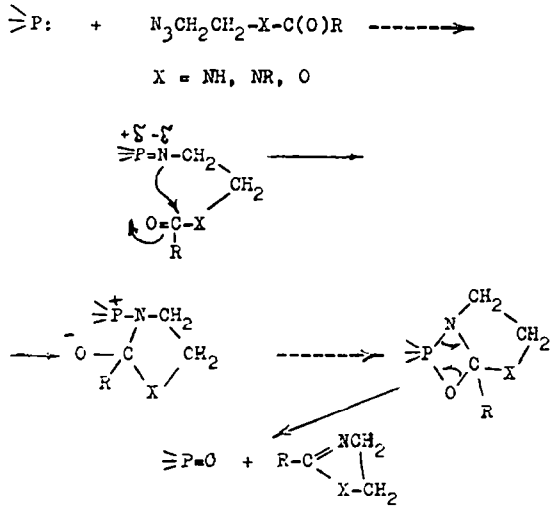
It is of extreme interest that the intramolecular decay of phosphazo-compounds with the CO group in the imine group into imidazolines is observed not only for monosubstituted amides discussed above but also for the totally substituted amides, such as **22**.



What this fact means is that in discussing the mechanism of heterocyclization it is not necessary to assume prototropic migrations. This is also corroborated by the reaction of oxazoline **25** formation from triphenyl phosphine and azide **24**.



These results permit to interpret the process as intramolecular imination via the following mechanism:

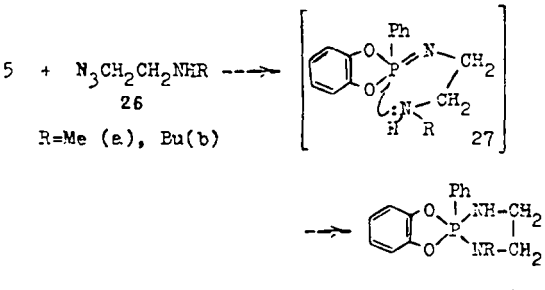


In the light of the above scheme it is easy to understand why trifluoroacetic acid compounds **6c**, **22** and **24** most readily produce imidazolines and oxazolines: the C of the CO group which attacks the nucleophilic N of phosphazo-compounds is most electrophilic.

Thus the reactions between carboxylic acid N-(2-azidoethyl) amides and trivalent P compounds yield phosphazo-compounds which, depending on the nature of the substituents in the starting compounds undergo dimerization, intramolecular imination of the CO group or imide–amide rearrangement. No prototropic migration from the amide to imine N have been observed in the investigated reactions. Apparently, in contrast to the H of carboxy group,

the acid properties of the amide H are insufficient for such motions.

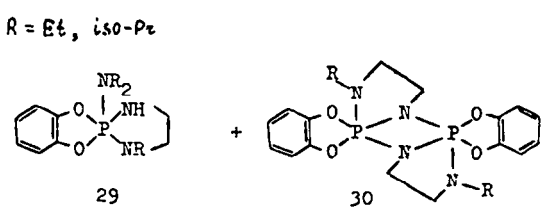
At the same time, reactions of azidoamines **26** that contain not an acyl but an alkyl group at the amine N with trivalent P compounds yield in some cases the products whose structure indicates that protonation of the imine N does ultimately occur despite the fact that the acid properties of the H-atom in secondary aliphatic amines (including phosphazo-compounds **27**) are much weaker than those in monosubstituted amides. For instance, reactions between azidoamines **26** with phenyl phosphonite **5** yield directly spirophosphoranes **28**.



That the structure of **28** is such is evidenced by the ^{31}P NMR spectra (δ_p = −25.4 for **28a** and δ_p = −27 ppm for **28b**) and the cryoscopic determinations of the molecular weight. Compounds **28** are well soluble in common organic solvents.

Proton migration from the amine to imine N also takes place during imination of cyclic amidophosphites **18** with azidoamines **26**. Thus reactions of azides **26** with phosphites **18** carried out at 80° without solvent yield two crystalline products in each case: compounds with a lower m.p. and readily soluble in ether that have the structure of spirocyclic phosphoranes **29** and ether-insoluble compounds **30** that have a polycyclic structure.

