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To the 85th Anniversary of birthday of late Yu.G. Gololobov

Synthesis and Spatial Structure of P^+–O(N)–C^- Bipolar Ions Based of Tris(diethylamino)phosphine and Some 1,3-Diketones

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Abstract—Reactions of tris(diethylamino)phosphine with indanetrione, 2-diazoindane-1,3-dione, 2-diazodimedone, and pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone (alloxan) afforded crystalline adducts of bipolar type, whose structure was established by X-ray diffraction analysis.

Keywords: polyketones, betaines, zwitterions, diazo compounds, X-ray diffraction analysis

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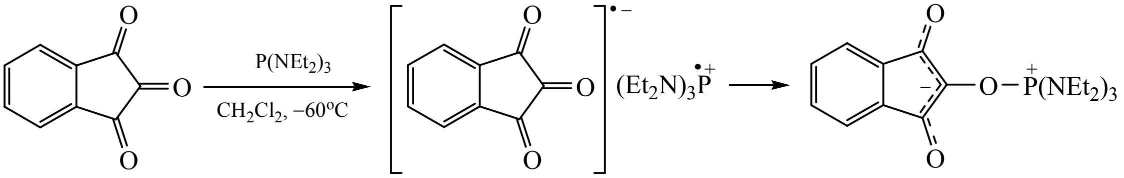
Reaction of trivalent phosphorus derivatives with carbonyl and dicarbonyl compounds is widely used for the preparation of various phosphorylated compounds and in organic synthesis. In addition, it allows obtaining non-phosphorylated substances as products of transformation of organic substrates and also compounds in which molecules the phosphorus atom is a part of a heterocyclic scaffold or is present in an exocyclic substituent [1–3]. At the same time, data on the interaction of P(III) derivatives with tri- and polycarbonyl compounds are scarce. For example, the reaction of indane-1,2,3-trione and 5,5-dimethylcyclohexane-1,2,3-trione with trialkyl phosphites is known to provide pentaalkoxyoxyphosphoranes containing dioxaphospholane fragment in which two diketone moieties are connected by the C–C bond [4, 5]. Unlike that Shajari and Ramazani [6] when performing the reaction in the absence of solvent indicated the formation of pentaalkoxyphosphorane containing one indenone fragment, which was analogous to the Kuhtin–Ramirez reaction product [2]. A similar result was obtained in the case of triphenylphosphine [7]. Depending on the structure of the substituent in the P(III) amide acyclic triketones like 1,3-diphenylpropane-1,2,3-trione reacted to form either spirophosphoranes or phosphabetaines, where the negative charge is localized on an oxygen atom [8]. In all the cases, the formation of bipolar ions of P^+–C–O^- and P^+–O–C^- types was postulated. Bipolar ion P^+–C–O^- obtained by reacting tris(tetrafluoropropyl)phosphite with chloral in the presence of antimony pentachloride has been characterized by ^{13}C and ^{31}P NMR spectroscopy [9]; the structure of P^+–O–C^- bipolar ions prepared by reacting tris(diethylamino)phosphine with tetrabromo-and tetrachloro-1,4-benzoquinone has been proved by X-ray diffraction (XRD) analysis [10].

This work is aimed at the synthesis of P^+–O(N)–C^- bipolar ions derived from hexaethyltriamidophosphite and hetero- and carbocyclic compounds containing dione or polyone fragments and also to study their structure by means of X-ray diffraction method. The reactions of these compounds is not accompanied with deoxygenation, as in the case of interaction of cyclic 1,2-dicarbonyl compounds with phosphorus(III) amides [3]. So, the reaction of indanetrione **1** with hexaethyltriamidophosphite under mild conditions (dichloromethane, –60°C, 30 min) was accompanied with a rapid change in the color of the reaction mixture from red to green and finally to brown, which indicated one-electron transfer from phosphite to acceptor indanetrione to form an intermediate radical ion pairs (**A**). According to ^{31}P NMR data, there was a complete conversion of the starting phosphite (δ_P = 128 ppm) to

Scheme 1.



