Synthesis and properties of functional derivatives of *N'*-phosphoryl- and *N'*-phosphonoyldiazene *N*-oxides; molecular structure of *N*-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)-*N'*-[methoxy(phenyl)phosphoryl]diazene *N*-oxide

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Methods for the synthesis of polyfunctional *N'*-phosphoryl- and *N'*-phosphonoyldiazene *N*-oxides containing hydroxyl, acetoxyl, and nitrate groups, and dibromoallyl and dibromopropyl fragments have been developed. The molecular structure of *N*-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)-*N'*-[methoxy(phenyl)phosphoryl]diazene *N*-oxide was established by X-ray structural analysis.

Key words: *N'*-phosphoryl- and *N'*-phosphonoyldiazene *N*-oxides; *N*-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)-*N'*-[methoxy(phenyl)phosphoryl]diazene *N*-oxide.

Previously[1—4] we reported the preparation of *N'*-phosphoryl- and *N'*-phosphonoyldiazene *N*-oxides, new classes of phosphorus—nitrogen—oxygen systems exhibiting insectoacaricide properties. In our opinion, the range of biological activity of compounds of this kind may be substantially extended when other heteroatoms and functional substituents are present in molecules.

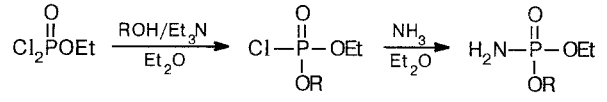
In the present work we studied the possibility of preparing substances of this type by the reaction of nitroso compounds with unsaturated amidophosphates and by oxidative condensation of amidophosphates with nitroso derivatives of acetals.

Unsaturated amidophosphates **3** and **4**, which have not been reported previously, were prepared by the reaction of dichloroethyl phosphate with 1 equiv. of allyl and propargyl alcohols, respectively, in the presence of triethylamine, and by the reaction of mixed chlorophosphates (**1** and **2**) with ammonia in an inert organic solvent (Scheme 1).

Amidophosphates **3** and **4** are viscous nondistillable liquids. The structures of these compounds were established by IR and ^{1}H NMR spectroscopy (see Experimental).

Compounds **3** and **4** react readily with nitroso compounds in the presence of dibromoisocyanurate (DBI) at room temperature; during the reaction, the formation of the diazene oxide group is accompanied by bromination of the multiple carbon—carbon bonds. As a result, halogen derivatives of *N'*-phosphoryldiazene

Scheme 1

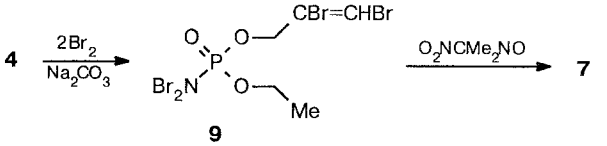


1, **3**: R = $CH_2CH{=}CH_2$ **1**, **2** **3**, **4**
2, **4**: R = $CH_2C{\equiv}CH$

N-oxides (**5**—**8**) were isolated in yields of 23—56 % (Scheme 2).

Apparently, the function of DBI is to brominate amides **3** and **4** to the corresponding *N,N*-dibromoamides,[5] which further react with nitroso compounds according to the scheme of the Kovacic reaction.[6]

Bromination of the C≡C bond during the reaction can occur through the action of the molecular bromine that is eliminated in the formation of the diazene oxide group. This suggestion is confirmed by the formation of (2,3-dibromo-2-propenyl) ethyl *N,N*-dibromoamidophosphate (**9**) in the reaction of **4** with bromine in the presence of Na_2CO_3, and by the synthesis of azoxy compound **7** from **9** and 2-nitro-2-nitrosopropane.



9

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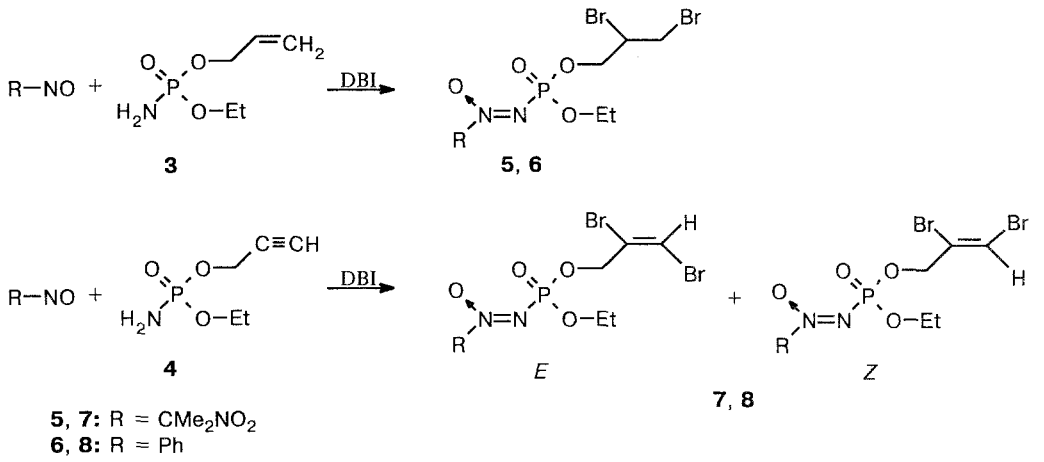
Scheme 2