The structure of phosphoranes **29** and **30** has been strictly identified by spectral and X-ray data.†



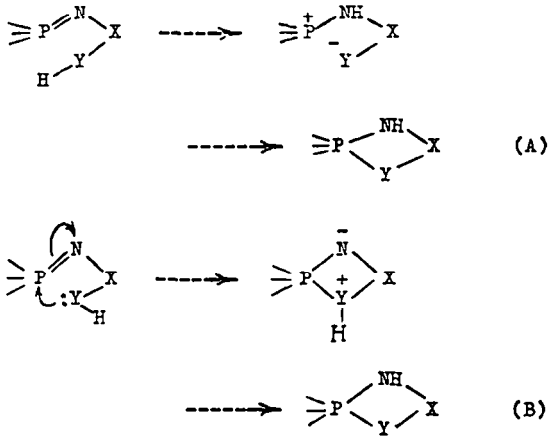
On heating spirophosphoranes **29** are converted with a good yield to the dimers **30**, producing the corresponding secondary amine as another product.

$$\mathbf{29} \dashrightarrow \mathbf{30} + R_2NH$$

†The X-ray analysis of **29** and **30** has been conducted by Yu. T. Struchkov, M. Yu. Antipin and A. N. Chernega and will be reported on in a separate paper.

This conversion is probably the first observed instance of formation of diazadiphosphetidines from spirophosphoranes through abstraction of the dialkylamine elements from the neighbour P and N atoms.

The above results allow one to make certain conclusions about the cyclization mechanism of phosphazo-compounds containing a group with a mobile H-atom in the group attached to the imine N. This fact has been commented in two different ways in the literature. Cadogan *et al.*[12] believe that the initial stage of cyclization is proton transfer to the imine N, whereby betaine is formed which is cyclized on approach of the oppositely charged atoms (Scheme A). On the other hand, Stegmann *et al.*[1] presume that the proton transfer is the concluding stage of the reaction, whereas the initial stage is the nucleophilic attack of the heteroatom to which the mobile H-atom is attached on P (Scheme B).‡



According to the data obtained in this work, however, it is untenable to consider the two points of view as contradictory. By all probability, depending on the nature of the substituents in the starting azide molecule, both the above cyclization mechanisms may work in different cases: route A when there is a highly mobile H-atom (derivatives of azidocarboxylic acids), route B when there is a highly nucleophilic protonbearing group (derivatives of secondary azidoamines **26**).

EXPERIMENTAL

M.p.s are uncorrected. The IR spectra were taken with the UR-20 spectrometer. The PMR spectra were recorded with the Tesla Bs-487B (60 MHz) spectrometer with HMDS as the external standard. The NMR spectra (^{31}P)—with the Tesla Bs-487B (30 MHz) or Bruker WP-200 (81 MHz) with 85% phosphoric acid as the external standard.

Reaction of triphenyl phosphine with azidoacetic acid. 2.4 g of azidoacetic acid were added dropwise at 20–25° (water cooling) to the soln of 6.24 g triphenyl phosphine in 25 ml anhydrous THF. After N_2 liberation stopped, the residue was separated and the additional quantity of product was isolated by evaporating the filtrate. This procedure gave 6.95 g (87.5%) betaine **2** (R=R'=H),

‡Refs. 1 and 12 refer to reactions of azidophenols with P(III)-compounds.

m.p. 178–182° (dec., from MeCN). IR (KBr): 3200, 1640 cm^{-1}. PMR ($CHCl_3$): δ 4.49 (d, 2H, CH_2), 5.92 (s, 1H, NH). NMR ^{31}P ($CHCl_3$): δ +25.2 ppm. Dipole moment ($CHCl_3$) 12.5 D. (Found: N 3.83, P 8.98. $C_{20}H_{18}NO_2P$ requires: N 4.18 P 9.24%).

Ethyl ester of N-*(diethoxyphosphoryl)-glycine* (3, R=R′=H,R″=Et). 2.38 g of azidoacetic acid were added dropwise at 15–20° (water cooling) to the soln of a minor excess of triethyl phosphite in anhyd benzene. The soln was agitated at room temp until N_2 liberation stopped and the azide group band disappeared from the IR spectrum. Evaporated and isolated by distillation 4.49 g (79.6%) of amidophosphate with b.p. 122–126°/0.05 mm Hg, n_D^{20} 1.4380, d_4^{20} 1.1367. IR (film): 3250, 1760, 1280, 1040. PMR (neat): δ 1.53 (t, 9H, CH_3), 3.88 (m, 2H, N–CH_2), 4.36 (m, 6H, O–CH_2), 5.21 (s, 1H, NH). (Found: N 5.84, P 12.95. $C_8H_{18}NO_5P$ requires: N 5.86, P 12.95%).

