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Structure and Properties of Phosponium Ylides-Betaines, Derivatives of 2-phenyl-2-oxazolin-5-one and its Thio- and Seleno-analogues

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Abstract: The combined chemical, spectral, and X-ray structural investigation has shown that the structure and properties of mesomeric triphenylphosponium ylides containing the 5-oxo-2-phenyl-4-oxazolidene moiety undergo considerable changes when the carbonyl oxygen atom is replaced by sulfur or selenium. This substitution leads to a clear decrease of the contribution of the ylide structure and an increased importance of the betaine structure, in contradiction with the electronegativity decrease in the O>S>Se series, but relates to the different ability of double bond formation of these elements. The deactivation of the ylide site by the thio- or selenocarbonyl group has been applied to regioselective syntheses.

Phosponium ylides are unique reagents in fine organic synthesis. Despite the works summarized in a recent monography¹, the structure-reactivity relationship for phosponium ylides still remains a problem. During the last years a systematical investigation of the cyclization of various phosponium reagents was performed by Ukrainian scientists²⁻⁴ and has resulted in the elaboration of original syntheses of a wide group of stabilized ylides, all derivatives of azoles. Among these compounds suitable representatives could be found for the comparative study of the influence of the carbonyl, thiocarbonyl and selenocarbonyl groups on the ylide site. In this work, a combined chemical and structural investigation of the mesomeric phosponium ylides, the oxazole derivatives 2-4, was carried out for the first time. Compounds 2-4 were prepared from the available precursor 1-benzoylamino-2,2-dichloroethenyltriphenylphosponium chloride

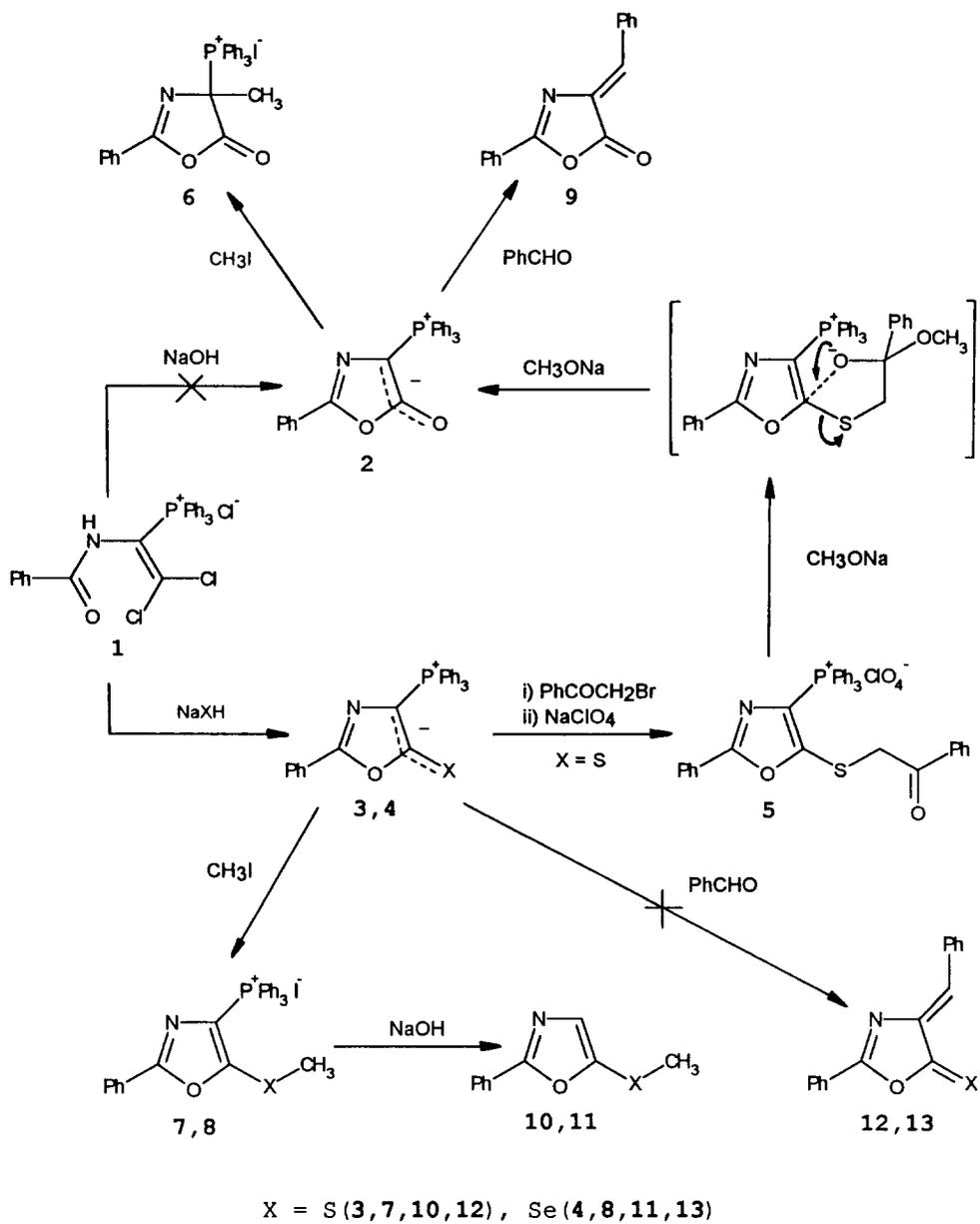
1⁵ (see Scheme).