1 **A** **2**

the reaction product (δ$_P$ = 36.9 ppm). Crystals of zwitter-ion **2** were obtained by slow evaporation of the solvent. Structure of **2** was established by XRD analysis (Scheme 1, Fig. 1).

Reactions of 2-diazoindane-1,3-dione **3** and 2-diazodimedone **4** with hexaethyltriamidophosphite provided the easy formation of compounds **5** and **6** of zwitterionic type. In their molecules the negative charge is predominantly localized on one of the oxygen atoms, as evidenced by the presence in ^{13}C NMR spectrum of two downfield signals at 180.78 and 190.15 ppm belonging to the carbon atoms of C–O$^-$ and C=O groups, respectively. The positive charge on the phosphorus atom is effectively stabilized by transfer of electron density from the nitrogen lone pairs to the *d*-orbitals of the phosphorus, which are lower in energy when an onium phosphorus center forms. Such structure of compounds **5** and **6** (with a predominant localization of the negative charge on one of the oxygen atoms, rather than over the entire system of multiple bonds) may be due to the possibility of convergence of electrostatic charges to form six-membered ring which is further stabilized by the presence of equilibrium (Scheme 2).

A very interesting object for possible deoxygenation reaction was alloxan **7** [pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone]. However, we found that this tetracarbonyl compound was not prone to deoxygenation under the action of hexaethyltriamidophosphite. The reaction afforded bipolar adduct **8** containing phosphorus–oxygen bond, which was isolated as a solvate with one molecule of dichloromethane. The latter was identified by the presence of a singlet at 39 ppm in ^{31}P–{^{1}H} NMR spectrum. Here, as in the cases described above,

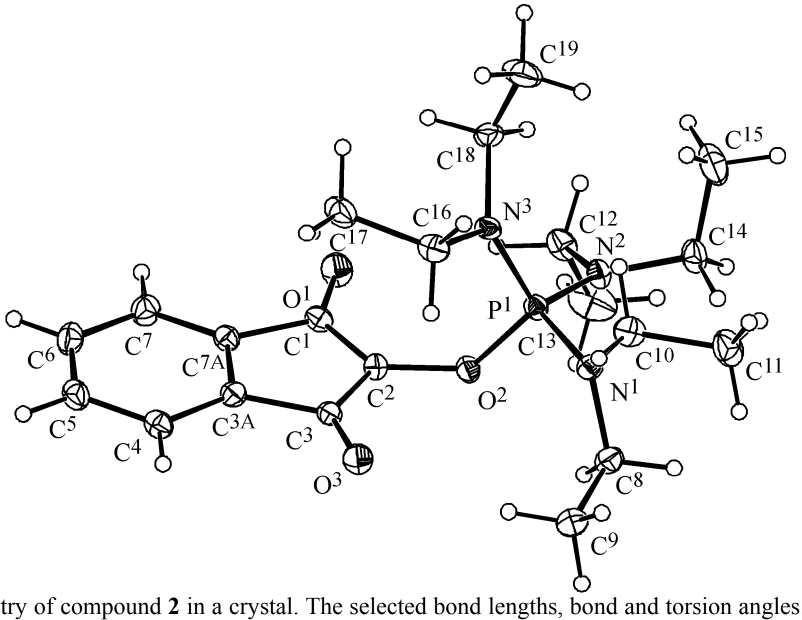
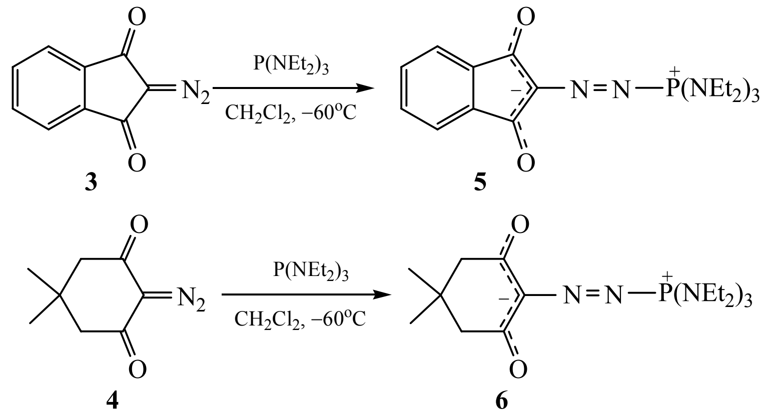
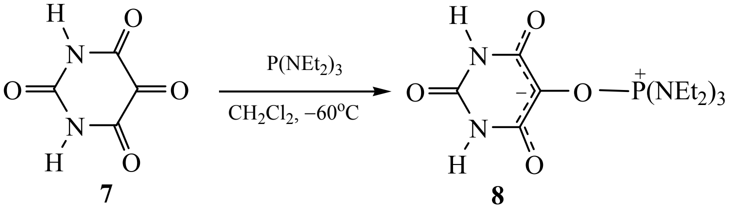


