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Phosphorylated Derivatives of 1-Morpholinocyclohexene and Cyclohexanone[1]

Andrew A. Tolmachev,[2] Alexander N. Kostyuk, Ernest S. Kozlov, Alexander N. Chernega, and Alexander M. Pinchuk

Institute of Organic Chemistry of the Ukrainian Academy of Sciences, Murmanskaya 5, Kiev-94, 253660, U.S.S.R.

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ABSTRACT

Phosphorylation of a relatively simple enamine with phosphorus (III) halides was first exemplified by the behavior of 1-morpholinocyclohexene. Novel types of functionalized P(III) derivatives have now been obtained and studied. The hydrolysis of (2-morpholino-1-cyclohexenyl) tetraethyldiamidophosphazidoarenes was found to be accompanied by the migration of the triazene group from the phosphorus atom to the carbon atom of the cyclohexene ring.

INTRODUCTION

Alkylation and acylation of enamines are widely used for synthesizing substituted aldehydes and ketones. However, phosphorylated derivatives of the simplest enamines were reported to be extremely unstable [1]. At the same time, some phosphorylated enamines of more complex structure have been isolated and characterized [2]. The synthesis and studies of the chemical reactivity of phosphorylated enamines of cyclic ketones are of theoretical and practical interest. Thus, for example, they can be the starting reagents for synthesizing α-phosphorylated derivatives of cyclic ketones, which are normally hard to obtain. Previously, we have described the phosphorylation of 1-morpholinocyclopentene with dichloro- and chlorophosphines [3]. This paper presents the results of the phosphorylation of 1-morpholinocyclohexene with phosphorus trichloride and tribromide that have enabled us to obtain key halophosphorylated 1-morpholinocyclohexenes and a wide range of derivatives derived from them.

RESULTS AND DISCUSSION

The reaction of enamine **1** with phosphorus trichloride in the presence of triethylamine leads to the formation of dichlorophosphine **2**, which is thermally unstable and cannot be isolated in a pure form. The resultant phosphonites **3, 4** are rather stable and vacuum distillable liquids, which can easily be transformed into the compounds of pentavalent phosphorus (**5–9**).

The reaction of two moles of enamine **1** with one mole of phosphorus trichloride leads to the formation of chlorophosphine **10**, which is characterized as thiophosphinates **11, 12.**

Even prolonged treatment of enamine **1** with the more active phosphorus tribromide in a 3:1 ratio, however, does not lead to the replacement of all three bromine atoms.

The phosphorylated enamine **9b** turned out to react readily with phosphorus tribromide to form the dibromophosphine **13,** which is characterized as diphosphonates **14, 15.** It should be noted that the two-fold electrophilic substitution in enamine molecules of cyclic ketones is typical of iodoalkanes, isocyanates, and sulfenyl chlorides, whereas it is not observed in the case of carboxylic and sulfonic acid halides [4].

[1] This paper is dedicated to the academician A. V. Kirsanov on the occasion of his 90th birthday.

[2] To whom correspondence should be addressed.

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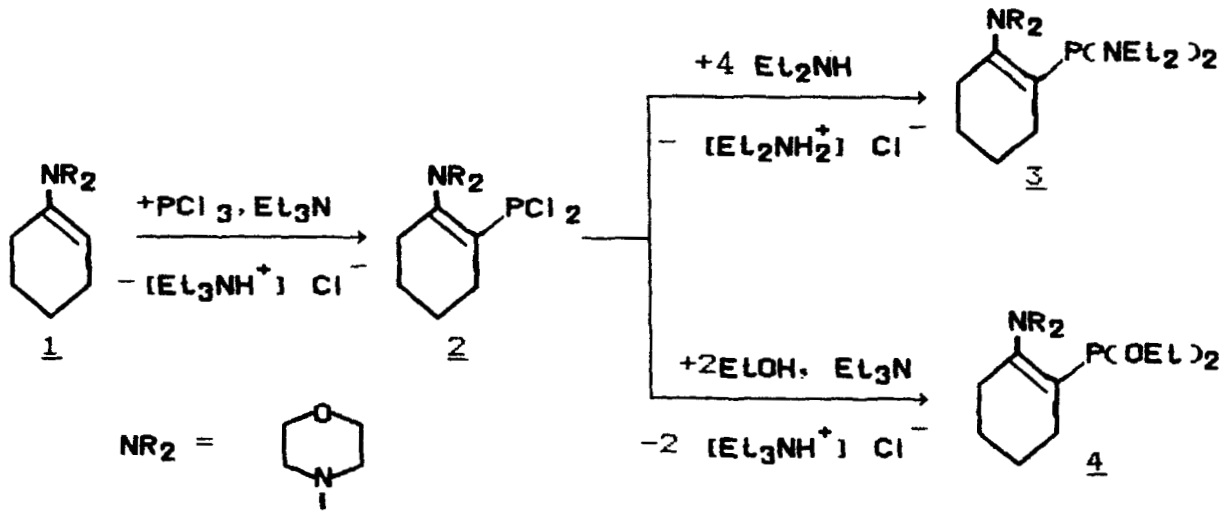
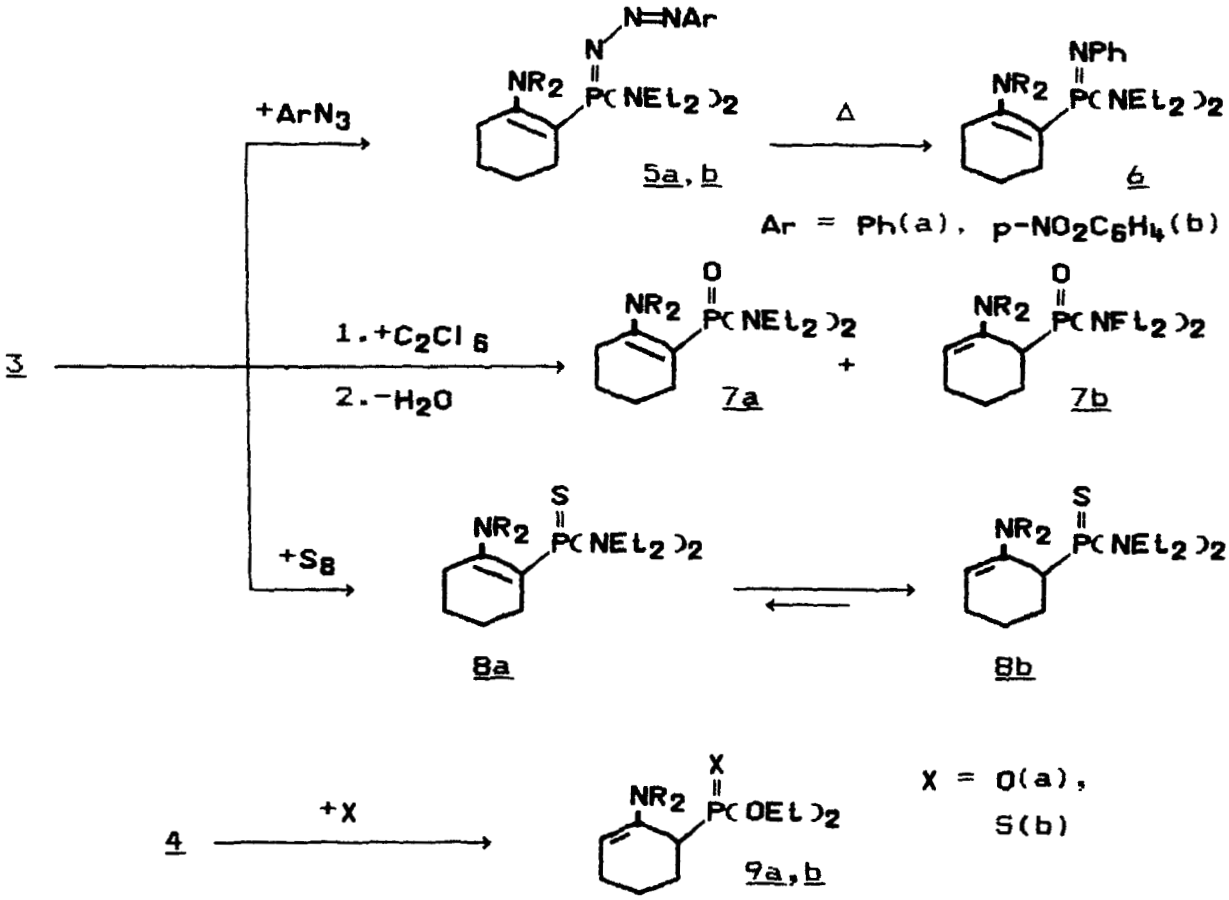
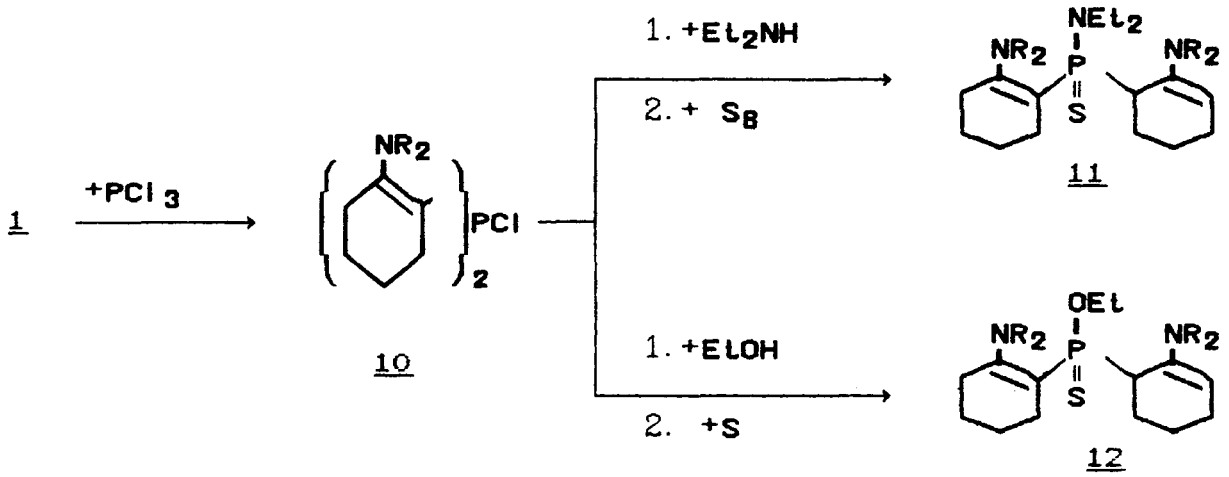


The structures of the compounds formed, including the position of the double bonds, have been determined by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The yields as well as the data on the elemental analyses and the ^{31}P NMR spectra are given in Table 1. Thus, all the phosphorylated enamines with trivalent phosphorus (**2–4**) exist only in the indicated form, that is, wherein the double bond encompasses the carbon atom bonded to phosphorus. The addition of sulfur to phosphonite **3** results initially in the formation of thiophosphonate **8a**; however, in due course, an equilibrium is established between the compounds **8a** and **8b** in a 2:3 ratio. In a similar reaction with phosphonite **4**, the position of the double bond is changed, thus leading to compound **9b**. Thiophosphinates **11**, **12** are initially formed as a mixture





with different positions of the double bonds; however, when allowed to stand, the substances, the double bonds of which are positioned as shown in the formulas, crystallize from the solution.