Compound **3** was prepared smoothly by treating the phenylphosphonium salt **1** with excess of sodium hydrosulfide; similar reaction with sodium hydroxide did not lead, however, to the ylide **2**, which could be prepared in a more complicated way: **1** → **3** → **5** → **2**. A plausible mechanism for the last step consists of the addition of a methoxide anion to the carbonyl group of compound **5** leading to the betaine intermediate presented in the Scheme, which transforms further into ylide **2**. This mechanism needs additional evidence. However, the structure of the end product of the interaction of the phosphonium salt **5** with sodium methoxide was out of doubt, since **2** could undergo the Wittig reaction with benzaldehyde to give *Z*-4-benzylidene-2-phenyl-2-oxazolin-5-one, which was prepared previously by the classical Plochl-Erlenmeyer reaction⁶.

The substitution of the exocyclic oxygen atom in structure **2** by a sulfur or selenium atom causes an obvious deactivation of the ylide site, despite the electronegativity decrease in the O>S>Se series. Compounds **3** and **4** did not undergo the Wittig reaction with benzaldehyde and even not with the more electrophilic *p*-nitrobenzaldehyde. On the other side, compounds **3** and **4** retained yet their nucleophilic properties since they reacted with methyl iodide readily. They were methylated on the S or Se nucleophilic site exclusively. Compound **2** was preferentially methylated on the C ylide site, rather than on the oxygen atom as confirmed by IR and NMR spectra (see Experimental Section).

Consequently, compound **2** is a typical stabilized phosphonium ylide, whereas the parent compounds **3** and **4** are rather phosphonium betaines with an increased electron density on the exocyclic X site. Considerable difference in the electron density distribution in the mesomeric compounds **2-4** has been revealed by the dipole moment measurement, as well as by spectral and X-ray structural methods. To rationalize these data, we should take into account the three most important resonance structures I-III presented in Table 1. The use of the sole non-polar structure I is not sufficient because the mesomeric compounds **2-4** are highly polar (their dipole moments measured in chlorobenzene were in the range of 6.5-9.4 D). Interestingly, the dipole moment increased considerably when the oxygen atom of the carbonyl group was replaced by a sulfur atom and especially when it was replaced by a selenium atom. The longest wavelength maximum and its pronounced bathochromic shift in polar solvents is characteristic for the UV spectrum of the highly polar compound **4** (see Table 1).

The clear difference in the structure of the mesomeric compounds **2** and **3** was also established on the basis of the X-ray structural analysis (see Tables 2-4 and Figs. 1-3). The lengths of the most important C(4)-P(13), C(4)-C(5) and C(5)-O(12) bonds in compound **2** are equal to 1.732(3), 1.409(4) and 1.257(3)Å, respectively, comparable to those of other moderately stabilized ylides for which, however the betaine structure does not play the principal role¹. On the other hand, compound **3** crystallized with two conformations (**a** and **b**) in the asymmetric unit, mainly differing in the orientation of the triphenylphosphonium group. For both of them the importance of the betaine structure is increased. The ylide bond length in modification **3b** is, for example, 1.762(4)Å which is only slightly less than the extreme value of 1.769Å found recently for a superstabilized ylide of a complicated structure⁷. At the same time, it approximates the length of the clearly ordinary C(4)-P(14) bond (1.773Å) in the phosphonium salt **7**. All these data corroborate strongly the dominant role of the betaine structure III at least for conformation **3b**.

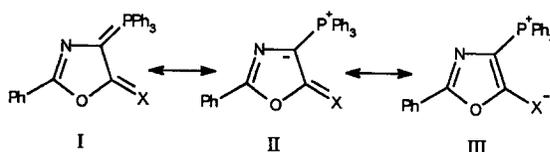


Scheme

We expected to find an even closer similarity by the comparison of the selenium-containing compounds **4** and **8**. However, our repeated attempts to prepare crystals of compound **4** suitable for an X-ray structural investigation failed. Nevertheless, taking into account the considerable increase of the dipole moment when replacing the sulfur by a selenium atom in the ylide-betaine **3**, it is clear that for compound **4** the betaine structure III contributes most to the real structure, having most of the negative charge mainly concentrated on the selenium atom.