Fig. 1. Molecular geometry of compound **2** in a crystal. The selected bond lengths, bond and torsion angles: P^1–O^2 1.578(3), P^1–N^1 1.617(3), P^1–N^2 1.615(3), P^1–N^3 1.618(3), O^1–C^1 1.240(4), O^2–C^2 1.411(4), O^3–C^3 1.246(4), C^1–C^2 1.418(5), C^1–C^{7A} 1.510(5), C^2–C^3 1.405(5), C^3–C^{3A} 1.508(5), C^{3A}–C^4 1.376(5), C^{3A}–C^{7A} 1.395(5), C^4–C^5 1.407(6), C^5–C^6 1.372(6), C^6–C^7 1.388(5), C^7–C^{7A} 1.369(5) Å; O^{2}P^{1}N^1 107.7(1)°, O^{2}P^{1}N^2 102.4(1)°, O^{2}P^{1}N^3 112.6(2)°, N^{1}P^{1}N^2 111.9(1)°, N^{1}P^{1}N^3 108.2(2)°, C^{1}C^{7A}C^{3A} 108.1(3)°, N^{2}P^{1}N^3 113.93(2)°, P^{1}O^{2}C^2 124.7(2)°, P^{1}N^{1}C^8 119.7(2)°, P^{1}N^{1}C^{10} 123.5(2)°, O^{1}C^{1}C^2 130.2(3)°, O^{1}C^{1}C^{7A} 124.8(3)°, C^{2}C^{1}C^{7A} 105.0(3)°, O^{2}C^{2}C^1 122.3(3)°, O^{2}C^{2}C^3 124.7(3)°, C^{1}C^{2}C^3 113.0(3)°, P^{1}O^{2}C^{2}C^1 96.3(4)°, P^{1}O^{2}C^{2}C^3 –87.1(4)°.

Scheme 2.



Scheme 3.



the addition of the phosphorus nucleophile occurred regioselectively at the position 5 of the heterocycle (Scheme 3).

The structure of the obtained phosphabetaines **2**, **5**, **6**, and **8** was also proved by XRD analysis (Figs. 1–4). Crystallographic data and experimental parameters for compounds **2**, **5**, **6**, and **8** are presented in the table.

EXPERIMENTAL

IR spectra were recorded on a Bruker Vector-22 spectrometer. ^{1}H (400 MHz), ^{13}C (100.6 MHz), and ^{31}P NMR spectra were registered on a Bruker Avance-400 instrument. Melting points were measured on a SMP10 Stuart instrument. Elemental analysis was performed using a CHNS-3 analyzer.