Diazene oxides **7** and **8** are the first representatives of phosphorus-containing azoxy compounds that contain olefin fragments. According to ^1H and ^{13}C NMR spectroscopy data, they exist as a mixture of *E*- and *Z*-isomers in the ratio of 4 : 1 and 11 : 8 for **7** and **8**, respectively. It is of interest that the *E* to *Z* ratio remains the same when **7** is prepared from either amidophosphate **4** or *N*,*N*-dibromoamidophosphate **9**.

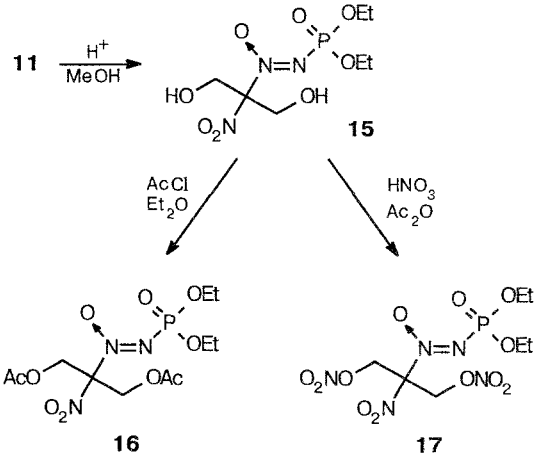
Synthesis of *N'*-phosphoryl- and *N'*-phosphonoyldiazene *N*-oxides with functional groups in the α and β positions with respect to the oxidized N atom of the diazene oxide group is performed using the oxidative condensation of amidophosphates and amidophosphonates with 2,2-dimethyl-5-nitro-5-nitroso-1,3-dioxane (**10**) in the presence of DBI. The choice of nitroso compound **10** is determined by the fact that the presence of the acetal protection conserves hydroxyl groups under the conditions of oxidative condensation; these groups can be subsequently released.[7]

In this way phosphoryl- and phosphonoyldiazene oxides (**11—14**) were obtained in yields of 46—63 % (Scheme 3).

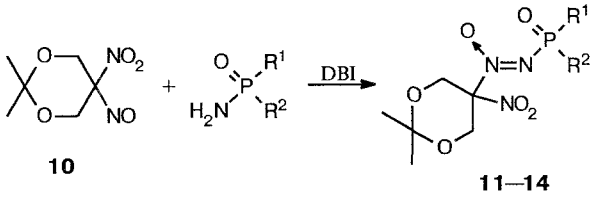
The protective group in **11** is readily removed when a catalytic amount of acetyl chloride is added to a methanolic solution of **11** to give *N*-(2-hydroxy-1-hydroxymethyl-1-nitroethyl)-*N'*-(diethoxyphosphoryl)diazene *N*-oxide (**15**) in a yield of 77 %; **15** is the first hydroxyl-containing compound in the series of phosphoryldiazene oxides.

Diol **15** undergoes acylation and nitration, which proceed under mild conditions with the retention of the diazene oxide function. Thus, the reaction of acetyl chloride and **15** affords diacetate (**16**) in a 65 % yield; nitration with an HNO_3—Ac_2O mixture yields bisnitrate (**17**) (Scheme 4).

Scheme 4



Scheme 3



11: $R^1 = R^2$ = OEt
12: R^1 = Me, R^2 = OPh
13: R^1 = OEt, R^2 = OPh
14: R^1 = OMe, R^2 = Ph

Thus, for the first time, a method has been developed for the synthesis of polyfunctional phosphoryldiazene oxides containing hydroxyl, acetoxyl, and nitrate groups, dibromoallyl and dibromopropyl fragments.

Functionalized diazene *N*-oxides **5—8** and **11—17** are crystalline or oily substances that are stable when stored for long periods at room temperature, but they decompose when heated to 80—100 °C. Their structures were established by IR spectral data and ^1H, ^{13}C, ^{14}N, and ^{31}P NMR spectroscopy (Tables 1—3).