Hence, we have found an effective way for stabilizing phosphonium ylides by substituting the oxygen atom in the $\text{Ph}_3\text{P}=\text{C}-\text{C}=\text{O}$ moiety with the less electronegative sulfur atom or selenium atom. This unexpected effect is obviously related to the different electronic structure of these elements, with their valence electrons placed in the second, third and fourth shell, respectively. The ability of double bond formation is drastically decreased in the $\text{O} > \text{S} > \text{Se}$ series, and the ylide structure of the $\text{Ph}_3\text{P}^+-\text{C}^--\text{C}=\text{Se}$ type becomes less favoured than the betaine structure of the $\text{Ph}_3\text{P}^+-\text{C}=\text{C}-\text{Se}^-$ type. A stabilization like this is not only characteristic for ylides-betaines of the oxazole type, but also for similar derivatives of thiazole², selenazole³ and imidazole⁴. Its importance for acyclic phosphonium ylides is also obvious (see for example ref. 8). The investigation of this effect for a wide range of various ylides is reasonable, since the sulfur- and selenium-containing phosphonium betaines may be used for series of specific regioselective syntheses. As an example, we can point out an interesting approach to the synthesis of the 5-substituted oxazoles by the conversions $3 \rightarrow 7 \rightarrow 10$ and $4 \rightarrow 8 \rightarrow 11$ also presented in the Scheme.

Table 1. Dipole Moments and UV Data of mesomeric Ylides-Betaines 2-4 for which the following resonance structures are the most important:



No of compound	X	Dipole moment (D) (C ₆ H ₅ Cl, 25°C)	UV maximum (nm) O(CH ₂ CH ₂)O (CH ₃) ₂ SO		Contribution of structures*
2	O	6.5	340	340	I + II > III
3	S	7.7	360	363	I + II ≤ III
4	Se	9.4	370	377	I + II ≪ III

*To estimate the contribution of the resonance structures, we have not only used data from this Table, but also differences in chemical properties of the compounds 2-4, as well as their X-ray structural data (see Tables 2-4)

Table 3. Selected Bond lengths (Å) and Angles (°) for Ylide-Betaine 3

O(1a)-C(2a)	1.366(6)	O(1b)-C(2b)	1.375(6)
C(2a)-N(3a)	1.287(6)	C(2b)-N(3b)	1.297(6)
N(3a)-C(4a)	1.409(6)	N(3b)-C(4b)	1.402(6)
C(4a)-C(5a)	1.390(7)	C(4b)-C(5b)	1.369(6)
O(1a)-C(5a)	1.405(5)	O(1b)-C(5b)	1.395(5)
C(2a)-C(6a)	1.463(6)	C(2b)-C(6b)	1.444(6)
C(4a)-P(13a)	1.745(5)	C(4b)-P(13b)	1.762(4)
C(5a)-S(12a)	1.654(5)	C(5b)-S(12b)	1.689(5)
P(13a)-C(14a)	1.804(4)	P(13b)-C(14b)	1.787(5)
P(13a)-C(20a)	1.800(4)	P(13b)-C(20b)	1.797(5)
P(13a)-C(26a)	1.783(5)	P(13b)-C(26b)	1.796(4)
C(2a)-O(1a)-C(5a)	106.4(3)	C(2b)-O(1b)-C(5b)	106.5(3)
O(1a)-C(2a)-N(3a)	114.3(4)	O(1b)-C(2b)-N(3b)	113.3(4)
C(2a)-N(3a)-C(4a)	104.4(4)	C(2b)-N(3b)-C(4b)	104.2(4)
N(3a)-C(4a)-C(5a)	110.6(4)	N(3b)-C(4b)-C(5b)	111.5(4)
C(4a)-C(5a)-O(1a)	104.1(4)	C(4b)-C(5b)-O(1b)	104.5(4)
O(1a)-C(2a)-C(6a)	116.8(4)	O(1b)-C(2b)-C(6b)	119.0(4)
N(3a)-C(2a)-C(6a)	128.8(4)	N(3b)-C(2b)-C(6b)	127.7(4)
N(3a)-C(4a)-P(13a)	123.6(4)	N(3b)-C(4b)-P(13b)	121.2(3)
C(5a)-C(4a)-P(13a)	125.7(3)	C(5b)-C(4b)-P(13b)	127.3(3)
S(12a)-C(5a)-O(1a)	120.3(2)	S(12b)-C(5b)-O(1b)	120.0(3)
S(12a)-C(5a)-C(4a)	134.7(4)	S(12b)-C(5b)-C(4b)	135.5(4)
C(4a)-P(13a)-C(14a)	108.3(2)	C(4b)-P(13b)-C(14b)	109.4(2)
C(4a)-P(13a)-C(20a)	112.0(2)	C(4b)-P(13b)-C(20b)	109.2(2)
C(4a)-P(13a)-C(26a)	109.4(2)	C(4b)-P(13b)-C(26b)	110.9(2)
C(14a)-P(13a)-C(20a)	110.4(2)	C(14b)-P(13b)-C(20b)	107.5(2)
C(14a)-P(13a)-C(26a)	108.7(2)	C(14b)-P(13b)-C(26b)	112.8(2)
C(20a)-C(13a)-C(26a)	108.1(2)	C(20b)-C(13b)-C(26b)	106.9(2)