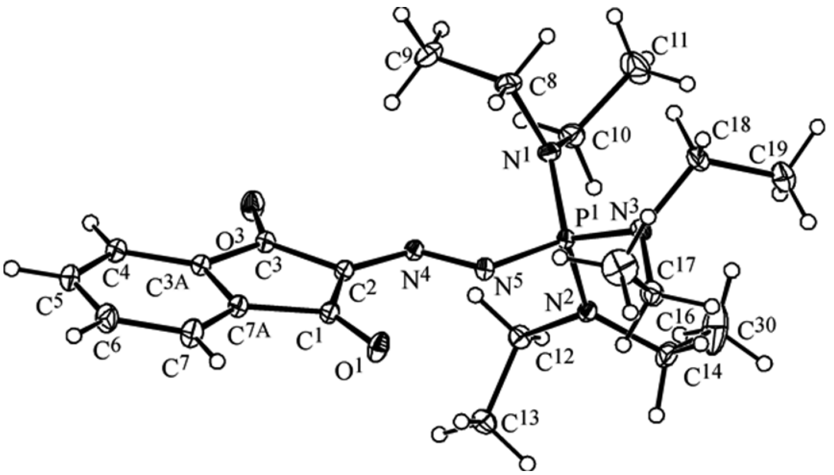


Fig. 2. Molecular geometry of compound **5** in a crystal. The selected bond lengths, bond and torsion angles: P^1–N^1 1.624(1), P^1–N^2 1.624(1), P^1–N^3 1.626(1), P^1–N^5 1.667(1), O^1–C^1 1.225(2), O^3–C^3 1.221(2), N^4–N^5 1.309(2), N^4–C^2 1.330(2), C^1–C^2 1.461(2), C^1–C^{7A} 1.501(2), C^2–C^3 1.462(2), C^3–C^{3A} 1.494(2), C^{3A}–C^4 1.387(2), C^{3A}–C^{7A} 1.386(2), C^4–C^5 1.386(2), C^5–C^6 1.384(2), C^6–C^7 1.391(2), C^7–C^{7A} 1.381(2) Å; N^{1}P^{1}N^2 109.85(6)°, N^{1}P^{1}N^3 110.98(6)°, N^{1}P^{1}N^5 112.61(6)°, N^{2}P^{1}N^3 109.83(6)°, N^{2}P^{1}N^5 109.01(6)°, N^{3}P^{1}N^5 104.43(6)°, N^{5}N^{4}C^2 118.3(1)°, P^{1}N^{5}N^4 112.05(9)°, O^{1}C^{1}C^2 130.0(1)°, O^{1}C^{1}C^{7A} 124.5(1)°, C^{2}C^{1}C^{7A} 105.5(1)°, N^{4}C^{2}C^1 131.6(1)°, N^{4}C^{2}C^3 118.8(1)°, C^{1}C^{2}C^3 109.4(1)°, N^{5}N^{4}C^{2}C^1 –0.3(2)°, N^{5}N^{4}C^{2}C^3 173.3(1)°.