Table 1. Yields and spectral characteristics of functional derivatives of *N'*-phosphoryl(phosphonoyl)diazene *N*-oxides

Compound	Yield (%)	IR, ν/cm^{-1}				^{1}H NMR* (δ, *J*/Hz)
		N=N→O	P=O	P—O—C	NO_2	
5	30	1510	1280	1030	1580	1.35 (t, 3 H, Me, *J* = 7.0); 2.24 (s, 6 H, Me_2C); 3.94 (m, 2 H, CH_2); 4.32 (m, 2 H, $\underline{CH_2}Me$); 4.58 (m, 3 H, CHBr—CH_2Br)
6	37	1490	1270	1030	—	1.39 (t, 3 H, Me); 3.97 (m, 2 H, CH_2); 4.38 (m, 2 H, $\underline{CH_2}Me$); 4.63 (m, 3 H, CHBr—CH_2Br); 7.65 (m, 2 H, *m*-H, Ph); 7.78 (t, 1 H, *p*-H, Ph, *J* = 7.5); 8.29 (d, 2 H, *o*-H, Ph, *J* = 7.5)
7 (*E,Z*)	23	1520	1280	1030	1580	1.34 (t, 3 H, Me, *J* = 7.0); 2.23 (s, 6 H, Me_2C); 4.31 (m, 2 H, $\underline{CH_2}Me$); 5.08 (m, 2 H, CH_2); 7.09 (s, 1 H, CH, *E*-isomer); 7.50 (t, 1 H, CH, *Z*-isomer, *J* = 1.1)
8 (*E,Z*)	56	1490	1270	1030	—	1.43 (t, 3 H, Me, *J* = 7.0); 4.42 (m, 2 H, $\underline{CH_2}Me$); 5.20 (m, 2 H, CH_2); 7.11 (s, 1 H, CH, *E*-isomer); 7.58 (t, 1 H, CH, *Z*-isomer, *J* = 1.1); 7.69 (m, 2 H, *m*-H, Ph); 7.82 (t, 1 H, *p*-H, Ph, *J* = 7.5); 8.33 (d, 2 H, *o*-H, Ph, *J* = 7.5)
11	46	1520	1280	1020	1580	1.32 (t, 6 H, Me, *J* = 7.0); 1.42 (s, 6 H, Me_2C); 4.27 (m, 4 H, $\underline{CH_2}Me$); 4.65 (s, 4 H, OCH_2, cycle)
12	62	1495	1240	1050	1580	1.32 (s, 6 H, Me_2C); 1.83 (d, 3 H, Me, *J* = 17.0); 4.57 (s, 4 H, OCH_2, cycle); 7.18 (s, 5 H, Ph)
13	63	1510	1295	1030	1580	1.34 (t, 3 H, Me); 1.42 (s, 6 H, Me_2C); 4.42 (m, 2 H, $\underline{CH_2}Me$); 4.62 (m, 4 H, OCH_2, cycle); 7.27 (m, 5 H, Ph)
14**	51	1510	1250	1020	1570	1.42, 1.46 (both s, 6 H, Me_2C); 3.93 (d, 3 H, OMe, $^3J_{H,P}$ = 11.0); 4.75 (m, 4 H, OCH_2, cycle); 7.57 (m, 2 H, *m*-H, Ph); 7.70 (t, 1 H, *p*-H, Ph, *J* = 8.0); 7.85 (dd, 2H, *o*-H, Ph, $^3J_{H,P}$ = 12.0, $^3J_{H,H}$ = 8.0)
15	77	1515	1250	1040	1580	1.32 (t, 6 H, Me); 4.28 (m, 4 H, $\underline{CH_2}Me$); 4.45 (s, 4 H, OCH_2)
16	65	1530	1220	1040	1580	1.32 (t, 6 H, Me); 2.05 (s, 6 H, Ac); 4.26 (m, 4 H, $\underline{CH_2}Me$); 4.93 (s, 4 H, OCH_2)
17***	30	1530	1280	1030	1590; 1680 (NO_3)	1.28 (t, 6 H, Me); 4.25 (m, 4 H, $\underline{CH_2}Me$); 5.43 (s, 4 H, OCH_2)

Note. For compounds **5, 8, 13,** and **14**, satisfactory elemental analysis data were obtained; products **5—8, 11—13,** and **15—16** were isolated as oil. * Relative to HMDS. ** M.p. 115—117 °C (4 : 1 hexane—chloroform). *** M.p. 39—40 °C (hexane).