Hydrolysis of the phosphorylated enamines (**6–9, 12**) occurs easily in aqueous acetic acid at 20°C.

At the same time, despite the mild conditions of the hydrolysis, we have failed to isolate diphosphorylated ketones. The reaction products turned out to be only monophosphorylated ketones.

The keto-enol tautomerism is typical of α-phosphorylated ketones. The compounds **17, 18, 20** exist completely in the form of the ketone, whereas the compound **16,** due to the high basicity of the iminophosphonate group, exists only in the enol form. For the compound **19**, a mixture of the keto and enol forms is observed. The ketone amount in the mixture increases with increasing polarity of the solvent. The structures of the compounds, as well as the relative keto and enol content of each mixture, were proved by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.

The ammonolysis of the phosphonium salt, obtained by the reaction between hexachloroethane and phosphonite **3**, with subsequent alkaline hydrolysis, led to iminophosphonate **21**, the first compound of the R_3P = NH type, which contains a hydroxyl group in the β-position **(21a)**.

As follows from the spectral data, iminophosphonate **21** exists as the enol in solutions and in the solid state. In its IR spectra the absorption band for the carbonyl group is absent, whereas the ^{13}C NMR spectrum taken in deuterochloroform and deuteromethanol indicates the presence of a bond between the atoms of phosphorus and an sp^2-carbon. The stability of the enol form in methanol is unusual, since ordinarily alcohols are known to shift equilibria of this type towards the keto form [5]. Due to the high basicity of the P = NH group, the enol form of **21a** is, most likely, in an equilibrium with the zwitterionic form **21b**.

In the PMR spectrum of this compound, the signals for two protons, capable of deutero exchange, are positioned at δ 5.3, that is, in the range typical of the signals for the NH_2 groups of analogous phos-

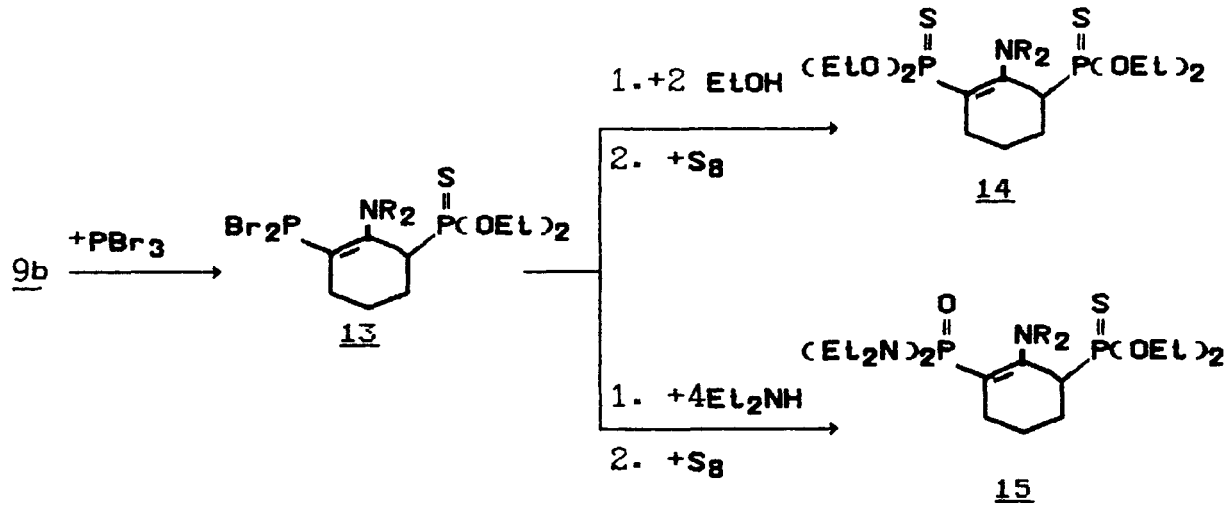


TABLE 1 Yields, Analytical Data and ^{31}P NMR Spectra of the Compounds 3–33

Compound	mp (°C) bp (°C/mm)	Yield %	Formula	$^{31}P\{^1H\}$ (Solvent)	Found (%) (calculated)		
					N	S	P
1	2	3	4	5	6	7	8
3	150-155/0.02	56	$C_{18}H_{36}N_3OP$	99.7,98.4 (benzene)	12.3 (12.3)		9.1 (9.1)
4	110-112/0.02	49	$C_{14}H_{26}NO_3P$	156.2,185.5 (benzene)	4.9 (4.9)		10.3 (10.8)
5a	145-147 (decomp.)	83	$C_{24}H_{41}N_6OP$	45.1 (chloroform)	17.9 (18.3)		6.5 (6.7)
5b	135-136 (decomp.)	72	$C_{24}H_{40}N_7O_3P$	44.9 (benzene)	18.9 (19.4)		
6	106-109	76	$C_{24}H_{41}N_4OP$	18.4 (benzene)	13.2 (13.0)		7.0 (7.2)
7	160-165/0.02	61	$C_{18}H_{36}N_3O_2P$	35.3 (benzene)	11.5 (11.8)		8.7 (8.7)
8	oil	96	$C_{18}H_{36}N_3OPS$	91.0,75.8 (benzene)	11.1 (11.3)		8.3 (8.3)
9a	115-120/0.02	53	$C_{14}H_{26}NO_4P$	30.3 (benzene)			9.7 (10.2)
9b	oil	95	$C_{14}H_{26}NO_3PS$	100.5,85.4 (benzene)	4.3 (4.4)	10.3 (10.0)	
11	132-135	7	$C_{24}H_{42}N_3O_2PS$	79.7 (benzene)	9.0 (9.0)	7.1 (6.9)	
12	157-159	22	$C_{22}H_{37}N_2O_3PS$	94.9 (benzene)		7.5 (7.3)	7.0 (7.0)
14	oil	61	$C_{18}H_{35}NO_5P_2S_2$	96.7,85.6 (benzene)		13.3 (13.6)	13.2 (13.1)
15	oil	59	$C_{22}H_{45}N_3O_4P_2S$	98.2,26.5 (benzene)		6.6 (6.3)	12.8 (12.5)
16	oil	34	$C_{20}H_{34}N_3OP$	36.5 (benzene)	11.2 (11.6)		8.3 (8.5)
18	105-110/0.02	43	$C_{10}H_{19}O_3PS$	92.8 (benzene)		12.4 (12.8)	12.2 (12.4)
19	123-125/0.02	39	$C_{14}H_{29}N_2O_2P$	39,8,31.0 (chloroform)	9.7 (9.7)		11.0 (10.7)
20	137-139	54	$C_{14}H_{23}O_3PS$	107.9 (benzene)		11.0 (10.6)	10.3 (10.2)
21	143-144	28	$C_{14}H_{30}N_3OP$	56.4 (chloroform)	14.3 (14.6)		10.8 (10.8)
22	oil	94	$C_{22}H_{40}N_3O_4PS$	45.8 (benzene)	8.8 (8.9)		7.1 (6.8)
24	oil	65	$C_{15}H_{31}N_3O_2P_2$	23.5,21.2 (benzene)	12.6 (12.1)		18.0 (17.8)
27	47-52	54	$C_{22}H_{38}N_4O_2P_2$	24.2,13.5 (benzene)	12.9 (12.4)		14.1 (13.7)
29	oil	76	$C_{16}H_{34}N_3OSiP$	21.9 (benzene)			9.0 (9.0)
31	oil	69	$C_{17}H_{34}N_4OPCl$	22.2 (chloroform)			8.1 (8.2)
33a	46-51	27	$C_{20}H_{34}N_5OP$	32.0 (heptane)	17.0 (17.9)		8.3 (7.9)
33b	148-154	26	$C_{20}H_{33}N_6O_3P$	33.3 (benzene)	19.1 (19.3)		7.4 (7.1)

phonium salts [6]. The existence of a zwitterionic form is also supported by the alkylation of the compound **21**, which proceeds at the oxygen and not at the nitrogen atom, with the formation of salt **22**. This is confirmed both by the analysis for the methoxy group and PMR spectra, in which the signals for the CH_3 group are positioned at δ 3.7, that is typical of the OCH_3 and not of the NCH_3 group.

Iminophosphonate **21** reacts with penta- and trivalent phosphorus acid dichlorides, dichloro-

TABLE 2 Selected Bond Lengths (Å), Bond Angles (°) and Torsion Angles of Molecule **5a**

P-N^1	1.623(1)	P-N^1-N^2	114.76(9)
P-N^4	1.646(1)	N^1-N^2-N^3	112.6(1)
P-N^5	1.659(1)	N^2-N^3-C^1	112.3(1)
P-C^{15}	1.808(1)	P-N^1-N^2-N^3	178.1(2)
N^1-N^2	1.342(2)	N^1-N^2-N^3-C^1	173.2(2)
N^2-N^3	1.273(2)	N^2-N^3-C^1-C^2	−6.5(4)
N^3-C^1	1.423(2)	P-C^{15}-C^{20}-N^6	1.8(3)

dimethylsilane and dichloromethylenedimethylammonium chloride in the presence of bases to form heterocyclic compounds **24, 27, 29, 31**.

The results of the hydrolysis of compounds **5a, b** turned out to be unexpected. The ^{13}C NMR spectra of the products were more consistent with the structures, **33a, b,** than with **32a, b**.

An X-ray diffraction analysis proved the structure of **5a**. The stereo view of a molecule of the compound **5a** is given in Figure 1 and its main geometrical parameters are given in Table 2.

The $P{=}N^1{-}N^2{=}N^3{-}C^1$ bonds system is planar within 0.014(3) Å, the C^{1-6} benzene ring being almost coplanar with it [the corresponding dihedral angle being only 7.8(6)°]. The $N^1N^2N^3C^1$ torsion angle is 177.3(2)°. The bond configuration for the N^4 and N^5 atoms is close to planar-trigonal and that for the N^6 atom is pyramidal [the bond angles sums being 359.3(4), 356.6(3) and 337.7(3)°, respectively]. A significant turn of the orbital of the lone electron pair of the N^6 atom relative to the π-system of the $C^{15}{-}C^{20}$ double bond (the corresponding torsion angle along the N^6 — C^{20} bond being about 70°) excludes the possibility of an appreciable N_n–$\pi_{C=C}$ conjugation.