2,3-*Benzo-5-phenyl-1,4,6-trioxa-5-phospha-9-azaspiro[4,4]-7-nonanone* (4, R=R′=H). A soln of 0.05 mol of 5 in 25 ml benzene was added dropwise to a soln of 0.05 mol azidoacetic acid in 25 ml anhyd benzene. This was accompanied by liberation of N_2, hazing of soln and precipitation. After N_2 liberation stopped (3–4 hr), the residue was separated, washed with anhyd benzene and spirophosphorane was obtained, yield 70%, m.p. 174° (benzene–hexane 4:1). IR (KBr): 3380, 1240. PMR: δ 3.81 (d, 2H, J 15 Hz, CH_2, 4.85 (m, 1H, NH), 7.4 (m, 9H, arom.). NMR ^{31}P (THF): δ −32 ppm. M.w. (ebullioscopy in dichloroethane) 291, calcd. 289. (Found: N 4.89, P 10.74. $C_{14}H_{12}NO_4P$ requires N 4.84, P 10.71%).

2,3-*Benzo-5-phenyl-8-isopropyl-1,4,6-trioxa-5-phospha-9-azaspiro[4,4]-7-nonanone* (4, R=iso–Pr, R′=H). Obtained by the above procedure from α-azidoisovaleric acid and 5, yield 91%, m.p. 154–156° (hexane–benzene 5:1). IR (KBr): 3300, 1745, 1260. NMR ^{31}P ($CHCl_3$): δ −35 ppm. (Found: N 4.44, P 9.33. $C_{17}H_{18}NO_4P$ requires: N 4.23, P 9.35%).

N-*[2-(Hexamethyltriamidophosphazo)-ethyl]-acetamide* (7, R=Me). To a soln of about 10 g of N-(2-azidoethyl)-acetamide in 100 ml of anhyd benzene was added dropwise at room temp an equivalent amount of hexamethyl triamidophosphite and stirred for 0.5 hr. The phosphotriazene residue was isolated and washed with hexane, yield 93.7%, m.p. 98° (dec). IR (KBr): 3200, 1670, 1565, 1300. (Found: N 33.65, P 10.65. $C_{10}H_{26}N_7OP$ requires: N 33.65, P 10.63%). Suspension of triazene in anhydrous benzene was boiled until N_2 liberation stopped, evaporated *in vacuo*, and 7 (R–Me) was obtained, yield 92%, m.p. 58–60° (hexane). Dipole moment ($CHCl_3$) 6.0D. IR (KBr): 3130, 1650, 1565, 1380, 1300. PMR (benzene): δ 1.85 (s, 3H, C–CH_3) 2.36 (d, 18H, J 6 Hz, N–CH_3), 3.36 (m, 4H, CH_2), 8.0 (broad, 1H, NH). NMR ^{31}P (benzene): δ +25.2 ppm. (Found: N 26.43, P 11.81. $C_{10}H_{26}N_5OP$ requires: N 26.60, P 11.75%).

N-*[2-(N-Ethyl-N-diethoxyphosphoryl)-ethyl]-acetamide* (9, R=Me, R′=Et). A soln of 0.05 mol of 6a in 25 ml anhyd benzene was added dropwise at room temp to the soln of 0.055 mol of triethyl phosphite in 25 ml anhyd benzene. After N_2 liberation stopped, the mixture was boiled for 30 min, cooled, evaporated *in vacuo* and the amidophosphate was isolated by distillation. Yield 80%, b.p. 128–132°/0.05 mm Hg, n_D^{20} 1.4599, d_4^{20} 1.0908. IR (film): 3300, 1670, 1240, 1030. PMR (neat): δ 1.47 (t, 9H, J 7 Hz, OCH_2CH_3 and NCH_2CH_3), 2.15 (s, 3H, $COCH_3$), 3.40 (broad, 6H, N–CH_2), 4.20 (t, 4H, J 8 Hz, OCH_2), 8.50 (broad, 1H, NH). NMR ^{31}P: δ +9.8 ppm. (Found: N 10.60, P 11.43. $C_{10}H_{23}N_2O_4P$ requires: N 10.52, P 11.63%).