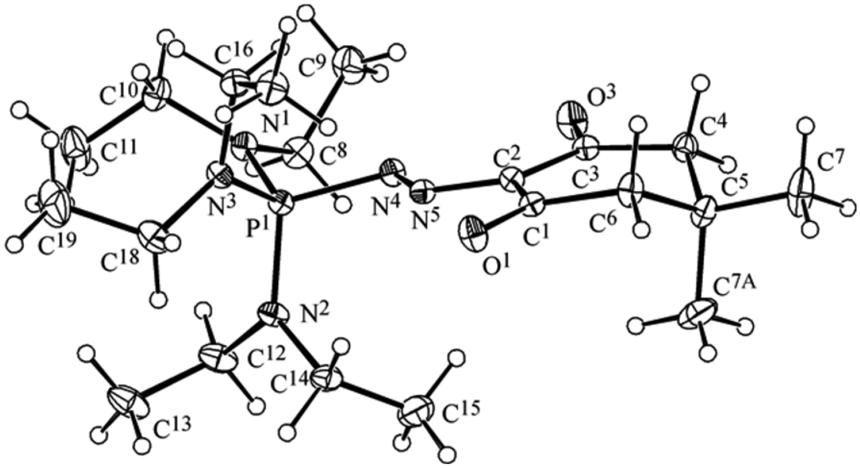


Fig. 3. Molecular geometry of compound **6** in a crystal. The selected bond lengths, bond and torsion angles: P^1–N^1 1.626(1), P^1–N^2 1.631(1), P^1–N^3 1.634(1), P^1–N^4 1.666(3), O^1–C^1 1.224 (2), O^3–C^3 1.225(2), N^4–N^5 1.314(2), N^5–C^2 1.335(2), C^1–C^2 1.474(2), C^1–C^6 1.505(2), C^2–C^3 1.466(2), C^3–C^4 1.517(2), C^4–C^5 1.523(2), C^5–C^6 1.530(2), C^5–C^7 1.530(3), C^5–C^{7A} 1.527(3) Å; N^{1}P^{1}N^2 109.89(6)°, N^{1}P^{1}N^3 110.54(7)°, N^{1}P^{1}N^4 104.49(6)°, N^{2}P^{1}N^3 109.82(7)°, N^{2}P^{1}N^4 109.53(7)°, N^{3}P^{1}N^4 112.46(6)°, P^{1}N^{4}N^5 110.1(1)°, N^{4}N^{5}C^2 120.9(1)°, O^{1}C^{1}C^2 123.1(1)°, N^{5}C^{2}C^1 112.8(1)°, N^{5}C^{2}C^3 126.3(1)°, C^{1}C^{2}C^3 120.8(1)°, O^{3}C^{3}C^2 123.4(1)°, C^{4}C^{5}C^7 109.9(1)°, P^{1}N^{4}N^{5}C^2 175.3(1)°, N^{4}N^{5}C^{2}C^1 179.8(1)°, N^{4}N^{5}C^{2}C^3 –2.0(2)°, C^{3}C^{4}C^{5}C^7 –170.5(1)°, C^{3}C^{4}C^{5}C^{7A} 68.0(2)°.

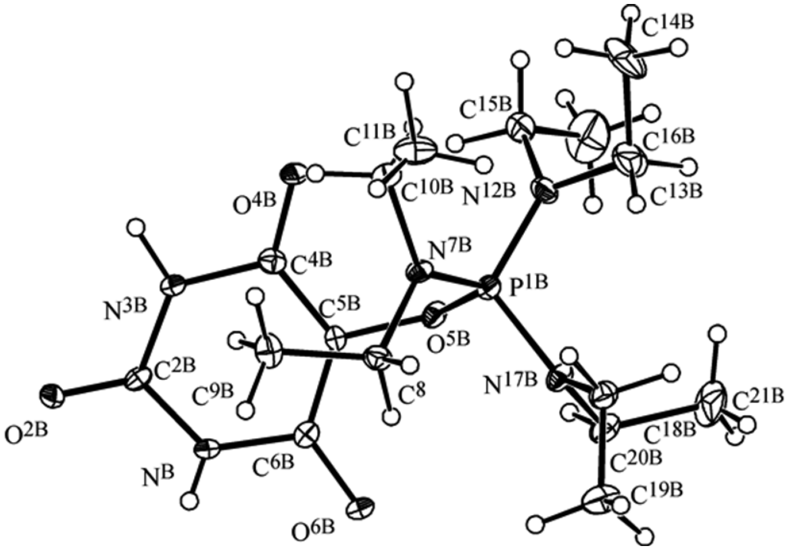


Fig. 4. Molecular geometry of compound **8** in a crystal (one of the two molecules is shown; solvate molecules of dichloromethane and water are not shown). The selected bond lengths, bond and torsion angles: N^{1b}–C^{6b} 1.401(6), N^{1b}–C^{2b} 1.367(6), N^{3b}–C^{4b} 1.403(6), N^{3b}–C^{2b} 1.383(6), P^{1b}–N^{7b} 1.604(4), P^{1b}–N^{12b} 1.626(4), P^{1b}–O^{5b} 1.581(3), P^{1b}–N^{17b} 1.615(4), O^{2b}–C^{2b} 1.225(6), O^{4b}–C^{4b} 1.255(6), O^{6b}–C^{6b} 1.263(6), O^{7b}–C^{5b} 1.419(5) Å; O^{5b}P^{1b}N^{12b} 103.0(2)°, O^{5b}P^{1b}N^{17b} 105.8(2)°, N^{12b}P^{1b}N^{17b} 112.3(2)°, N^{7b}P^{1b}N^{17b} 107.6(2)°, N^{7b}P^{1b}N^{12b} 113.8(2)°, O^{5b}P^{1b}N^{7b} 114.3(2)°, P^{1b}O^{5b}C^{5b} 120.8(3)°.