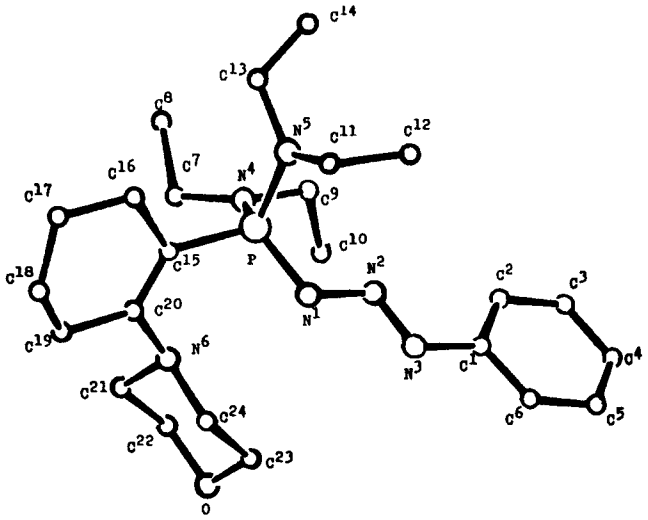


FIGURE 1 General view of molecule **5a**, including the numbering scheme (H atoms omitted for clarity).

The X-ray structure analysis of the hydrolysis product of compound **5b** showed it to have the structure **33b**.

One can assume that the compounds **33a, b** result from the hydrolysis of the compounds **32a, b** at the P = N bond with a subsequent reaction taking place between the hydrolysis products, that is, Ar — N = N — NH_2, the triazene, and the phosphorylated ketone. However, it should be noted that similar reactions always proceed with evolution of nitrogen [7]. Therefore, it is quite possible that the

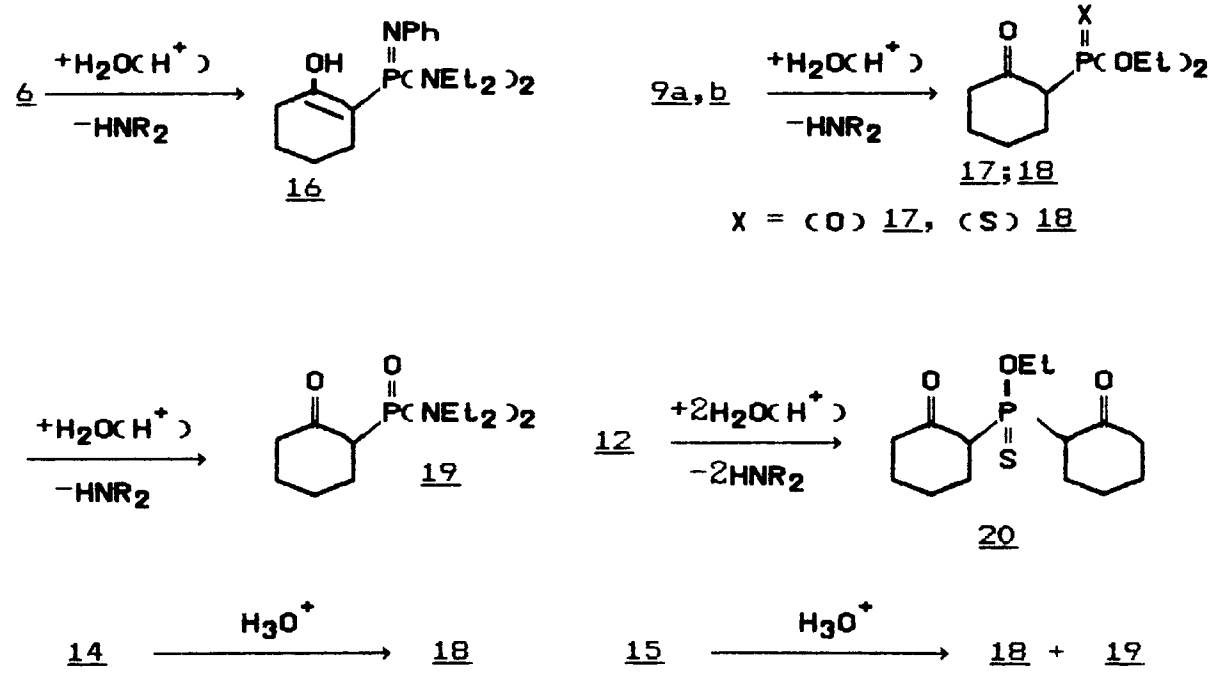


TABLE 3 Selected Bond Lengths (Å), Bond Angles (°) and Torsion Angles of Molecule **33b**

P-O^1	1.485(1)	N^2-N^1-C^{20}	122.0(2)
P-N^4	1.637(1)	N^1-N^2-N^3	112.4(1)
P-N^5	1.650(1)	N^2-N^3-C^1	112.22(9)
P-C^{15}	1.807(1)	P-C^{15}-C^{20}-N^1	2.9(3)
N^1-N^2	1.319(1)	C^{15}-C^{20}-N^1-N^2	−175.6(2)
N^1-C^{20}	1.382(2)	C^{20}-N^1-N^2-N^3	−178.8(2)
N^2-N^3	1.237(1)	N^1-N^2-N^3-C^1	−179.3(2)
N^3-C^1	1.412(1)	N^2-N^3-C^1-C^2	−169.4(2)

compounds **33a, b** are formed by an intra- or intermolecular Witting-type rearrangement.

The stereo view of a molecule of **33b** is given in Figure 2 and its main geometrical parameters are given in Table 3.

The $P-C^{15} = C^{20}-N^1-N^2 = N^3-C^1$ bonds system is planar within 0.055(2) Å, the c^{1-6} benzene ring being turned relative to it by 17.3(2)°. The geometrical parameters of the $C^{20}N^1N^2N^3C^1$ group indicate considerable delocalization of the electron density: the N^1-C^{20} and N^3-C^1 bonds are shortened to 1.388(2) and 1.412(1) Å, respectively, as compared to the standard value of 1.45 Å for the $N(sp^2)-C(sp^2)$ bonds [8]. The N^2-N^3 bond is longer (1.273(4) Å), and the N^1-N^2 bond (1.319(1) Å) is appreciably shorter than the standard values of 1.23 and 1.41 Å, respectively, for the N = N and $N(sp^2)-N(sp^2)$ bonds [8]. The N^1, N^4 and N^5 atoms have practically the planar-trigonal configurations. A specific feature of the molecular structure of the compound **33b** is the intramolecular $N^1-H...O^1$ hydrogen bond. The geometrical parameters of this bond are: $N^1...O^1$ 2.624(1) N^1-H 0.77(2), $H...O^1$ 1.95(2) Å, N^1HO^1 144.8(1.6)°. The value of the $N^1...O^1$ distance is considerably shorter than the average statistical value of 2.89 Å, typical for hydrogen bridges of this type [9], and this is, most likely, evidence for its strength.

The ^{13}C and ^{31}P NMR spectra of triazene **33a, b** are rather similar, and the PMR spectra in deuterobenzene are almost identical, the signals for the protons of the NH groups being positioned in the range of δ 14.5. The PMR spectrum of the compound **33b** in deuterochloroform is the same as that in deuterobenzene, but the proton signal for the NH group of compound **33a** is at δ 3. The signal shift by 11 ppm is apparently explained by a breaking of the intramolecular hydrogen bond due to either the

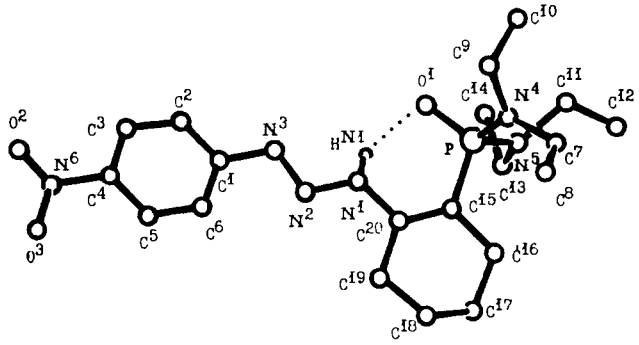


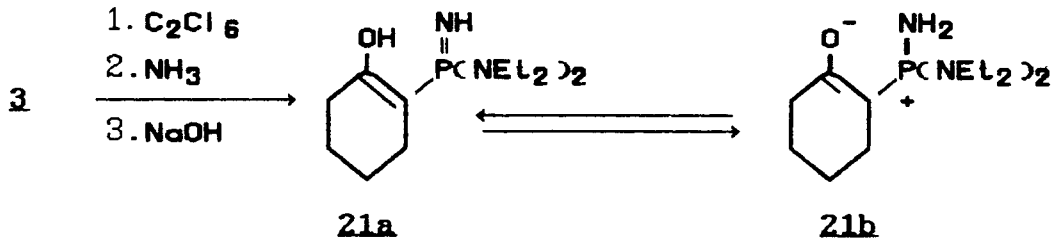
FIGURE 2 General view of molecule **33b**, including the numbering scheme.

effect of deuterochloroform or to a proton migration to the nitrogen atom bonded to the phenyl group. The latter is typical of triazenes, though it seems to be hardly probable, since no changes in the PMR spectra of the aromatic protons are observed when the solvent is changed. In the compound **33b** the proton of the NH group is more acidic and forms a more stable hydrogen bond, which is retained in deuterochloroform. In the IR spectra of the compounds **33a, b** in tetrachloromethane low-intensity absorption bands for the NH groups are in the range of 3400 cm^{-1} and do not shift on dilution.