Table 2. ^{13}C NMR spectra of functional derivatives of *N'*-phosphoryl(phosphonoyl)diazene *N*-oxides

Compound	δ, J_{C-P}/Hz					
	$O\underline{C}H_2Me$	$OCH_2\underline{Me}$	$O\underline{C}H_2CBr$	$OCH_2\underline{C}Br$	C—N(O)	Other signals
5	66.2 (*J* = 6)	16.6 (*J* = 6)	69.9*(*J* = 5); 70.0*(*J* = 5)	49.6 (*J* = 8)	116.1 (*J* = 15)	25.1 ($\underline{Me}$CN); 33.5 (*J* = 4, CH_2Br)
6	65.6 (*J* = 6)	16.8 (*J* = 6)	69.6*(*J* = 5); 69.7*(*J* = 5)	50.0 (*J* = 8)	148.6 (*J* = 15)	33.9 (*J* = 3, CH_2Br); 123.8 (*o*-C, Ph); 130.5 (*m*-C, Ph); 135.2 (*p*-C, Ph)
7 (*E,Z*)	66.3 (*J* = 6)	16.6 (*J* = 6)	69.0 (*J* = 5, *E*); 71.5 (*J* = 5, *Z*)	120.5 (*J* = 8)	116.2 (*J* = 15)	25.1 ($\underline{Me}$CN); 109.4 (CHBr, *E*); 114.5 (CHBr, *Z*)
8 (*E,Z*)	65.7 (*J* = 6)	16.7 (*J* = 6)	68.7 (*J* = 5, *E*); 71.7 (*J* = 5, *Z*)	121.5 (*J* = 8)	148.6 (*J* = 15)	109.0 (CHBr, *E*); 114.1 (CHBr, *Z*); 123.8 (*o*-C, Ph); 130.4 (*m*-C, Ph); 135.2 (*p*-C, Ph)
13	66.6 (*J* = 7)	16.1 (*J* = 6)	—	—	108.4 (*J* = 13)	21.6, 24.1 ($\underline{Me}_2C$); 62.3 (*J* = 6, $\underline{CH_2}CN$); 100.7 ($Me_2\underline{C}$); 120.3 (*J* = 5, *o*-C, Ph); 125.7 (*p*-C, Ph); 129.7 (*m*-C, Ph); 149.8 (*J* = 8, *i*-C, Ph)
14	—	—	—	—	108.7 (*J* = 8)	22.3, 24.7 ($\underline{Me}_2C$); 53.5 (*J* = 6, OMe); 63.0 (*J* = 12, $\underline{CH_2}CN$); 101.2 ($Me_2\underline{C}$); 127.2 (*J* = 166, *i*-C, Ph); 129.6 (*J* = 15, *m*-C, Ph); 133.3 (*J* = 11, *o*-C, Ph); 134.7 (*p*-C, Ph)

* The signals for diastereomers.

Table 3. ^{14}N (δ, $\Delta\nu_{1/2}$/Hz) and ^{31}P (δ) NMR spectra of functional derivatives of *N'*-phosphoryl(phosphonoyl)diazene *N*-oxides

Compound	$^{14}N(O)$		$^{14}NO_2$		^{31}P
	δ	$\Delta\nu_{1/2}$	δ	$\Delta\nu_{1/2}$	δ
5	−27.6	115	−0.6	70	−1.9
6	−32.9	230	—	—	0.2
7	−27.6	95	−0.6	60	−1.5
8	−32.6	190	—	—	0.4
13	−38.9	170	−13.8	125	−10.9
14	−42.0	95	−11.6	95	19.0

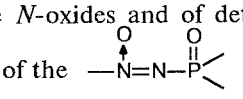
In the IR spectra of compounds **5—8** and **11—17**, intense absorption bands are observed for the diazene oxide (1490—1530 cm^{-1}), alkoxyphosphoryl (1220—1295 and 1020—1050 cm^{-1}), and other functional groups that are present in the molecules.

The structure of the *E*- and *Z*-isomers of compounds **7** and **8**, which we failed to separate into individual components by TLC, was established from the analysis of the shape of the signals of the vinylic protons in the ^1H NMR spectra. The signals at δ 7.09 (for **7**) and 7.11 (for **8**), which are characterized by high intensity and exhibit spin coupling constants ^4J with allylic protons < 0.5 Hz, are assigned, according to the literature data,[8] to the *E*-isomers; the signal at δ 7.50 (for **7**) and 7.58 (for **8**), the spin coupling constant ^4J for which is 1.1 Hz, is assigned to the *Z*-isomers. The validity of these assignments is confirmed by a comparison of the chemical shifts of the vinylic carbon atoms in the ^{13}C NMR spectra of compounds **7** and **8** (δ ~109.4 and 109.0 for predominant *E*-isomers; 114.5 and 114.1 for *Z*-isomers) (see Table 2), which correlate well with the corresponding parameters for *trans*- and *cis*-1,2-dibromoethylenes.[9]

The characteristic feature of the ^{13}C NMR spectra of compounds **5—8, 13**, and **14** is the splitting of signals for the C atoms separated from the P atom by one—four bonds into doublets owing to $^{31}P—^{13}C$ spin coupling ($J_{^{13}C,^{31}P}$ = 3 to 166 Hz).