Reaction of tributyl phosphite with azide 6c. To the soln of 0.036 mol of phosphite in 30 ml benzene was added dropwise at room temp an equivalent amount of 6c. After N_2 liberation stopped, the mixture was evaporated *in vacuo*, kept for 2 hr at 70° under a 0.05 mm vacuum. No sublimation of 11c occurred. The properties of the product corresponded to 8c (R′=Bu). The PMR spectrum is similar to that of 9c (R′=Bu) (see below) but with a different proton ratio of the N–CH_2 (6H) and O–CH_2 (4H) groups. (Found: N 6.75, P 7.66. $C_{16}H_{32}F_3N_2O_4P$ requires: N 6.93, P 7.66%). The product was heated for 2 hr at 120° and 1.33 g of 11c were obtained by sublimation *in vacuo*. It was kept for another 2 hr at 150° and 0.5 g more of the imidazoline were recovered. Total yield 37%, m.p. 112° (hexane–benzene 2:1). IR (KBr): 3150, 1640. (Found: N 20.33. $C_4H_5F_3N_2$ requires: N 20.29%). Lit. date[13]: m.p. 112°.

Tributyl phosphate was isolated by distillation of the residue *in vacuo*; yield 40%, b.p. 156–158°/0.05 mm Hg, n_D^{20} 1.4329. IR (film): 3240, 1730, 1220, 1030. PMR (CCl_4): δ 1.18 (m, 9H, CH_3), 1.65 (m, 12H, C–CH_2), 3.40 (m, 6H, N–CH_2), 4.05 (t, 4H, J 6 Hz, O–CH_2), 8.25 (broad., 1H, NH). NMR ^{31}P: δ +9.5 ppm. (Found: N 7.32, P 7.70. $C_{16}H_{32}F_3N_2O_4P$ requires: N 6.93, P 7.66%).

Hydrolysis of the amidophosphate 9b (R′=Et). The mixture of 0.02 mol of amidophosphate and 100 ml of 10% HCl was boiled for 3 hr, extracted with $CHCl_3$, the extract was dried with $MgSO_4$, evaporated *in vacuo*, amine 10 was isolated by distillation of the residue, yield 50%, b.p. 117°/0.05 mm Hg, n_D^{20} 1.5497. IR (CCl_4): 3320, 1680. PMR (neat): δ 1.15 (t, 3H, J 6 Hz, C–CH_3), 1.82 (s, 1H, NH–amine), 2.75 (m, 4H, $\underline{CH_2}$NH–amine), 3.66 (broad., 2H, $\underline{CH_2}$NH–amide), 7.50–8.09 (m, 5H, arom.), 8.85 (broad., 1H, NH–amide). (Found: N 14.85. $C_{11}H_{16}N_2O$ requires: N 14.57%).

N-*(2-Triphenylphosphazoethyl)-acylamides* (12). To a soln of 0.03 mol of triphenyl phosphine in anhyd benzene was added dropwise a soln of 0.03 mol of the corresponding 6 in benzene; after N_2 liberation stopped, the mixture was evaporated *in vacuo*, the residue was rubbed with ether and 12a,b,c were obtained.

Compound 12a. Yield 83%, m.p. 105–107°. IR (Nujol): 3260, 1650, 1380. (Found: N 7.58, P 8.41. $C_{22}H_{23}N_2OP$ requires: N 7.72, P 8.55%).

Compound 12b. Yield 80%, m.p. 125–127°. IR (KBr): 3360, 1640, 1310. (Found: N 6.56, P 7.33. $C_{27}H_{25}N_2OP$ requires: N 6.59, P 7.30%).

Compound 12c. Yield 92%, m.p. 112–115°. IR (KBr): 3350, 1710. (Found: N 6.66, P 7.58. $C_{22}H_{20}F_3N_2OP$ requires: N 6.73, P 7.44%). Compound 12c also partially transforms into 11c and triphenylphosphine oxide already when attempts are made to recrystallize it from benzene–petroleum ether mixture.