X-Ray diffraction analysis was performed on a Bruker Smart APEX II CCD automated diffractometer [graphite monochromator, λ(MoK_α) 0.71073 Å, ω-scanning]. Semi-empirical correction for extinction was performed using SADABS software [11]. The structure was solved by the direct method and refined first in isotropic and then in anisotropic approximation using SHELX software [12]. Hydrogen atoms were placed in the geometrically calculated positions and involved into refinement with a *rider* model. All calculations were performed using WinGX software [13]. Data collection, indexing, and processing were performed using APEX2 software package [14]. The figures were made using ORTEP software [15].

The crystallographic data of compounds **2**, **5**, **6** and **8** were deposited in the Cambridge Crystallographic Data Center (CCDC 1053210–1053213).

Crystallographic parameters for compounds **2**, **5**, **6**, **8**

Parameter	Compounds			
	2	**5**	**6**	**8**
Empirical formula	$C_{21}H_{34}N_3O_3P$	$C_{21}H_{34}N_5O_2P$	$C_{20}H_{40}N_5O_2P$	$C_{16}H_{32}N_5O_4P\cdot CH_2Cl_2\cdot 1/4H_2O$
M	407.48	419.50	413.54	478.36
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	Cc	P-1	$P2_1/c$	$P2_1/c$
T, K	150	150	150	150
a, Å	14.488(4)	8.9294(18)	12.4344(14)	28.823(7)
b, Å	12.780(4)	9.789(2)	10.4276(11)	11.648(3)
c, Å	12.497(4)	13.453(3)	19.006(2)	15.071(3)
α, deg	90	96.154(2)	90	90
β, deg	108.054(4)	92.648(2)	106.451(2)	104.790(3)
γ, deg	90	98.636(2)	90	90
V, Å^3	2200.0(12)	1153.6(4)	2363.5(4)	4892(2)
Z	4	2	4	8
d_{calc}, g/cm^3	1.230	1.208	1.162	1.299
μ, cm^{-1}	1.51	1.45	1.40	3.63
Number of measured reflections (R_{int})	13556 (0.052)	14022 (0.031)	29010 (0.045)	9615 (0.000)
Number of reflections with $I \geq 2\sigma(I)$	4234	4690	4716	5910
Number of variables	259	268	261	563
Flack parameter	0.10(9)	–	–	–
R_1 [$I \geq 2\sigma(I)$]	0.0508	0.0402	0.0441	0.0705
wR_2 (all reflections)	0.1025	0.1118	0.1142	0.1739

General procedure for the synthesis of phosphabetaines 2, 5, 6, and 8. To a solution of the appropriate carbonyl compound in 20 mL of CH_2Cl_2 at –60°C under argon was added an equimolar amount of hexaethyltriamidophosphite within 10 min. The reaction mixture was kept for 20 min, then allowed to spontaneously warm to room temperature and subsequently the solvent evaporated through a tube filled with $CaCl_2$ to a volume of 5 mL. The resulting precipitate was filtered off and dried in a vacuum (18 mmHg).

1-Oxo-2-[tris(diethylamino)phosphoniooxy]-1*H*-indene-3-oate (2). Yield 85%, dark brown crystals, mp 70°C. IR spectrum (film), ν, cm^{-1}: 2975 (C–H), 1735 (C=O), 1616 (C=C), 1213 (P–O). ^{1}H NMR spectrum, δ, ppm: 1.11–1.14 m (18H, CH_3), 3.20–3.30 m (12H, NCH_2), 7.11–7.14 m (4H, H^4, H^5). ^{13}C NMR spectrum, δ_C, ppm (J, Hz) (the data given in parentheses are for the ^{13}C–{^{1}H} spectra): 13.05 d.q (br.s) (CH_3, $^1J_{HC}$ 126.9, $^3J_{PC}$ 2.9), 39.96 t.m (d) (CH_2, $^1J_{HC}$ 138.7, $^2J_{PC}$ 4.4), 117.24 d.m (s) (C^5, $^1J_{HC}$ 161.4, $^3J_{HC}$ 5.9, $^2J_{HC}$ 2.9), 122.79 d (d) (C^2, $^2J_{PC}$ 8.4), 129.54 d.d (s) (C^4, $^1J_{HC}$ 162.1, $^3J_{HC}$ 4.4), 136.35 m (s) (C^{3a}), 180.51 d (d) (C^3, $^3J_{PC}$ 1.8). ^{31}P–{^{1}H} NMR spectrum: δ_P 36.9 ppm. Found, %: C 61.68; H 8.09; N 10.28. $C_{21}H_{34}N_3O_3P$. Calculated, %: C 61.90; H 8.41; N 10.31.