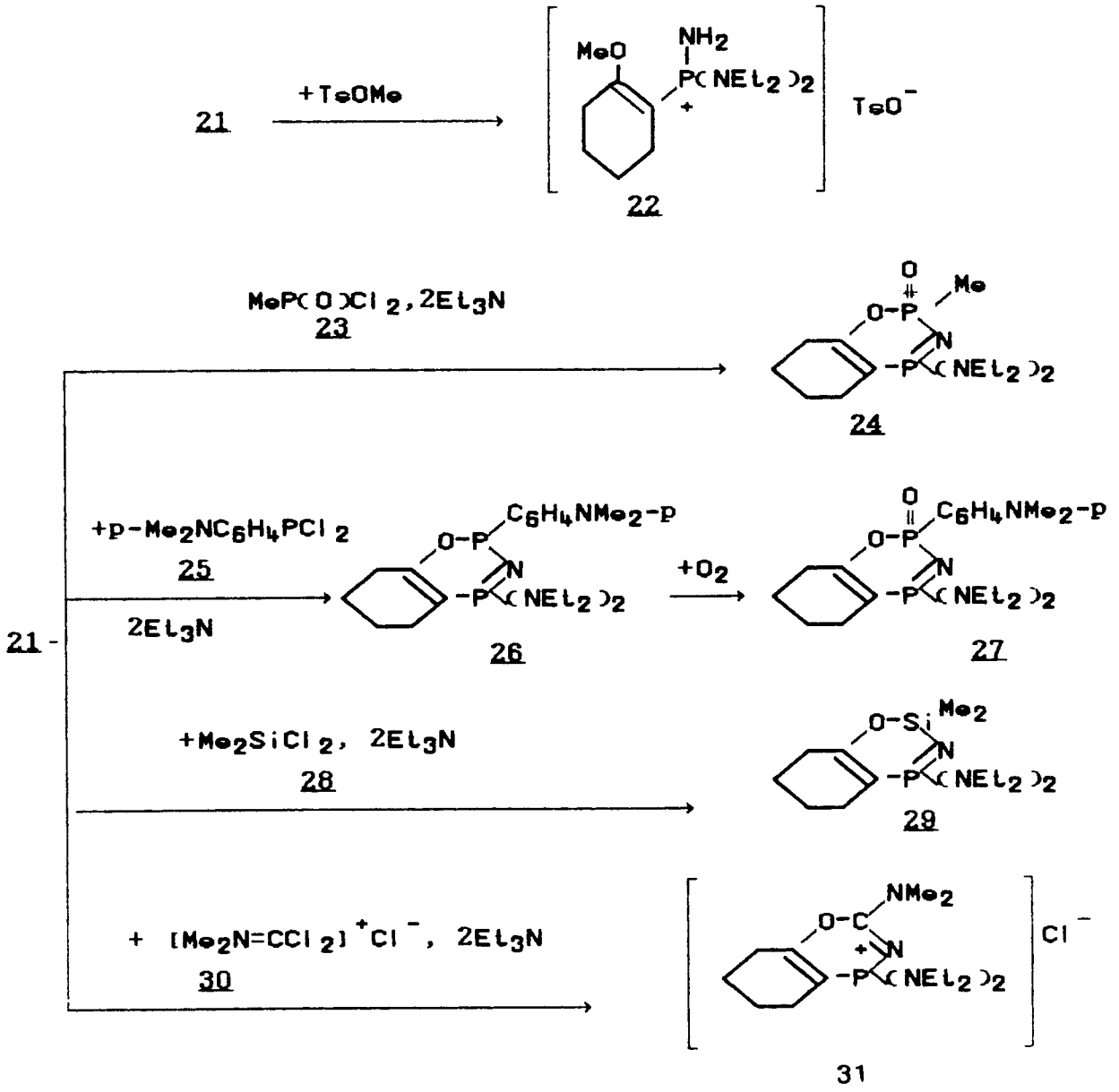
EXPERIMENTAL

A Bruker WP-200 spectrometer was used to take the ^{31}P NMR spectra and a Varian Gemini-200 to take the ^1H and ^{13}C NMR spectra. The ^1H and ^{13}C signals were registered with respect to the internal standard, tetramethylsilane, and the ^{31}P signals to the external standard, 85% H_3PO_4.

An X-ray structural study of the compounds **5a** and **33b** has been performed with a CAD-4-ENRAF-NONIUS diffractometer using graphite monochromated Cu-K_α radiation ($\bar{\lambda}$ = 1.54184 Å, the ratio of the scanning rates ω/ϑ = 1.2). The main crystallographic data for **5a** and **33b** are listed in Table 4. Both structures were solved by the direct methods and refined by full-matrix least squares. The reflections with $I > 3\sigma$ were used in the refinement with the weighting scheme based on counting statistic



21a **21b**



$$\omega = \frac{4F_o^2}{[\sigma^2(F_o)]^2}$$

Only part (about 30% for **5a** and 40% for **33b**) of the hydrogen atoms were located in the difference Fourier maps; the positions of the remaining H atoms were calculated. The hydrogen atoms in both structures were included in the final refinement with the fixed positional and thermal (B_{iso} = 6Å^2) parameters. Only the H^{N1} atom in **33b** was refined isotropi-

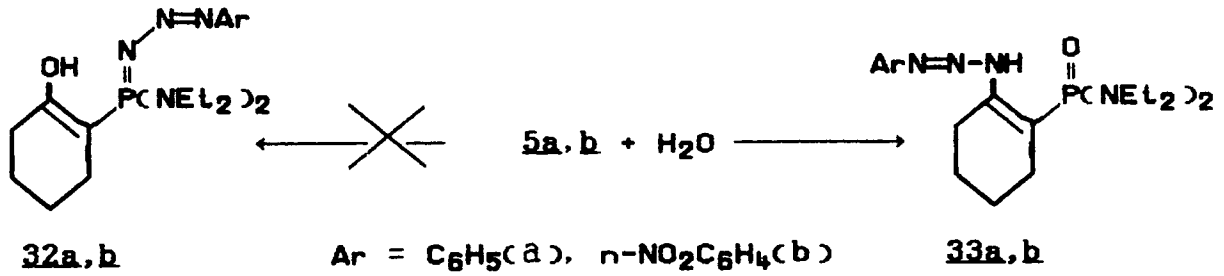


TABLE 4 Crystal and Data Reduction Parameters for **5a** and **33b**

	5a	33b
a, Å	9.481(4)	11.195(4)
b, Å	21.027(5)	11.607(7)
c, Å	13.954(9)	18.410(8)
β, °	111.68(4)	99.20(3)
V, Å	2584.9	2361.4
Z	4	4
d_{calc}, g cm^{-3}	1.18	1.23
Space group	$P2_1/c$	$P2_1/c$
μ, cm^{-1}	11.3	12.8
ϑ_{max}, °	65	65
The number reflection:		
measured (unique)	4430	4011
used in the refinement	3506	3139
R	0.072	0.055
R_w	0.107	0.080
The number of parameters refined	289	347
Largest difference peak e• Å^{-3}	0.45	0.34

cally. Corrections for Lorentz and polarization effects but not for absorption were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [10]. Atomic coordinates and their thermal parameters are listed in Table 5 and 6. All crystallographic data including the tables of the atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre [11].

*(2-Morpholino-1-cyclohexenyl)dichlorophosphine (**2**)*

To a solution of PCl_3 (0.28 mole) in petroleum ether, b.p. 70–100°C (500 mL), which had been cooled to 10°C, a mixture of the compound **1** (0.28 mole) and triethylamine (0.30 mole) was added with stirring for 30 min. The ^{31}P NMR spectrum (of the solution): δ 165.0. The substance was not isolated but used for further transformations.

*(2-Morpholino-1-cyclohexenyl)phosphonus acid tetraethyldiamide (**3**)*

To a solution of dichlorophosphine **2** (0.28 mole) in petroleum ether (500 mL), diethylamine (1.4 mole)

TABLE 5 Coordinates of nonhydrogen atoms and their equivalent isotropic temperature factors B_{equ} (Å) in structure **5a**

Atom	*x*	*y*	*z*	*B*
P	0.03265(6)	0.20061(3)	0.20761(4)	2.95(1)
O	0.5097(2)	0.0938(1)	0.4901(2)	5.37(5)
N^1	0.1348(2)	0.24019(9)	0.3095(2)	3.44(4)
N^2	0.2252(2)	0.28452(9)	0.2930(1)	3.15(4)
N^3	0.2997(2)	0.3156(1)	0.3743(2)	3.84(4)
N^4	0.1098(2)	0.17069(9)	0.1295(2)	3.65(4)
N^5	−0.1032(2)	0.2488(1)	0.1347(2)	4.17(5)
N^6	0.1989(2)	0.10068(9)	0.3638(1)	3.15(4)
C^1	0.4004(3)	0.3605(1)	0.3575(2)	3.42(5)
C^2	0.4298(3)	0.3668(1)	0.2677(2)	4.83(6)
C^3	0.5329(4)	0.4104(2)	0.2606(2)	5.62(7)
C^4	0.6121(3)	0.4484(2)	0.3438(2)	5.17(7)
C^5	0.5817(3)	0.4436(2)	0.4320(2)	5.20(7)
C^6	0.4769(3)	0.4002(1)	0.4391(2)	4.47(6)
C^7	0.1114(4)	0.1038(1)	0.1029(2)	4.98(6)
C^8	0.0594(4)	0.0920(2)	−0.0119(3)	6.60(8)
C^9	0.2074(3)	0.2126(1)	0.0963(2)	4.28(6)
C^{10}	0.3752(4)	0.1999(2)	0.1528(3)	6.26(8)
C^{11}	−0.1576(3)	0.3002(1)	0.1837(3)	5.54(8)
C^{12}	−0.1038(5)	0.3654(2)	0.1698(4)	7.7(1)
C^{13}	−0.2080(4)	0.2307(2)	0.0315(3)	6.58(9)
C^{14}	−0.2133(6)	0.2735(3)	−0.0526(4)	9.7(1)
C^{15}	−0.0492(2)	0.1357(1)	0.2545(2)	3.19(5)
C^{16}	−0.2217(3)	0.1296(2)	0.2092(2)	4.67(7)
C^{17}	−0.2774(3)	0.0700(2)	0.2417(3)	7.7(1)
C^{18}	−0.1964(5)	0.0455(3)	0.3434(4)	5.6(1)
C^{19}	−0.0277(3)	0.0393(2)	0.3646(3)	5.53(7)
C^{20}	0.0374(2)	0.0933(1)	0.3237(2)	3.28(5)
C^{21}	0.2852(3)	0.0420(1)	0.3706(2)	4.03(6)
C^{22}	0.4492(3)	0.0602(2)	0.3952(2)	4.90(6)
C^{23}	0.4221(3)	0.1492(2)	0.4866(2)	4.82(7)
C^{24}	0.2583(3)	0.1331(1)	0.4634(2)	3.85(5)

TABLE 6 Coordinates of nonhydrogen atoms and their equivalent isotropic temperature factors B_{equ} (Å^2) in structure **33b**