It is noteworthy that in the ^{13}C NMR spectra the carbon atoms of the $POCH_2$ fragment in diazene oxides **5** and **6** give two signals of equal intensities, which is associated with the presence of two diastereomers.

The parameters of the ^{14}N and ^{31}P NMR spectra of compounds **5—8, 13**, and **14** (see Table 3) and of compounds prepared previously,[2—4] in which the azoxy group is linked to the P atom, are similar.

With the aim of establishing the structure of the synthesized functionalized *N'*-phosphoryl- and *N'*-phosphonoyldiazene *N*-oxides and of determining the geometric features of the  structural fragment we performed X-ray structural analysis of compound **14**. Phosphorus-containing azoxy compounds have not previosuly been studied by this method.[10]

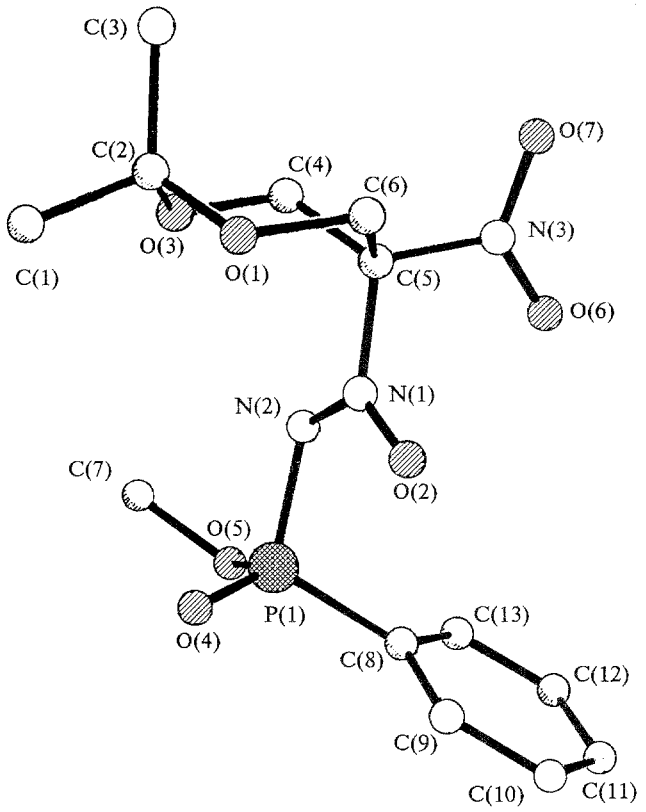


Fig. 1. Molecular structure of phosphonoyldiazene oxide **14**.

The overall view of the molecule and the atomic numbering are shown in Fig. 1. The bond lengths and bond angles are given in Tables 4 and 5. The 1,3-dioxane cycle adopts a chair conformation (the torsion angles in the cycle are from 56.9 to 67.1°). The nitro group has the equatorial orientation, and the *N'*-phosphonoyl *N*-oxide fragment is in the axial position. The C(5) atom lies within the plane of the diazene oxide group; the P(1) and O(4) atoms are displaced from this plane in the same direction by 0.198 and 1.506 Å, respectively. The N(1) atom has a planar-trigonal

Table 4. Bond lengths in molecule **14**

Bond	*d*/Å	Bond	*d*/Å
P(1)—O(4)	1.465(5)	N(1)—C(5)	1.503(6)
P(1)—O(5)	1.570(4)	N(3)—C(5)	1.515(7)
P(1)—N(2)	1.727(4)	C(1)—C(2)	1.505(9)
P(1)—C(8)	1.781(6)	C(2)—C(3)	1.524(8)
O(1)—C(2)	1.439(7)	C(4)—C(5)	1.533(8)
O(1)—C(6)	1.426(7)	C(5)—C(6)	1.520(8)
O(2)—N(1)	1.260(6)	C(8)—C(9)	1.388(8)
O(3)—C(2)	1.432(7)	C(8)—C(13)	1.405(9)
O(3)—C(4)	1.418(7)	C(9)—C(10)	1.387(9)
O(5)—C(7)	1.473(8)	C(10)—C(11)	1.40(1)
O(6)—N(3)	1.217(7)	C(11)—C(12)	1.36(1)
O(7)—N(3)	1.225(6)	C(12)—C(13)	1.398(9)
N(1)—N(2)	1.275(6)		