Phosphazoamide 12a *decomposition*. 11 g of 12a were heated for 5 hr at 180° and then at 100° and the vacuum of 0.05 mm Hg in a sublimation apparatus. The total of 2.5 g (72%) of 11a were sublimated, m.p. 100° (benzene). PMR (benzene): δ 1.35 (s, 3H, CH_3), 2.95 (s, 4H, CH_2), 4.07 (broad, 1H, NH). (Found: N 33.49. $C_4H_8N_2$ requires: N 33.80%). Lit. date[14]: m.p. 100–103°. The sublimation residue was dissolved in benzene, extracted with HCl (1:1), washed with water, evaporated, and triphenylphosphine oxide was obtained, yield 80%. The m.p. of the mixed sample with an *a priori* sample did not show a tendency for depression.

Decomposition of phosphazoamide 12b. The procedure was the same as for 12a; 11b was isolated by distillation, yield 91%, b.p. 120°/0.05 mm Hg, m.p. 100–101° (benzene). PMR ($CDCl_3$): δ 4.02 (s, 4H, CH_2), 5.86 (s, 1H, NH), 7.34–8.02 (m, 5H, arom.). (Found: N 19.22. $C_9H_{10}N_2$ requires: N 19.16%). Lit. date[15]: m.p. 99°. From the residue triphenylphosphine oxide was obtained with the yield of 89%.

Decomposition of phosphazoamide 12c. 4 g of 4 were heated for 4 hr at 120° and a vacuum of 0.05 mm Hg in the sublimation apparatus; 11c was isolated, yield 80%. Triphenylphosphine oxide was separated from the residue, yield 75%.

Reaction of triphenylphosphine with azide 13. Carried out as for 6, the residue after rubbing with ether is triphenylphosphine oxide, yield 90%. The ether soln was evaporated and the residue was distilled to yield 78% of 14, b.p. 104°/10 mm Hg, n_D^{20} 1.4866. PMR (CCl_4): δ 1.05 (dd, 3H, J 37 and 6 Hz, C–CH_3), 2.90 (s, 3H, N–CH_3), 3.39 (m, 1H, PhC$\underline{H}$), 4.85 (dd, 1H, J 37 and 12 Hz, MeC$\underline{H}$), 7.25 (m, 5H, arom.).

(Found: N 12.83, F 25.80. $C_{12}H_{13}F_3N_2$ requires: N 12.84, F 26.12%). Chlorohydrate, m.p. 201° (benzene–acetone). (Found: N 9.46, Cl 12.11. $C_{12}H_{14}ClF_3N_2 \cdot H_2O$ requires: N 9.48, Cl 11.94%).

1,3-Bis-(2-trifluoroacetamidoethyl)-2,4-diphenyl-2,4-bis-(o-phenylenedioxy)-1,3,2λ⁵,4λ⁵-diazadiphosphetidine (**15c**). The soln of 0.033 mol of **5** in ether was added dropwise to the ether soln of 0.03 mol of **6c** and the mixture was left overnight. The crystals formed were separated, washed with a small quantity of ether and **15c** was obtained with a yield of 83%, m.p. 210° (MeCN). Molecular weight (ebullioscopy in dichloroethane) 738, calc. 740. IR (KBr): 3360, 1730, 1720, 1210. (Found: N 7.68, P 8.31. $C_{32}H_{28}F_6N_4O_6P_2$ requires: N 7.57, P 8.37%).

1,3-Bis-(2-benzamidoethyl)-2,4-diphenyl-2,4-bis-(o-phenylenedioxy)-1,3,2λ⁵,4λ⁵-diazadiphosphetidine (**15b**). Obtained by the previous procedure from **6b** and **5**, yield 90%, m.p. 220° (dec., MeCN–THF). IR (KBr): 3390, 1660, 1240. (Found: N 7.39, P 8.17. $C_{42}H_{38}N_4O_6P_2$ requires: N 7.40, P 8.19%).