1-Oxo-2-{[tris(diethylamino)phosphonio]diazenyl}-1*H*-indene-3-oate (5). Yield 97%, red crystals, mp 89°C. IR (paraffin oil), ν, cm^{-1}: 1657 (C=O), 1591 (C=C), 1460 (C=N), 1285 (P–N). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.09 t (18H, CH_3, $^3J_{HH}$ 7.1), 3.04–3.11 m (12H, CH_2), 7.49–7.53 m (2H, H^4, H^7), 7.66–7.72 m (2H, H^5, H^6). ^{13}C NMR spectrum, δ_C, ppm (J, Hz): 13.27 d.q (d) (CH_3, $^1J_{HC}$ 126.2, $^3J_{PC}$ 1.8), 39.45 t.m (d) (CH_2, $^1J_{HC}$ 137.2, $^2J_{PC}$ 2.2, $^2J_{HC}$ 4.4), 121.01 d.m (s) (C^5, $^1J_{HC}$ 162.1, $^3J_{HC}$ 5.1), 121.83 d.m (s) (C^7), 132.37 d.m (s) (C^6), 133.00 d.d (s) (C^4, $^1J_{HC}$ 160.7, $^3J_{HC}$ 6.6), 139.11 d.d (s) (C^5, $^3J_{HC}$ 6.6, $^3J_{HC}$ 6.6), 139.39 d (d) (C^2, $^3J_{PC}$ 47.3), 139.85 d.d (s) (C^{3a}, $^3J_{HC}$ 5.9, $^3J_{HC}$ 5.9), 180.78 d (d) (C^3, $^4J_{PC}$ 1.5), 190.15 d (d) (C^1, $^3J_{HC}$ 2.2). ^{31}P–{^{1}H} NMR spectrum: δ_P 42.4 ppm. Found, %: C 61.85; H 8.02; N 16.38. $C_{21}H_{34}N_5O_2P$. Calculated, %: C 60.12; H 8.17; N 16.69.

5,5-Dimethyl-3-oxo-2-{[tris(diathylamino)phosphonio]diazenyl}cyclohex-1-ene-2-oate (6). Yield 95%, dark pink crystals, mp 76°C. IR spectrum (KBr), ν, cm^{-1}: 3141, 2976 (C–H), 1693 (C=O), 1609 (C=C), 1467 (C=N), 1392 (C–N), 1301 (P–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.03 s (6H, CH_3), 1.10 t (18H, CH_3, $^3J_{HH}$ 7.1), 2.42 br.s (4H, CH_2), 3.10 d.q (12H, NCH_2, $^3J_{PH}$ 10.0, $^3J_{HH}$ 7.1). Due to low solubility of the compound in a number of organic solvents ^{13}C NMR spectrum was not recorded. ^{31}P–{^{1}H} NMR spectrum: δ_P 41.3 ppm. Found, %: C 57.70; H 9.59; N 16.58. $C_{20}H_{40}N_5O_2P$. Calculated, %: C 58.09; H 9.75; N 16.94.

2,6-Dioxo-5-[tris(diathylamino)phosphoniooxy]-1,2,3,6-tetrahydropyrimidine-4-oate (7). Yield 55%, pale purple crystals, mp 46°C. IR (mineral oil), ν, cm^{-1}: 2968 (N–H), 1709 (C=O), 1466 (C–N), 1212 (P–O). ^{1}H NMR spectrum, δ, ppm: 1.16 br.s (18H, CH_3), 2.92 br.s (12H, NCH_2), 8.05 br.s (2H, NH). Due to low solubility of the compound in a number of organic solvents ^{13}C NMR spectrum was not recorded. ^{31}P–{^{1}H} NMR spectrum: δ_P 41.3 ppm. Found, %: C 49.20; H 8.09; N 17.73. $C_{16}H_{32}N_5O_4P$. Calculated, %: C 49.35; H 8.28; N 17.98.

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