Table 5. Bond angles in molecule **14**

Angle	ω/deg	Angle	ω/deg
O(4)—P(1)—O(5)	117.4(2)	O(1)—C(2)—C(3)	112.4(4)
O(4)—P(1)—N(2)	110.8(2)	O(3)—C(2)—C(3)	111.5(5)
O(5)—P(1)—N(2)	98.9(2)	C(1)—C(2)—C(3)	113.2(6)
O(4)—P(1)—C(8)	116.8(3)	O(3)—C(4)—C(5)	107.4(5)
O(5)—P(1)—C(8)	102.7(2)	N(1)—C(5)—N(3)	106.1(4)
N(2)—P(1)—C(8)	108.5(2)	N(1)—C(5)—C(4)	111.7(4)
C(2)—O(1)—C(6)	114.7(5)	N(3)—C(5)—C(4)	109.9(4)
C(2)—O(3)—C(4)	115.7(4)	N(1)—C(5)—C(6)	109.8(5)
P(1)—O(5)—C(7)	119.6(4)	N(3)—C(5)—C(6)	109.4(4)
O(2)—N(1)—N(2)	127.2(4)	C(4)—C(5)—C(6)	109.8(5)
O(2)—N(1)—C(5)	116.4(4)	O(1)—C(6)—C(5)	107.9(4)
N(2)—N(1)—C(5)	116.4(4)	P(1)—C(8)—C(9)	119.4(5)
P(1)—N(2)—N(1)	116.3(4)	P(1)—C(8)—C(13)	120.7(4)
O(6)—N(3)—O(7)	124.8(5)	C(9)—C(8)—C(13)	119.9(5)
O(6)—N(3)—C(5)	119.1(4)	C(8)—C(9)—C(10)	120.6(6)
O(7)—N(3)—C(5)	116.1(5)	C(9)—C(10)—C(11)	119.1(6)
O(1)—C(2)—O(3)	108.5(5)	C(10)—C(11)—C(12)	120.5(6)
O(1)—C(2)—C(1)	105.0(5)	C(11)—C(12)—C(13)	121.0(6)
O(3)—C(2)—C(1)	105.7(4)	C(8)—C(13)—C(12)	118.8(6)

configuration (the sum of the bond angles is 360°); the N(1)—C(5) bond (1.503(6) Å) is slightly longer than the standard N_{sp^2}—C_{sp^3} bond (1.485(5) Å).[11] The P atom has a substantially distorted tetrahedral coordination (the bond angles are from 98.9(2) to 117.4(2)°); the P(1)—N(2) bond length corresponds to a single P—N bond[12] and correlates well with that found in diethyl *m*-nitrophenylazophosphonate (1.733(5) Å).[13] The N(1)—N(2) bond (1.275(6) Å) is substantially longer than the standard N=N double bond (1.240 Å),[11] which is indicative of the possibility of conjugation in the N(2)N(1)O(2) diazene oxide fragment. The N(1)—N(2) and N(1)—O(2) bond lengths (1.275(6) and 1.260(6) Å, respectively) correlate well with the corresponding distances (1.272(2) and 1.261(1) Å) in the molecule of 1-methyl-2-methoxydiazene *N*-oxide.[14]

All intermolecular contacts in the crystal of compound **14** have typical values.

Experimental

Single crystals of phosphonoyldiazene oxide 14 are triclinic, mol. weight 359.3, $C_{13}P_{18}N_3O_7P$, space group $P\bar{1}$, $Z = 2$; at −110 °C: a = 5.698(3), b = 10.048(6), c = 15.053(7) Å, α = 107.75(4), β = 92.10(4), γ = 98.21(5)°, V = 809.5(1.6) Å^3, d_{calc} = 1.474 g cm^{-3}. The unit-cell parameters and intensities for 1901 independent reflections with $I \geq 3.5\ \sigma(I)$ were measured on a Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $2\theta \leq 60°$). The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares method (for nonhydrogen atoms). All H atoms, except for the H atoms at C(1), C(10), and C(11), which were placed in the calculated positions, were located from the electron density difference synthesis. Coordinates for H atoms were refined isotropically at the final cycles. The final values of the R factors are R = 0.067, R_w = 0.074. All calculations were performed using the SHELXTL (PC Version) program. The atomic coordinates are given in Table 6.