Atom	*x*	*y*	*z*	*B*
P	0.15169(4)	0.07198(4)	0.37021(3)	4.13(1)
O^1	0.1610(1)	0.1843(1)	0.40933(9)	5.84(3)
O^2	−0.4736(2)	0.7632(2)	0.4989(2)	8.99(5)
O^3	−0.5986(2)	0.6678(2)	0.4246(1)	8.94(5)
N^1	−0.0688(1)	0.2261(1)	0.36260(9)	4.11(3)
N^2	−0.1597(1)	0.2946(1)	0.37077(9)	3.96(3)
N^3	−0.1293(1)	0.3719(1)	0.41929(9)	4.12(3)
N^4	0.1572(2)	−0.0397(2)	0.4249(1)	5.31(4)
N^5	0.2630(2)	0.0524(2)	0.3226(1)	5.71(4)
N^6	−0.4983(2)	0.6827(2)	0.4585(1)	6.07(4)
C^1	−0.2271(2)	0.4442(2)	0.4286(1)	3.90(4)
C^2	−0.1980(2)	0.5425(2)	0.4709(1)	4.50(4)
C^3	−0.2862(2)	0.6215(2)	0.4816(1)	4.95(4)
C^4	−0.4036(2)	0.5991(2)	0.4494(1)	4.68(4)
C^5	−0.4358(2)	0.4995(2)	0.4097(1)	4.98(4)
C^6	−0.3473(2)	0.4222(2)	0.3995(1)	4.64(4)
C^{7A}	0.0596(4)	−0.1036(4)	0.4357(2)	4.95(9)
C^{7B}	0.1399(6)	−0.1655(5)	0.4084(4)	7.1(1)
C^{8A}	0.0746(7)	−0.2310(5)	0.4126(4)	8.1(2)
C^{8B}	0.0177(7)	−0.2220(7)	0.4152(4)	8.5(2)
C^{9A}	0.2746(4)	−0.0551(6)	0.4730(3)	6.9(1)
C^{9B}	0.1671(6)	−0.0234(7)	0.5102(3)	7.8(1)
C^{10A}	0.2712(6)	−0.0088(8)	0.5509(3)	8.6(2)
C^{10B}	0.2902(9)	−0.0318(9)	0.5430(4)	10.5(2)
C^{11A}	0.3022(4)	−0.0483(4)	0.2947(2)	5.14(9)
C^{11B}	0.3740(5)	−0.0143(6)	0.3606(3)	7.0(1)
C^{12A}	0.4475(6)	−0.0644(9)	0.3099(6)	11.4(3)
C^{12B}	0.4282(4)	−0.0823(4)	0.3063(3)	5.6(1)
C^{13A}	0.2745(5)	0.1257(6)	0.2655(3)	7.7(1)
C^{13B}	0.3168(8)	0.1751(7)	0.2923(6)	10.3(2)
C^{14A}	0.258(2)	0.197(1)	0.2159(7)	19.2(5)
C^{14B}	0.3792(7)	0.2233(6)	0.2987(6)	11.8(2)
C^{15}	0.0105(2)	0.0632(2)	0.3073(1)	4.01(4)
C^{16}	−0.0016(2)	−0.0298(2)	0.2490(1)	5.25(5)
C^{17}	−0.1138(3)	−0.0201(3)	0.1924(2)	8.38(8)
C^{18}	−0.2175(3)	0.0189(3)	0.2195(2)	8.67(7)
C^{19}	−0.2029(2)	0.1286(2)	0.2633(1)	5.36(5)
C^{20}	−0.0812(2)	0.1374(2)	0.3118(1)	3.92(4)
H^{N1}	−0.004(2)	0.242(2)	0.381(1)	2.8(5)

[a]The atoms C^7–C^{14} of diethylamino groups are disordered by two positions (A and B) with equal populations

was added with stirring for 1 hr. The preciptated solid was filtered off and the filtrate was evaporated to the 250 mL volume. The solution was added with stirring to liquid ammonia, and sodium (~20 g) was added with stirring for 3 hrs, until the bleaching of the solution was complete. After evaporation of ammonia, the mixture was filtered, the solvent was evaporated from the filtrate, and the residue was distilled (Table 1 lists physical contants) ^{1}H NMR (C_6D_6) δ 1.08 (t, J_{HH} 7 Hz, 12 H CH_3), 1.3–2.6 (m, 8H, CH_2), 2.6-2.8 (m, 4H, NCH_2CH_2), 2.8–3.1 (m, 8H, NCH_2CH_3), 3.5-3.9 (m, 4H, OCH_2). ^{13}C NMR (C_6D_6) δ 130.4 (d, J_{cp} 12.7 Hz, C^1), 149.1 (d, J_{cp} 22.5 Hz, C^2), 22.4 (d, J_{cp} 1.3 Hz, C^3), 21.1 (s, C^4), 21.9 (s, C^5), 25.8 (s, C^6), 49.2 (s, NCH_2CH_2O), 65.7 (s, NCH_2CH_2O) 43.1 (d, J_{cp} 19.3 Hz, NCH_2CH_3), 13.7 (d, J_{cp} 3.7 Hz, CH_3).

Diethyl ester of (2-Morpholino-1-cyclohexenyl)phosphonous acid (**4**)

To a solution of dichlorophosphine **2** (0.30 mole) in petroleum ether (700 mL), a mixture of ethyl alcohol (0.6 mole) and triethylamine (0.62 mole) was added, with stirring for 1,5 hr. The mixture was then stirred for 2 hr. The precipitated solid was filtered off, the filtrate evaporated and the residue distilled (Table 1); ^{1}H NMR ($CDCl_3$) δ 1.17 (t, 6H, CH_3), 1.4–2.3 (m, 8H, CH_2), 2.6–2.8 (m, 4H, NCH_2), 3.5–4.2 (m, 8H, OCH_2).

^{13}C NMR ($CDCl_3$) δ 132.7 (d, J_{cp} 15.6 Hz, C^1), 154.1 (d, J_{cp} 24.1 Hz, C^2), 22.6 (s, C^3), 20.8 (s, C^4), 20.0 (d, J_{cp} 1.4 Hz, C^5), 20.9 (s, C^6), 48.8 (s, NCH_2CH_2O), 65.0 (s, NCH_2CH_2O), 60.3 (d, J_{cp} 15.0 Hz, OCH_2), 15.4 (d, J_{cp} 5.4 Hz, CH_3).

General method of synthesizing the compounds **5a,b**

To a solution of the compound **3** (0.03 mole) in benzene (30 mL), a solution of the corresponding aryl azide (0.03 mole) in benzene (20 mL) was added, with stirring at 10°C. In a month a pure product, either **5a** or **5b**, crystallized.

*(2-Morpholino-1-cyclohexenyl)tetraethyldiamidophosphazidobenzene (**5a**)*

^1H NMR ($CDCl_3$) δ 1.12 (t, J_{HH} 7 Hz, 12H, CH_2CH_3), 1.5–2.5 (m, 8H, CH_2), 2.8–3.0 (m, 4H, NCH_2CH_2O), 3.0–3.5 (m, 8H, NCH_2CH_3), 3.6–3.9 (m, 4H, NCH_2CH_2O), 7.1–7.6 (m, 5H, Ar-H). ^{13}C NMR ($CDCl_3$) δ 110.7 (d, J_{cp} 136.3 Hz, C^1), 162.6 (d, J_{cp} 3.4 Hz, C^2), 25.6 (d, J_{cp} 11.6 Hz, C^3), 22.7 (s, C^4), 23.1 (d, J_{cp} 8.4 Hz, C^5), 27.9 (d, J_{cp} 7.4 Hz, C^6), 50.9 (s, NCH_2CH_2O), 66.9 (s, NCH_2CH_2O), 39.9 (d, J_{cp} 3.1 Hz, NCH_2), 13.8 (d, J_{cp} 2.3 Hz, CH_3), 153.5-(s,i–Ph), 120.7 (s, o–Ph, 128.7 (s, m-Ph), 124.3 (s, p-Ph).

*(2-Morpholino-1-cyclohexenyl)tetraethyldiamidophosphazido-4-nitrobenzene (**5b**)*

^1H NMR ($CDCl_3$) δ 1.14 (t, J_{HH} 7 Hz, 12H, CH_2CH_3), 1.5-2.4 (m, 8H, CH_2), 2.7–3.0 (m, 4H, NCH_2CH_2O), 3.0–3.4 (m, 8H, NCH_2CH_3), 3.5–3.8 (m, 4H, NCH_2CH_2O), 7.4–8.2 (m, 4H, Ar-H). ^{13}C NMR ($CDCl_3$) δ 110.3 (d, J_{cp} 354.9 Hz, C^1), 164.6 (d, J_{cp} 4.6 Hz, C^2), 26.9 (d, J_{cp} 11.2 Hz, C^3) 23.0 (s, C^4), 23.4 (d, J_{cp} 6.2 Hz, C^5), 28.3 (d, J_{cp} 7.3 Hz, C^6), 51.1 (s, NCH_2CH_2O), 67.1 (s, NCH_2CH_2O), 40.0 (d, J_{cp} 3.3 Hz, NCH_2), 13.9 (s, CH_3), 159.8 (s, $C^{1'}$, Ar), 120.2 (s, $C^{2'}$, Ar), 125.9 (s, $C^{3'}$, Ar), 144.0 (s, $C^{4'}$, Ar).

HEATING OF THE COMPOUNDS **5A** *AND* **5B**

*(2-Morpholino-1-cyclohexenyl)phenyliminophosphonic acid tetraethyldiamide (**6**)*

The compound **5a** (0.07 mole) was heated to 140°C, accompanied by rapid nitrogen evolution. The cooled mass was stirred with petroleum ether and crystallized from heptane (Table 1) ^1H NMR ($CDCl_3$) δ 1.08 (t, J_{HH} 7 Hz, 12 H, CH_2CH_3), 1.5–2.4 (m, 8H, CH_2), 2.7–3.3 (m, 12 H, NCH_2), 3.5–3.7 (m, 4H, NCH_2CH_2O), 6.4–7.2 (m, 5H, Ar-H). ^{13}C NMR ($CDCl_3$) δ 114.2 (d, J_{cp} 143.5 Hz, C^1), 157.4 (d, J_{cp} 3.1 Hz, C^2) 23.2 (d, J_{cp} 11.9 Hz, C^3), 20.9 (s, C^4), 21.2 (d, J_{cp} 8.3 Hz, C^5), 26.3 (d, J_{cp} 8.1 Hz, C^6), 49.1 (s, NCH_2CH_2O), 65.0 (s, NCH_2CH_2O), 37.4 (d, J_{cp} 4.8 Hz, NCH_2), 11.7 (d, J_{cp} 2.7 Hz, CH_3), 150.9 (s, i-Ph), 120.7 (d, J_{cp} 18.5 Hz o-Ph), 126.6 (s, m-Ph), 113.5 (s, p-Ph).

On attempted distillation of compound **5b**, individual substances were not separated.

*(2-Morpholino-1-cyclohexenyl)phosphonic acid tetraethyldiamide (**7a,b**)*

To a solution of the compound **3** (0.03 mole) in petroleum ether (50 mL), a solution of hexachloroethane (0.03 mole) in petroleum ether (30 mL) was added. The precipitated solid was filtered off, dissolved in chloroform (70 mL), and washed with water (30 mL). The organic layer was separated and dried. The solvent was evaporated and the residue was distilled (Table 1); ^1H NMR (C_6D_6) δ 1.09 (t, J_{HH} 7 Hz, 12H, CH_3), 1.3–2.6 (m, 8H, CH_2), 2.7–3.3 (m, 12 H, NCH_2), 3.5–3.9 (m 4H, OCH_2). ^{13}C NMR (C_6D_6) for **7a** δ 117.5 (d, J_{cp} 149.1 Hz, C^1) 158.1 (d, J_{cp} 2.5 Hz, C^2); for **7b** 33.8 (d, J_{cp} 112.7 Hz, C^1), 144.2 (s, C^2), 107.4 (d, J_{cp} 8.3 Hz, C^3), 19.0 (d, J_{cp} 6.8 Hz, C^4), 21.1 (d, J_{cp} 8.7 Hz, C^5), 23.8 (d, J_{cp} 3.3 Hz, C^6), 49.6 (s, NCH_2CH_2O), 65.3 (s, NCH_2CH_2O), 37.8 (d, J_{cp} 3.6 Hz, NCH_2), 36.5 (d, J_{cp} 2.4 Hz, NCH_2), 12.9 (d, J_{cp} 2.8 Hz, CH_3), 12.0 (d, J_{cp} 2.7 Hz, CH_3).