Thermolysis of the dimer **15c**. 2.4 g of the dimer were heated for 1 hr at 250° (in molten state); **11c** was isolated by sublimation under a vacuum of 0.05 mm Hg, yield 84%. The residue was crystallized to give **17** with a yield of 76%, m.p. 124° (petroleum ether–CH_2Cl_2 1:1). IR (KBr): 3380, 1600, 1500, 1270, 1220. (Found: P 12.39. $C_{12}H_{11}O_4P$ requires: P 12.38%). Lit. date[11]: m.p. 123–124.5°C.

Reaction between amidophosphite **18a** *and azidoamide* **6c**. 0.015 mol of **6c** without solvent were added dropwise to 0.015 mol of the amidophosphite and the mixture is left overnight. The mixture was rubbed with ether and **20a** was isolated, yield 58%, m.p. 179° (hexane–benzene 1:5). Mol. wt. (ebullioscopy in benzene) 675, calc. 674. IR (KBr): 3380, 1740, 1220. PMR (deuteroacetone): δ 2.25 (t, 6H, J 6 Hz, CH_3), 3.32 (m, 4H, CH_2), 6.65 (s, 4H, arom.), 7.39 (broad, 1H, NH). NMR ^{31}P (THF): δ −51 ppm. (Found: N 12.86, P 9.41. $C_{24}H_{30}F_6N_6O_6P_2$ requires: N 12.46, P 9.18%). The filtrate was evaporated and the residue was subjected to sublimation *in vacuo* (0.05 mm Hg at 60–80°) to recover **11c**, yield 2.9%.

Reaction between amidophosphite **18b** *and azidoamide* **6c**. Carried out at room temp as the previous reaction and obtained **20b**, yield 57%, m.p. 181° (hexane–benzene 1:4). Mol. wt. (ebullioscopy in benzene) 740, calc. 730. IR (KBr): 3320, 1710, 1220. NMR ^{31}P (THF): δ −45 ppm. (Found: N 11.84, P 8.62. $C_{28}H_{38}F_6N_6O_6P_2$ requires: N 11.50, P 8.48%). Sublimation of the residue gave **11c**, yield 6.6%. The dimer **20b** and **11c** were obtained in a similar reaction at 70° with the yields of 46% and 24%, respectively; and at 110° **20b** and **11c** were obtained with the yields of 26% and 47%, respectively.

Reaction between amidophosphite **18c** *and azidoamide* **6c**. Carried out at 120° by the previous procedure and isolated **21c**, yield 91%, m.p. 144° (hexane). IR (CCl_4): 1500, 1250, 1040, 1015. PMR (CCl_4): δ 1.63 (d, 12H, J 7 Hz, CH_3), 3.60 (m, 2H, OCH), 7.32 (s, 4H, arom.). NMR ^{31}P (THF): δ + 14.9 ppm. (Found: N 5.37, P 12.27. $C_{12}H_{18}NO_3P$ requires: N 5.49, P 12.13%). Also **11c** was obtained, yield 97%.

Reaction between amidophosphite **18c** *and azidoamide* **22**. Azide **22** (0.02 mol) was added dropwise at 80° to 0.02 mol of molten **18c** and the mixture was kept at 80° until N_2 liberation stopped. The liquid product was run off *in vacuo* and again distilled to recover **23**, yield 70%, b.p. 78°/10 mm Hg, n_D^{20} 1.4175, d_4^{20} 1.1262. PMR (neat): δ 1.02 (t, 3H, J 6 Hz, CH_3), 1.52 (m, 4H, C–CH_2), 3.25 (m, 6H, N–CH_2). (Found: N 14.59. $C_8H_{13}F_3N_2$ requires: N 14.43%). The imidazoline distillation residue was rubbed with hexane and **21c** was recovered, yield 91%.

Reaction between triphenylphosphine and azide **24**. To 7 g of triphenylphosphine 4.7 g of **24** were added dropwise under cooling. Distillation *in vacuo* gave **25**, yield 80%, b.p. 42°/55 mm Hg, n_D^{20} 1.3550, d_4^{20} 1.3553. MR_D 22.36, calc. 22.48. (Found: F 40.72, N 10.14. $C_4H_4F_3NO$ requires: F 40.98, N 10.07%). Lit. date[13]: b.p. 39–41°/55 mm Hg, n_D^{20} 1.3735. The solid residue was washed with ether and triphenylphosphine oxide was obtained, yield 84%.