Table 6. Atomic coordinates (×10^4; ×10^3 for H atoms) for molecule **14**

Atom	*x*	*y*	*z*
P(1)	508(3)	9719(1)	1907(1)
O(1)	2530(7)	14756(4)	2397(2)
O(2)	822(7)	12393(4)	3329(3)
O(3)	5041(7)	13321(4)	1523(2)
O(4)	−1419(8)	10171(4)	1456(3)
O(5)	1751(7)	8514(4)	1274(2)
O(6)	5615(8)	12399(4)	4268(3)
O(7)	7410(8)	14505(4)	4393(3)
N(1)	2636(8)	12183(4)	2885(3)
N(2)	2944(8)	11051(4)	2260(3)
N(3)	5974(9)	13434(5)	4003(3)
C(1)	2417(13)	14318(8)	779(5)
C(2)	4059(11)	14593(6)	1644(4)
C(3)	6003(12)	15873(6)	1808(5)
C(4)	6331(11)	13239(6)	2323(4)
C(5)	4646(9)	13410(5)	3107(3)
C(6)	3653(12)	14783(6)	3266(4)
C(7)	2954(14)	8733(8)	468(4)
C(8)	−198(10)	9101(5)	2870(3)
C(9)	−2204(10)	9444(6)	3329(4)
C(10)	−2783(12)	8988(6)	4087(4)
C(11)	−1288(12)	8197(6)	4398(4)
C(12)	671(12)	7847(6)	3946(4)
C(13)	1259(11)	8279(6)	3172(4)
H(11)	116(16)	1361(9)	78(6)
H(12)	175(15)	1527(9)	83(6)
H(13)	343(16)	1418(9)	28(6)
H(31)	706(13)	1562(7)	129(5)
H(32)	674(13)	1612(7)	244(5)
H(33)	522(12)	1657(8)	176(5)
H(41)	674(12)	1234(7)	223(5)
H(42)	771(13)	1402(7)	250(5)
H(61)	499(13)	1554(7)	350(5)
H(62)	237(13)	1484(7)	367(5)
H(71)	198(13)	910(7)	9(5)
H(72)	446(14)	926(7)	67(5)
H(73)	315(12)	775(8)	18(5)
H(91)	−321(13)	999(7)	316(5)
H(101)	−415(15)	910(9)	434(6)
H(111)	−199(15)	788(8)	486(6)
H(121)	162(12)	730(7)	415(5)
H(131)	265(13)	799(7)	285(5)

IR spectra for liquid substances were recorded in a thin layer samples, spectra for solid samples were recorded for pellets with KBr on a Specord IR-75 spectrometer. ^{1}H, ^{13}C, ^{14}N, and ^{31}P NMR spectra were recorded on a Bruker AM-300 spectrometer for solutions in a CCl_4 + $CDCl_3$ (15 %) mixture. ^{14}N and ^{31}P chemical shifts were measured relative to $MeNO_2$ and H_3PO_4 external standards and are given without corrections for diamagnetic susceptibility.

2-Nitro-2-nitrosopropane,[10] 2,2-dimethyl-5-nitro-5-nitroso-1,3-dioxane,[11] dibromoisocyanurate (DBI),[12] amidophosphates,[13] and amidophosphonates[13] were prepared according to the known procedures. Diazene *N*-oxides were isolated by TLC (Silpearl, ether as the eluent).

Allyl ethyl chlorophosphate (1). A mixture of 1.06 g (18 mmol) of allyl alcohol and 1.86 g (18 mmol) of Et_3N was slowly added dropwise to a stirred solution of 3 g (18 mmol) of ethyl dichlorophosphate in 30 mL of absolute ether at −50 °C. The reaction mixture was allowed to warm to ~20 °C; the precipitate of $Et_3N \cdot HCl$ was filtered off, the solvent was evaporated, and the residue was distilled *in vacuo*. Chlorophosphate **1** was obtained in a yield of 0.88 g (26 %), b.p. 70—73 °C (3 Torr). ^1H NMR (δ): 1.37 (t, 3 H, Me); 4.39 (m, 4 H, CH_2O); 5.42 (m, 3 H, $CH=CH_2$).

Ethyl propargyl chlorophosphate (2) was prepared using the same procedure as in the synthesis of **1**; the yield was 38 %, b.p. 82—84 °C (3 Torr). ^1H NMR (δ, *J*/Hz): 1.35 (t, 3 H, Me); 2.62 (t, 1 H, CH, $J = 2.5$); 4.23 (m, 2 H, CH_2Me); 4.73 (t, 2 H, CH_2, $J_1 = J_2 = 12.0$).

Allyl ethyl amidophosphate (3). Dry NH_3 was passed through a solution of 0.8 g (4 mmol) of dichlorophosphate **1** in 15 mL of absolute ether at −50 °C until the formation of the precipitate ceased. The precipitated NH_4Cl was filtered off and washed with ether, the solvent was removed from the filtrate *in vacuo*, and 0.67 g (94 %) of amidophosphate **3** (oil) was obtained. IR (ν/cm^{-1}): 1030 (P—O—C); 1220 (P=O); 3100—3400 (NH_2). ^1H NMR (δ): 1.28 (t, 3 H, Me); 4.25 (m, 4 H, OCH_2); 5.30 (m, 3 H, $CH=CH_2$).