General method of synthesizing the compounds **8** *and* **9b**

To a solution of the corresponding phosphonite **3** or **4** (0.05 mole) in benzene (50 mL), finely powdered sulfur (0.05 mole was added with stirring. When the sulfur had dissolved, the solution was filtered, the solvent was evaporated, and the residue was kept *in vacuo* (oil pump pressure).

*(2-Morpholino-1-cyclohexenyl)thiophosphonic acid tetraethyldiamide (**8**)*

^1H NMR (C_6) δ 1.07 (t, J_{HH} 7Hz, 12H, CH_3), 1.3–2.5 (m, 7H, CH_2) 2.8–3.3 (m, 12H, NCH_2) 3.5–3.8 (m, 4H, OCH_2), 5.17 (dt, J_{HH} 4 Hz, J_{Hp} 4.4 Hz, 0.4H NC = CH). ^{13}C NMR (C_6D_6) for **8a** δ 123.2 (d, J_{cp} 120.1 Hz, C^1), 158.6 (d, J_{cp} 3.4 Hz, C^2), for **8b** 146.8 (d, J_{cp} 8.3 Hz, C^2), 114.0 (d, J_{cp} 9.7 Hz, C^3).

*(2-Morpholino-1-cyclohexenyl)thiophosphonic acid diethylester (**9b**)*

^1H NMR ($CDCl^3$) δ 1.30 (t, J_{HH} 7Hz, 6H, CH_3), 1.5–3.3 (m, 7H, CH_2, CHP), 3.3–3.8 (m, 4H, OCH_2), 4.0–4.3 (m, 4H, OCH_2), 5.03 (dt, J_{HH} 3.3 Hz, J_{HP} 4.1 Hz, 1H, NC = CH). ^{13}C NMR ($CDCl_3$) δ 41.1 (d, J_{CP} 70.6 Hz, C^1), 143.1 (d, J_{CP} 5.9 Hz, C^2), 108.6 (d, J_{CP} 7.6 Hz, C^3), 25.0 (d, J_{CP} 2.0 Hz, C^4), 19.3 (d, J_{CP} 2.7 Hz, C^5), 24.3 (d, J_{CP} 2.3 Hz, C^6), 50.1 (s, NCH_2CH_2O), 67.0 (s, NCH_2 CH_20), 62.7 (d, J_{CP} 5.1 Hz, OCH_2), 62.0 (d, J_{CP} 5.0 Hz, OCH_2), 16.4 (d, J_{CP} 1.5 Hz, CH_3), 16.3 (d, J_{CP} 1.3 Hz, CH_3).

*Diethyl ester of the (2-morpholino-1-cyclohexenyl)phosphonic acid (**9a**)*

A solution of the compound **4** (0.05 mole) in benzene (50 mL) was purged with oxygen (5 L), the solvent evaported and the residue distilled (Table 1). ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J_{HH} 6.7 Hz, 6H, CH_3), 1.4–2.2 (m, 7H CH_2), 2.7–2.9 (m, 4H, NCH_2), 3.5–3.8 (m, 4H, OCH_2), 3.8–4.3 (m, 4H, OCH_2CH_3), 4.7–5.0 (s, 1H, CHP). ^{13}C NMR ($CDCl_3$) δ 34.2 (d, J_{CP} 87.0 Hz, C^1), 142.8 (d, J_{CP} 9.9 Hz, C^2), 107.1 (d, J_{CP} 10.2 Hz, C^3), 24.3 (s, C^4), 20.1 (d, J_{CP} 5.3 Hz, C^5), 24.9 (d, J_{CP} 5.3 Hz, C^6), 50.1 (s, NCH_2CH_2O), 67.2 (s, NCH_2CH_2O), 62.3 (d, J_{cp} 7.0 Hz, OCH_2CH_3), 16.3 (d, J_{cp} 4.6 Hz, CH_3).

*Bis (2-morpholino-1-cyclohexenyl)chlorophosphine (**10**)*

To a solution of PCl_3 (0.04 mole) in benzene (200 mL), a mixture of enamine **1** (0.08 mole) and triethylamine (0.085 mole) was added with stirring at 10°C. Two hours later, the precipitate was filtered off. ^{31}P NMR (solution): δ 99.9 ppm. The solution obtained was used for further transformations.

*Diethylamide of the (2-morpholino-1-cyclohexenyl)(2-morpholino-2-cyclohexenyl)thiophosphinic acid (**11**)*

To a solution of the chlorophosphine **10** (0.03 mole) in benzene (120 mL), diethylamine (0.08 mole) was added at 10°C with stirring for 30 min. Two hr later the precipitated solid was filtered off. Sulfur (0.03 mole) was added to the filtrate. After 12 hr, the solution was filtered and the solvent was evaporated from the filtrate. The residue was added to petroleum ether (200 mL), heated to the boiling point and filtered. The filtrate was partially evaporated, and the precipitated solid was filtered off and dried. ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J_{HH} 7 Hz, 6H,CH_3), 1.3–2.62 (m, 17H), 2.92–3.84 (m, 18H), 4.31–4.43 (m, 1H, NC=CH). ^{13}C NMR ($CDCl_3$) δ 127.5 (d, J_{CP} 79.8 Hz, C^1), 154.4 (d, J_{CP} 3.6 Hz, C^2), 24.8 (d, J_{CP} 3.5 Hz, C^3), 22.9 (s, C^4), 25.0 (s, C^5), 27.4 (d, J_{CP} 8.1 Hz, C^6), 38.4 (d, J_{CP} 56.3 Hz, $C^{1\prime}$), 145.2 (d, J_{CP} 9.3 Hz, $C^{2\prime}$), 110.4 (d, J_{CP} 9.6 Hz, $C^{3\prime}$), 26.0 (s, $C^{4\prime}$), 19.1 (s, $C^{5\prime}$), 23.5 (d, J_{cp} 7.4 Hz, $C^{6\prime}$), 51.8, 50.8 (2s, NCH_2CH_2O), 67.3 (s, NCH_2CH_2O), 41.4 (d, J_{cp} 3.2 Hz, NCH_2CH_3), 15.8 (d, J_{cp} 3.0 Hz, CH_3).

*Ethyl ester of the (2-morpholino-1-cyclohexenyl)(2-morpholino-2-cyclohexenyl)thiophosphinic acid (**12**)* was obtained in the same way as the compound **11**. It was crystallized from isopropyl alcohol (Table 1). ^{1}H NMR ($CDCl_3$) δ 1.2–1.4 (m, 3H, CH_3), 2.0–3.4 (m, 21H), 3.5–4.2 (m, 12H), 5.11 (m, 1H, CHP). ^{13}C NMR ($CDCl_3$) δ 130.8 (d, J_{cp} 100.3 Hz, C^1), 154.6 (d, J_{cp} 5.7 Hz, C^2), 24.2 (d, J_{cp} 3.0 Hz, C^3), 23.0 (s, C^4), 22.8 (d, J_{cp} 11.8 Hz, C^5), 25.8 (d, J_{cp} 5.5 Hz, C^6), 41.6 (d, J_{cp} 64.3 Hz, $C^{1\prime}$), 146.0 (d, J_{cp} 10.1 Hz, $C^{2\prime}$), 110.9 (d, J_{cp} 9.3 Hz, $C^{3\prime}$), 25.0 (s, $C^{4\prime}$), 19.4 (d, J_{cp} 2.6 Hz, $C^{5\prime}$), 22.3 (d, J_{cp} 7.0 Hz, $C^{6\prime}$), 51.0, 50.6 (2s, NCH_2CH_2O), 67.3, 67.1 (2s, NCH_2CH_2O), 60.1 (d, J_{cp} 7.3 Hz, OCH_2CH_3), 16.4 (d, J_{cp} 7.4 Hz, CH_3).

*The reaction between phosphorus tribromide and phosphonate **9b***

To a solution of phosphorus tribromide (0.04 mole) in benzene (100 mL), a mixture of phosphonate **9b** (0.04 mole) and triethylamine (0.05 mole) in benzene (70 mL) was added with stirring. The ^{31}P NMR spectrum of the (3-diethoxythiophosphoryl-2-morpholino-1-cyclohexenyl)dibromophosphine **(13)**: δ 159.7, 96.7.

*Diethyl ester of the (3-diethoxythiophosphoryl-2-morpholino-1-cyclohexenyl)thiophosphonic acid (**14**)*

To a suspension of dibromophosphine **13** (0.04 mole) in benzene (150 mL), a mixture of ethyl alcohol (0.08 mole) and triethylamine (0.09 mole) was added with stirring. An hour later, the precipitated triethylammonium bromide was filtered off. To the filtrate, sulfur (0.04 mole) was added. After one hour, the mixture was filtered and the filtrate evaporated. The compound **14** was purified by freezing from heptane (Table 1). ^{1}H NMR ($CDCl_3$) δ 1.25–1.45 (m, 12H, CH_3), 1.5–3.8 (m, 15H), 3.9–4.3 (m, 8H, OCH_2). ^{13}C NMR ($CDCl_3$) δ 125.7 (dd, J_{cp} 147.2, 11.2 Hz, C^1), 154.5 (dd, J_{cp} 5.3, 5.3 Hz, C^2), 42.7 (dd, J_{cp} 104.1, 13.4 Hz, C^3), 18.9 (dd, J_{cp} 10.8, 3.6 Hz, C^4), 25.5 (s, C^5), 26.6 (dd, J_{cp} 8.9, 3.2 Hz, C^6), 50.7 (s, NCH_2CH_2O), 67.0 (s, NCH_2CH_2O), 64.4, 64.3, 63.5, 63.3, 62.4, 62.3, 62.2, 62.1, 62.05 (OCH_2CH_3), 16.5, 16.4, 16.3, 16.25, 16.2, 16.0, 15.9 (CH_3).