2,3-Benzo-5-phenyl-6-methyl-1,4-dioxa-6,9-diaza-5-phosphaspiro[4,4]nonane **28a**. To the soln of 3 g of **5** in 20 ml anhyd benzene were added dropwise at room temp 1.7 g of **26a**, the mixture was boiled until N_2 liberation stopped, evaporated *in vacuo*, kept under the vacuum of 0.04 mm Hg for 1 hr at room temp and 1 hr at 50°. Obtained 3.5 g of glassy **28a** (87%). IR (CCl_4): 3480, 1500, 1230, 1030. PMR (CCl_4): δ 2.52 (d, 3H, J 9 Hz, CH_3), 3.13 (m, 4H, CH_2), 3.75 (m, 1H, NH), 7.16 (m, 9H, arom.). NMR ^{31}P (neat): δ −27 ppm. Mol. wt. (cryoscopy in benzene) 289.5, calc. 288.3. (Found: N 9.21, P 10.80. $C_{15}H_{17}N_2O_2P$ requires: N 9.72, P 10.74%).

2,3-Benzo-5-phenyl-6-butyl-1,4-dioxa-6,9-diaza-5-phosphaspiro[4,4]nonane **28b**. To 2.7 g of **5** were added dropwise at room temp 1.78 g of **26b** and the mixture was exposed to a vacuum of about 0.04 mm Hg to yield oily **28b**. Mol. wt. (cryoscopy in benzene) 380, calc. 380. PMR (CCl_4): δ 1.10 (m, 4H, CH_3 and NH), 1.48 (m, 4H, C–CH_2), 2.20–3.80 (m, 6H, N–CH_2), 6.90 and 7.53 (m, 9H, arom.). NMR ^{31}P ($CHCl_3$): δ −25.4 ppm. (Found: N 8.68, P 9.36. $C_{18}H_{23}N_2O_2P$ requires: N 8.48, P 9.38%).

Reaction between amidophosphite **18c** *and azide* **26b**. To 0.03 mol of phosphite were added dropwise at 80° 0.03 mol of the azide, heated at 80° until N_2 liberation stopped. After cooling the mixture was kept under a vacuum of about 0.04 mm Hg, the liquid condensed in the liquid N_2-cooled collector was identified by its IR spectrum as diisopropyl amine. The residue was treated with anhydrous ether and **30b** was isolated, yield 26%, m.p. 186° (hexane–benzene 4:1). Mol. wt. (cryoscopy in benzene) 514, calc. 504. IR (KBr): 1490, 1255, 980. PMR ($CDCl_3$): δ 1.48 (m, 14H, C–$CH_2CH_2CH_3$), 3.45 (m, 12H, N–CH_2), 7.22 (m, 8H, arom.). NMR ^{31}P (benzene): δ −48.57 ppm. (Found: N 11.07, P 12.07. $C_{24}H_{34}N_4O_4P_2$ requires: N 11.11, P 12.28%). The ether soln was evaporated *in vacuo* and the residue was an oil whose NMR ^{31}P spectrum showed one signal with δ_p −28 ppm. The product dissolved in a minor amount of hexane was kept in a refrigerator for several days and the crystalline **29b** was isolated, m.p. 80–82° (hexane). Mol. wt. (cryoscopy in benzene) 344, calc. 353. IR (KBr): 3430, 1500, 1000. PMR (CCl_4): δ 1.45 (m, 19H, $CH_3CH_2CH_2$– and CH_3CH), 3.22 (m, 9H, NCH_2, NH, CH), 6.98 (m, 4H, arom.). NMR ^{31}P (benzene): δ −23 ppm. (Found: N 11.83, P 8.68. $C_{18}H_{32}N_2O_2P$ requires: N 11.89, P 8.76%). On heating of **29b** for 4 hr at 120° the dimer of **30b** was obtained with the yield of 64%.

Reaction between amidophosphite **18b** *and azide* **26b**. Carried out like before and after treating the mixture with anhyd ether the dimer **30b** was isolated, yield 20%. An oil was concentrated from the ether soln whose NMR ^{31}P spectrum contained one signal with δ_p −30 ppm. Long-term exposure of the product to a low temp in hexane did not result in crystallization, but after heating for 4 hr at 120° and treating with ether an additional quantity of dimer **30b** was recovered, yield (total) 55%.