Ethyl propargyl amidophosphate (4) was prepared in the same manner as described for **3**; the yield of amidophosphate **4** was 83 % (oil). IR (ν/cm^{-1}): 1040 (P—O—C); 1230 (P=O); 3100—3400 (NH_2). ^1H NMR (δ, *J*/Hz): 1.28 (t, 3 H, Me); 2.60 (t, 1 H, CH, $J = 2.5$); 4.04 (m, 2 H, $O\underline{CH_2}Me$); 4.57 (t, 2 H, CH_2, $J_1 = J_2 = 10.0$).

(2,3-Dibromo-2-propenyl) ethyl *N,N*-dibromoamidophosphate (9). Bromine (1.96 g, 12 mmol) was added dropwise with stirring at 0 °C to a solution of 1 g (6 mmol) of amidophosphate **4** and 0.93 g (7 mmol) of K_2CO_3 in 11 mL of water. Stirring was continued for ~30 min at 0 °C and for 1 h at 20 °C. 5 mL of CH_2Cl_2 was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×3 mL). The combined organic layer was washed with cold water and dried with $MgSO_4$, and the solvent was evaporated to give 1.4 g (48 %) of amidophosphate **9** (oil). ^1H NMR (δ, *J*/Hz): 1.37 (t, 3 H, Me); 4.24 (m, 2 H, $O\underline{CH_2}Me$); 4.99 (m, 2 H, CH_2); 6.67 (t, 1 H, CH, $J = 2.5$).

***N*-(1-Methyl-1-nitroethyl)-*N'*-[(2,3-dibromo-2-propenyloxy)ethoxyphosphoryl]diazene *N*-oxide (7).** A mixture of 1 g (2 mmol) of **9** and 0.29 g (2.5 mmol) of 2-nitro-2-nitrosopropane in 10 mL of CH_2Cl_2 was stirred for 12 h at 20 °C. The solvent was removed *in vacuo*, the residue was chromatographed on silica gel (ether as the eluent), and 0.2 g (22 %) of diazene *N*-oxide **7** identical, according to the ^1H NMR spectrum, to the product obtained from 2-nitro-2-nitrosopropane and **4** in the presence of DBI, was isolated.

***N'*-Phosphoryl(phosphonoyl)diazene *N*-oxides (5—8 and 11—14).** A mixture of 10 mmol of a nitroso compound, 10 mmol of amidophosphate (amidophosphonate), and 20 mmol of DBI in 10 mL of CH_2Cl_2 was stirred for 12—24 h at 20 °C. The excess DBI and cyanuric acid were filtered off and washed with CH_2Cl_2 (2×5 mL), the filtrate was evaporated *in vacuo*, and diazene oxides were obtained. Spectral data for compounds **5—8** and **11—14** are given in Tables 1—3.

***N*-(2-Hydroxy-1-hydroxymethyl-1-nitroethyl)-*N'*-(diethoxyphosphoryl)diazene *N*-oxide (15).** Acetyl chloride (0.3 g, 3.7 mmol) was added with stirring at ~20 °C to a solution of 0.5 g (1.5 mmol) of **11** in 7 mL of absolute MeOH. The mixture was kept for 19 h at ~20 °C, the solvent was removed *in vacuo*, and compound **15** (0.34 g, 77 %) was isolated by TLC (Silpearl, 6 : 1 ether—benzene mixture as the eluent) (see Table 1).

***N*-(2-Acetoxy-1-acetoxymethyl-1-nitroethyl)-*N'*-(diethoxyphosphoryl)diazene *N*-oxide (16).** Acetyl chloride (0.1 g, 1.3 mmol) was added dropwise with stirring at −20 °C to a solution of 0.1 g (0.3 mmol) of **15** in 2 mL of ether. The reaction mixture was allowed to warm to ~20 °C, then the solvent was removed under a vacuum, and 0.08 g (65 %) of diacetate **16** was isolated (see Table 1).

***N*-(1-Nitro-2-nitroxy-1-nitroxymethyl)ethyl-*N'*-(diethoxyphosphoryl)diazene *N*-oxide (17).** 0.07 g (1.1 mmol) of HNO_3 ($d = 1.506$ g cm^{-3}) was added at 0 °C to a solution of 0.1 g (1.1 mmol) of acetic anhydride in 1 mL of absolute CH_2Cl_2. The mixture was allowed to stand for ~30 min, the temperature was gradually increased to ~20 °C, and then a solution of **15** (0.08 g, 0.266 mmol) in 1 mL of absolute CH_2Cl_2 was added. The reaction mixture was kept for 20 min at 20 °C and poured into 3 mL of water. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×3 mL). The combined organic extract was dried with $MgSO_4$, the solvent was evaporated, and diazene *N*-oxide **17** was isolated (see Table 1).

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