*(3-Diethoxythiophosphoryl-2-morpholino-1-cyclohexenyl)phosphonic acid tetraethyldiamide (**15**)*

To a suspension of dibromophosphine **13** (0.05 mole) in benzene (150 mL), diethylamine (0.25 mole) was added with stirring. An hour later, the precipitated solid was filtered off. A solution of hexachloroethane (0.05 mole) in petroleum ether (60 mL) was added to the filtrate. An oily precipitate was decanted and dissolved in chloroform (150 mL). Then it was treated with a 10% solution of Na_2CO_3 (two time by 100 mL). The organic layer was separated and dried over Na_2SO_4. The solvents were evaporated. The oil was purified by freezing from heptane (Table 1). ^{1}H NMR ($CDCl_3$) δ 1.04–1.19 (m, 12H, NCH_2CH_3), 1.27–1.42 (m, 6H, OCH_2CH_3), 1.56–2.56 (m, 7H), 2.88–3.47 (m, 12H, NCH_2), 3.62–4.28 (m, 8H, OCH_2). ^{13}C NMR ($CDCl_3$) δ 119.2 (dd, J_{cp} 149.3, 11.0 Hz, C^1), 155.1 (dd, J_{cp} 8.9, 4.5 Hz, C^2), 44.4 (dd, J_{cp} 104.1, 11.9 Hz, C^3), 19.1 (dd, J_{cp} 9.4, 3.8 Hz, C^4), 25.2 (s, C^5), 26.8 (dd, J_{cp} 8.8, 3.4 Hz, C^6), 50.8 (s, NCH_2CH_2O), 67.5 (s, NCH_2CH_2O), 63.3 (d, J_{cp} 7.7 Hz, OCH_2CH_3), 62.1 (d,

J_{cp} 8.3 Hz, OCH_2CH_3), 39.6 (d, J_{cp} 4.8 Hz, NCH_2CH_3), 38.7 (d, J_{cp} 5.5 Hz, NCH_2CH_3),16.4 (d, J_{cp} 4.4 Hz, CH_3), 16.3 (d, J_{cp} 4.7 Hz, CH_3), 14.4 (d, J_{cp} 2.4 Hz, CH_3), 13.7 (d, J_{cp} 2.5 Hz, CH_3).

General method of the hydrolysis of the compounds **6, 7, 9, 12, 14, 15**

To a solution of the corresponding enamine (0.05 mole) in glacial acetic acid (50 mL), water (0.06 mole) was added. After 12 hr the acetic acid was evaporated. Chloroform (50 mL) was added to the solution and then washed with three portions of water (30 mL each). The organic layer was separated, and dried over Na_2SO_4 and the cloroform evaporated.

*(2-Hydroxy-1-cyclohexenyl)(phenylimino)phosphonic acid tetratethyldiamide (***16***).*

The compound was purified by reprecipitation with petroleum ether from benzene (Table 1). ^1H NMR ($CDCl_3$) δ 1.08 (t, J_{HH} 7 Hz, 12H, CH_2CH_3), 1.5–1.8 (m, 4H, CH_2), 2.01 (dt, J_{HH} 6.2, J_{PH} 6 Hz, 2H, $CH_2C(P)$), 2.25 (t, J_{HH} 6.2 Hz, 2H, $CH_2C(OH)$), 3.11–3.23 (m, 8H, CH_2N), 3.62–3.70 (m, 1H, OH), 6.9–8.3 (m, 5H, H-Ph). ^{13}C NMR ($CDCl_3$) δ 70.8 (d, J_{cp} 284.0 Hz, C^1), 180.1 (d, J_{cp} 7.3 Hz, C^2), 34.9 (d, J_{cp} 17.0 Hz, C^6), 38.8 (d, J_{cp} 9.5 Hz, NCH_2), 12.8 (d, J_{cp} 3.4 Hz, CH_3), 143.5 (d, J_{cp} 6.6 Hz, i-Ph), 120.5, 120.2, 120.0 (s, Ph), 24.4, 24.3, 24.2, 24.1, 23.7 (s, C^3,C^4,C^5).

*2-Oxocyclohexylphosphonic acid diethyl ester (***17***)*

The yield: 64% [12].

*2-Oxocyclohexylthiophosphonic acid diethyl ester (***18***)*

^1H NMR ($CDCl_3$) δ 1.31 (t, J_{HH} 6.8 Hz, 6H, CH_3), 1.5–3.4 (m, 9H), 4.5–4.8 (m, 4H, OCH_2). ^{13}C NMR ($CDCl_3$) δ 56.5 (d, J_{cp} 101.8 Hz, C^1), 206.4 (d, J_{cp} 4.4 Hz, C^2), 42.0 (d, J_{cp} 1.8 Hz, C^3), 26.5 (s, C^4), 22.3 (d, J_{cp} 5.8 Hz, C^5), 28.3 (d, J_{cp} 3.3 Hz, C^6), 63.3 (d, J_{cp} 7.3 Hz, OCH_2CH_3), 63.0 (d, J_{cp} 6.7 Hz, OCH_2CH_3), 16.3 (d, J_{cp} 3.7 Hz, CH_3), 16.1 (d, J_{cp} 3.7 Hz, CH_3).

*2-Oxocyclohexylphosphonic acid tetraethyldiamide (***19***)*

^1H NMR ($CDCl_3$) δ 1.05 (t, 12H, CH_3), 1.4–2.2 (m, 9H), 2.9–3.1 (m, 8H, NCH_2). ^{13}C NMR ($CDCl_3$) δ 50.1 (d, J_{cp} 100.9 Hz, C^1), 209.0 (d, J_{cp} 2.1 Hz, C^2), 42.2 (s, C^3), 27.7 (s, C^4), 29.1 (d, J_{cp} 4.2 Hz, C^5), 23.0 (d, J_{cp} 8.8 Hz, C^6), 39.0, 38.9, 38.87, 38.8, 38.2, 38.1 (NCH_2), 14.31, 14.26, 14.06, 14.0, 13.72, 13.66 (CH_3). The signals for the enol form 92.6 (d, J_{cp} 147.9 Hz, C^1), 167.6 (d, J_{cp} 4.0 Hz, C^2), 22.1 (d, J_{cp} 2.4 Hz, C^3) 22.5 (d, J_{cp} 1.0 Hz, C^4), 24.3 (d, J_{cp} 1.0 Hz, C^5), 29.4 (d, J_{cp} 8.8 Hz, C^6).

*Bis(2-oxocyclohexyl)thiophosphinic acid ethyl ester (***20***)* was purified by reprecipitation from benzene with petroleum ether. ^1H NMR ($CDCl_3$) δ 1.29 (t, J_{HH} 7 Hz, 3H, CH_3), 1.42–2.7 (m, 16H), 2.96–3.14 (m, 2H, CHP), 3.91–4.26 (m, 2H,OCH_2). ^{13}C NMR ($CDCl_3$) δ 57.6 (d, J_{cp} 44.9 Hz, C^1), 50.6 (d, J_{cp} 65.6 Hz, C^1, 209.36, 209.33, 209.30 (s, C^2), 36.6 (d, J_{cp} 13.0 Hz, C^3), 28.7 (s, C^4), 30.3 (s, C^4) , 26.2 (s, C^5), 26.0 (s, C^5), 19.6 (d, J_{cp} 4.3 Hz, C^6), 21.2 (d, J_{cp} 1.5 Hz, C^6), 62.2 (d, J_{cp} 7.0 Hz, OCH_2), 61.0 (s, OCH_2), 16.3 (d, J_{cp} 5.9 Hz, CH_3), 18.9 (d, J_{cp} 1.3 Hz, CH_3).

On hydrolysis of the compound **14**, the monophosphorylated ketone **18** was obtained in 15% yield.

The products of the hydrolysis of the diphosphorylated enamine **15** were identified by ^{31}P NMR spectroscopy. Two monophosphorylated ketones **18, 19** were revealed in the reaction mixture.

*(2-Hydroxy-1-cyclohexenyl)iminophosphonic acid tetraethyldiamide (***21***).*

To a solution of phosphonite **3** (0.83 mole) in petroleum ether (700 mL), a solution of hexachloroethane in heptane (1 L) was added. After 12 hr the solvent was removed from the oily salt. The latter was dissolved in dichloromethane (1.5 L), and the solution was purged with ammonia until the end of the absorption. The precipitate was separated by filtration. The mother solution was evaporated. The residue was dissolved in dichloromethane (1 L), and the solution was shaken three times with portions of 50% aqueous potassium hydroxide (500 mL each). The alkaline solution was washed with two portions of methylene chloride (200 mL each). The combined portions of dichloromethane were dried over Na_2SO_4 and evaporated. The residue was recrystallized twice from heptane. ^1H NMR ($CDCl_3$) δ 1.12 (t, J_{HH} 7 Hz, 12H, CH_3), 1.4–2.4 (m, 8H), 2.8–3.4 (m, 8H CH_2), 5.0–5.3 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) δ 69.6 (d, J_{cp} 147.0 Hz, C^1), 184.4 (d, J_{cp} 8.5 Hz, C^2), 24.4 (d, J_{cp} 10.8 Hz, C^3), 24.2 (s, C^4), 24.9 (d, J_{cp} 10.6 Hz, C^5), 36.5 (d, J_{cp} 15.1 Hz, C^6), 39.5 (d, J_{cp} 5.1 Hz, NCH_2), 14.1 (d, J_{cp} 3.1 Hz, CH_3).

*Bis(diethylamino)amino(2-methoxy-1-cyclohexenyl)phosphonium tosylate (***22***)*

To a solution of the compound **21** (3 mmole) in acetonitrile (20 mL), a solution of methyl tosylate (3 mmole) in acetonitrile (10 mL) was added. The mixture was kept for 24 hr. at 20°C. The mixture was filtered. Acetonitrile was evaporated from the filtrate, and the residue was kept in a vacuum (0.03 mm.m.c.) at 60°C for 2 hr. ^1H NMR ($CDCl_3$) δ 1.12 (t, J_{HH} 7 Hz, 12H, CH_2CH_3), 1.5–2.5 (m, 8H, CH_2), 2.33 (s, 3H, CH_3-Ar), 2.9–3.4 (m, 8H, CH_2N), 3.73 (s, 3H, OCH_3), 4.77 (d, J_{PH} 4.4 Hz, 2H, NH_2), 7.2–7.8 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ 142.9 (d, J_{cp} 107.5 Hz, C^1), 170.6 (s,

C^2), 26.2 (s, C^3), 23.0 (s, C^4), 23.1 (d, J_{cp} 11.3 Hz, C^5), 26.0 (d, J_{cp} 4.5 Hz, C^6), 41.1 (d, J_{cp} 5.8 Hz, NCH_2), 14.3 (d, J_{cp} 2.1 Hz, NCH_2CH_3), 21.3 (s, CH_3-Ar), 131.2 130.0, 127.2, 129.3 (Ar).

General method of synthesizing the compounds **24, 27, 29, 31**

To a solution of the corresponding dichloride **23, 25, 28, 30** (7 mmole) in benzene (50 mL) a mixture of the compound **21** (7 mmole) and triethylamine (16 mmole) was added. Two hr. later the precipitated solid was filtered off, the filtrate evaporated, and the residue purified either by freezing or by the reprecipitation.