Reaction between amidophosphite **18c** *and azide* **26a**. Carried out as previously and isolated **30a**, yield 13%, m.p. 300° (dec., MeCN–THF 1:6); IR (KBr): 1490, 1250, 940. NMR ^{31}P (benzene): δ −48.23 ppm. (Found: N 13.38, P 14.59. $C_{18}H_{22}N_4O_4P_2$ requires: N 13.33, P 14.74%). From the ether soln, **29** (R=Me, R′=iso-Pr) was isolated, yield 62%, m.p. 95–97° (hexane). Mol. wt. (cryoscopy in benzene) 301, calc. 311. IR (CCl_4): 3500, 1500, 990. PMR (CCl_4): δ 1.47 (d, 12H, 7 Hz, C–CH_3), 2.82 (d, 3H, J 10 Hz, N–CH_3) 3.29 (m, 7H, N–CH and NH), 7.39 (m, 4H, arom.). NMR ^{31}P (THF): δ −25.3 ppm. (Found: N 13.38, P 9.60. $C_{15}H_{26}N_2O_2P$ requires: N 13.50, P 9.95%). At 120° the spirophosphorane was converted to dimer **30a** with the yield of 74%.

N-(1-Azido-1-phenylpropyl-2)-methylamine chlorhydrate **31**. The soln of 2.6 g of sodium azide and 8 g of N-(1-chloro-1-phenylpropyl-2)-methylamine chlorhydrate in water was heated for 6 hr on water bath. After cooling it was alkalinated with 20% soln of NaOH, distilled with water

vapor into dil HCl, the acid soln was evaporated to dryness *in vacuo*, and the residue was recrystallized from acetone. The product was 4.3 g (52%) of the salt, m.p. 176° (dec.). IR (KBr): 2110 (N_3). (Found: Cl 15.81, N 24.84. $C_{10}H_{15}ClN_4$ requires: Cl 15.63, N 24.71%).

N-Methyl-N-(1-phenyl-1-azidopropyl-2)-trifluoroacetamide **13**. The aqueous soln of 3.8 g of **31** was treated with a soln of 2 g of K_2CO_3 in water, extracted with benzene, the extract was dried with $MgSO_4$, 4.2 g of trifluoroacetic anhydride were added and the mixture was stirred for several hr at room temp, evaporated *in vacuo*, and the residue was distilled to give 4.5 g of a compound (94%) with the b.p. of 90°/0.05 mm Hg, n_D^{20} 1.4940, d_4^{20} 1.2550. IR (film): 2115, 1700. PMR (CCl_4): δ 1.35 (dd, 3H, J 18 and 6 Hz, C–CH_3), 3.19 (m, 3H, N–CH_3), 4.87 (m, 2H, CH), 7.49 (s, 5H, arom.). (Found: F 19.79, N 19.70. $C_{12}H_{13}F_3N_4O$ requires: F 19.91, N 19.57%).

N-Methyl-N-(2-azidoethyl)-trifluoroacetamide. 0.25 mol of trifluoroacetic anhydride were added under cooling to the soln of 0.2 mol of N-(2-azidoethyl)-methylamine in anhyd benzene. The mixture was stirred for several hours at room temp, evaporated and the azide was recovered by distillation, yield 99%, b.p. 109°/20 mm Hg, n_D^{20} 1.4250, d_4^{20} 1.3531. IR (film): 2120, 1700, 1255, 1150. (Found: N 28.58. $C_5H_7F_3N_4O$ requires: N 28.57%).

2-Azidoethyltrifluoroacetate, **24**. The soln of 7.2 g of 2-azidoethanol and 12 ml of Et_3N in 50 ml of anhyd benzene were added dropwise under cooling 17.4 g of trifluoroacetic acid anhydride, stirred under cooling for another hour, 3 hr at room temp and 2 hr at 50°, the mixture was poured into water, extracted with benzene, the extract was dried with $MgSO_4$, evaporated, distillation gave **24**, yield 75%, b.p. 50°/10 mm Hg, n_D^{20} 1.3838, d_4^{20} 1.3807. IR (film): 2115, 1805. (Found: F 31.10, N 22.96. $C_4H_4F_3N_3O_2$ requires: F 31.12, N 22.95%).

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