4-Methyl-4-oxo-2,2-bis(diethylamino)-5-oxa-3-aza-2,4-diphosphabicyclo[4.4.0] deca-1(6), 2-diene (**24**) was purified by freezing from heptane and dried *in vacuo* (0.03 mm.m.c.) at 60°C for 2 hr. ^{1}H NMR ($CDCl_3$) δ 1.13 (dt, J_{HH} 7 Hz, J_{ph} 2.8 Hz, 12H, CH_2CH_3), 1.52 (dd, J_{ph} 16.8, 1.2 Hz, 3H, PCH_3), 1.56–2.35 (m, 8H, CH_2), 2.9–3.3 (m, 8H CH_2N). ^{13}C NMR ($CDCl_3$) δ 100.1 (dd, J_{cp} 130.0, 10.1 Hz, C^1), 163.2 (dd, J_{cp} 8.3, 3.8 Hz, C^2), 30.2 (dd, J_{cp} 9.2, 5.1 Hz, C^3), 22.5 (s, C^4), 22.3 (d, J_{cp} 3.0 Hz, C^5), 24.0 (d, J_{cp} 4.1 Hz, C^6), 38.1 (dd, J_{cp} 7.4, 5.1 Hz, NCH_2), 13.3 (dd, J_{cp} 3.6, 6.0 Hz,NCH_2CH_3), 16.8 (dd, J_{cp} 139.0, 6.0 Hz, CH_3P).

4-(p-Dimethylaminophenyl)-2,2-bis(diethylamino)-5-oxa-3-aza-2, 4-diphosphabicyclo[4.4.0]deca-1(6), 2-diene (**26**) was not separated, but instead it was oxidized with oxygen of the air to the compound **27**.

4-(p-Dimethylaminophenyl)-4-oxo-2,2-bis(diethylamino)-5-oxa-3-aza-2, 4-diphosphabicyclo[4.4.0]deca-1(6), 2-diene (**27**)

The compound **(27)** was purified by reprecipitation with petroleum ether from a benzene solution. ^{1}H NMR ($CDCl_3$) δ 1.16 (dt, J_{HH} 7 Hz, J_{pH} 6.8 Hz, 12H, CH_2CH_3), 1.60–2.41 (m, 8H, CH_2), 2.8–3.4 (m, 8H, CH_2N), 2.96 (s, 6H, NCH_3), 6.6–8.0 (m, 4H, H-Ar), ^{13}C NMR ($CDCl_3$) δ 99.7 (dd, J_{cp} 131.8, 8.8 Hz, C^1), 163.9 (dd, J_{cp} 8.3, 3.8 Hz, C^2), 30.3 (dd, J_{cp} 9.4, 6.2 Hz, C^3), 22.6 (s, C^4), 22.4 (d, J_{cp} 1.8 Hz, C^5), 24.1 (d, J_{cp} 3.9 Hz, C^6), 38.2 (d, J_{cp} 4.3 Hz, NCH_2), 13.6 (d, J_{cp} 2.4 Hz, NCH_2CH_3), 40.3 (s, NCH_3), 121.2 (dd, J_{cp} 198.3, 7.4 Hz, $C^{1'}$), 133.1 (d, J_{cp} 11.6 Hz, $C^{2'}$), 111.3 (d, J_{cp} 15.9 Hz, $C^{3'}$), 152.5 (d, J_{cp} 2.8 Hz, $C^{4'}$).

4,4-dimethyl-2,2-bis(diethylamino)-5-oxa-3-aza- 2-phospha-4-silabicyclo[4.4.0]deca-1(6),2-diene (**29**) was purified by freezing from heptane. ^{1}H NMR ($CDCl_3$) δ 0.5 (d, J_{pH} 1.0 Hz, 6H, $SiCH_3$), 1.09 (dt, J_{pH} 1.4, J_{HH} 7 Hz, 12H, CH_2CH_3), 1.5–2.2 (m, 8H, CH_2), 2.8–3.3 (m, 8H, CH_2N). ^{13}C NMR ($CDCl_3$) δ 100.8 (d, J_{cp} 127.5 Hz, C^1), 164.1 (d, J_{cp} 4.3 Hz, C^2), 25.0 (d, J_{cp} 3.8 Hz, C^3), 23.0 (s, C^4), 23.1 (s, C^5), 31.7 (d, J_{cp} 9.3 Hz, C^6), 37.7 (d, J_{cp} 4.5 Hz, NCH_2), 13.3 (d, J_{cp} 3.6 Hz, NCH_2CH_3), 2.4 (s, $SiCH_3$).

4,4-Dimethyl-2, 2-bis(diethylamino)-5-oxa-3-aza- 2-phosphoniabicyclo[4.4.0]deca-1(6),3-diene chloride (**31**) was purified by reprecipitation with petroleum ether from a dichloromethane solution. ^{1}H NMR ($CDCl_3$) δ 1.19 (t, J_{pH} 7 Hz, 12H, CH_2CH_3), 1.4–2.6 (m, 8H, CH_2), 2.94–3.3 (m, 8H, CH_2N), 3.15 (s, 3H, NCH_3), 3.21 (s, 3H, NCH_3). ^{13}C NMR ($CDCl_3$) δ 98.3 (d, J_{cp} 126.0 Hz, C^1), 163.9 (s, C^2), 20.7 (d, J_{cp} 7.6 Hz, C^3), 20.5 (s, C^4), 21.6 (s, C^5), 27.1 (d, J_{cp} 7.2 Hz, C^6), 37.9 (d, J_{cp} 4.6 Hz, NCH_2), 12.8 (d, J_{cp} 2.9 Hz, NCH_2CH_3), 37.0 (s, C = N), 36.2 (s, NCH_3).

2-(3-Phenyl-2-triazeno)-1-cyclohexenylphosphonic acid tetraethyldiamide (**33a**)

The compound **5a** (2 mmole) was dissolved in a 1:1 mixture (50 mL) of acetonitrile and water. After four weeks the solution was evaporated at 20°C. Petroleum ether (50 mL) was added to the residue. The mixture was filtered and the solvent was evaporated from the filtrate at 20°C. The residue was kept *in vacuo* (0.03 mm.m.c.) at 60°C for 2 hr. ^{1}H NMR ($CDCl_3$) δ 1.11 (t, J_{HH} 7 Hz, 12H, CH_2CH_3), 1.5–2.9 (m, 8H, CH_2), 3.0–3.3 (m, 8H, NCH_2), 3.6 (s, 0.7H, OH), 7.1–7.6 (m, 5H, Ar-H), ^{13}C NMR ($CDCl_3$) δ 99.7 (d, J_{cp} 145.9 Hz, C^1), 149.7 (d, J_{cp} 4.1 Hz, C^2), 25.7 (s, C^3), 22.0 (s, C^4), 22.7 (d, J_{cp} 8.5 Hz, C^5), 26.0 (d, J_{cp} 12.1 Hz, C^6), 38.3 (d, J_{cp} 4.3 Hz, NCH_2), 13.7 (d, J_{cp} 3.0 Hz, CH_3), 150.4 (s, i-Ph), 121.8 (s, o-Ph), 128.7 (s, m-Ph), 126.6 (s, p-Ph).

2-(3-(4-Nitrophenyl)-2-triazeno)-1-cyclohexenylphosphonic acid tetraethyldiamide (**33b**)

The compound **5b** (2 mmole) was dissolved in a 1:1 mixture (50 mL) of acetonitrile and water. In a month the precipitated crystals of the compound **(33b)** were filtered off and dried. ^{1}H NMR ($CDCl_3$) δ 1.31 (t, J_{HH} 11 Hz, 12H, CH_2CH_3), 1.6–2.8 (m, 8H, CH_2), 2.9–3.3 (m, 8H, NCH_2), 7.5–8.3 (m, 4H, Ar-H), 14.3 (s, 0.6H, OH). ^{13}C NMR ($CDCl_3$) δ 104.4 (d, J_{cp} 170.9 Hz, C^1), 149.5 (d, J_{cp} 4.8 Hz, C^2), 26.0 (s, C^3), 22.0 (s, C^4), 22.7 (d, J_{cp} 8.3 Hz, C^5), 25.8 (d, J_{cp} 4.0 Hz, C^6) 38.5 (d, J_{cp} 4.1 Hz, NCH_2), 13.9 (d, J_{cp} 2.8 Hz, CH_3), 155.1 (s, $C^{1'}$, Ph), 121.8 (s, $C^{2'}$, Ph), 125.2 (s, $C^{3'}$, Ph), 146.0 (s, $C^{4'}$, Ph).

REFERENCES

[1.] L. A. Lazukina, V. P. Kukhar, V. G. Pesotskaya, *Zh. Obshch. Khim., 44,* 1974, 2355. H. Weingarten, J. S. Wager, Synth. *Inorg. and Metal-org. Chem, 1,* 1972, 7.

[2.] N. Gamon, C. Reichardt, *Liebigs Ann. Chem, 12,* 1980, 2072. I. I. Krasavtsev, E. D. Basalkevich, M. O.

Lozinskii, *Zh. Org. Khim, 20,* 1984, 1167. V. N. Zemlianoy, O. J. Kolodiazhnyi, *Zh. Obshch. Khim., 59,* 1989, 467. A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, *Zh. Obshch. Khim, 59,* 1989, 719. A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, A. M. Pinchuk, *Zh. Obshch. Khim, 60,* 1990, 1752.

[3.] A. A. Tolmachev, L. N. Morozova, A. N. Kostyuk, R. D. Lampeka, E. S. Kozlov, A. M. Pinchuk, *Zh. Obshch. Khim, 59,* 1989, 2388.

[4.] A. G. Cook: *Enamines: Synthesis, Structure and Reactions,* Marcel Dekker. New York. 1969.

[5.] B. A. Arbuzov, V. S. Vinogradova, N. A. Polezhaeva, *DAN SSSR, 137,* 1961, 855.

[6.] I. S. Zaltsman, G. N. Koidan, A. P. Marchenko, A. M. Pinchuk, *Zh. Obshch. Khim, 54,* 1984, 2788.

[7.] V. Ya. Pochinok: *Triazeny,* Kiev, KGU, 1968.

[8.] M. Burke-Laing, M. Laing, *Acta Cryst., 12,* 1976. 3216.

[9.] A. N. Vereshchagin, *Usp. Khim., 52,* 1983, 1879.

[10.] B. A. Frenz; in H. Schenk, R. Olthof-Hazelkamp, H. van Konigsfeld, G. C. Bassi (eds). *Computing in Crystallography,* Delft Univ. Press, Delft, Holland, pp. 64–75 (1976).

[11.] CCDC, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

[12.] C. Herzig, J. Gasteiger, *Chem. Ber., 115,* 1982, 601.