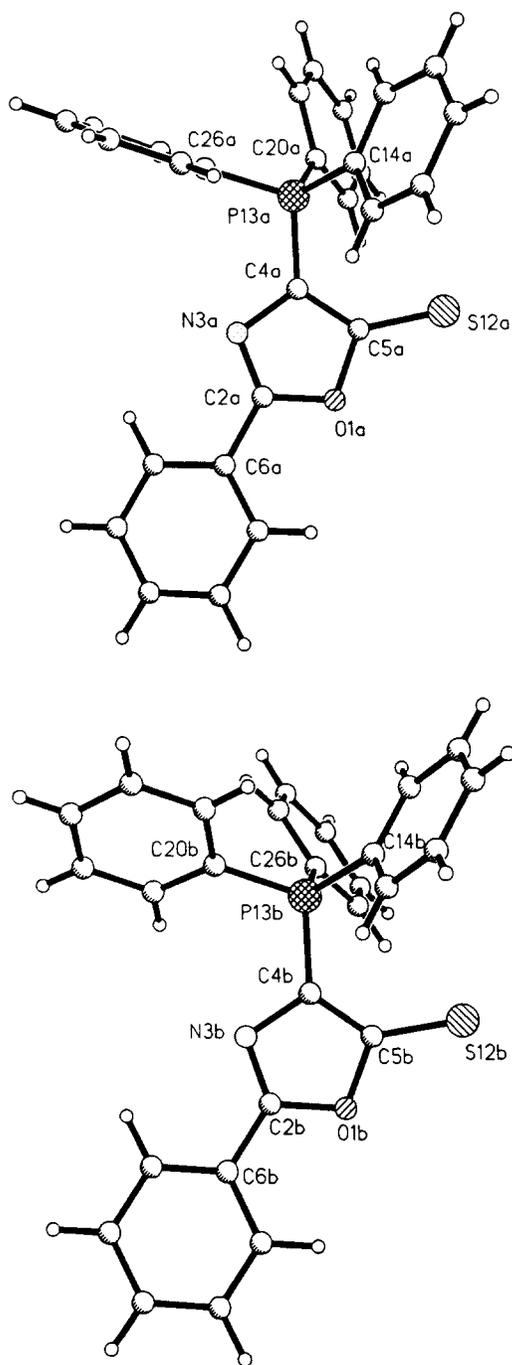


Fig. 2. Molecular Structure of Ylide-Betaine 3 (conformations a and b)

Table 4. Selected Bond lengths (Å) and Angles (°) for Phosphonium Salt 7

O(1)-C(2)	1.378(7)	C(4)-P(14)	1.773(6)
C(2)-N(3)	1.278(8)	C(5)-S(12)	1.715(6)
N(3)-C(4)	1.398(8)	S(12)-C(13)	1.787(8)
C(4)-C(5)	1.376(9)	P(14)-C(15)	1.794(7)
O(1)-C(5)	1.369(8)	P(14)-C(21)	1.780(7)
C(2)-C(6)	1.454(9)	P(14)-C(27)	1.780(6)
C(2)-O(1)-C(5)	104.5(5)	S(12)-C(5)-O(1)	120.2(4)
O(1)-C(2)-N(3)	114.7(5)	S(12)-C(5)-C(4)	132.3(5)
C(2)-N(3)-C(4)	104.5(5)	C(5)-S(12)-C(13)	100.7(4)
N(3)-C(4)-C(5)	109.2(5)	C(4)-P(14)-C(15)	108.8(3)
C(4)-C(5)-O(1)	107.1(5)	C(4)-P(14)-C(21)	110.8(3)
O(1)-C(2)-C(6)	117.5(5)	C(4)-P(14)-C(27)	107.2(3)
N(3)-C(2)-C(6)	127.8(6)	C(15)-P(14)-C(21)	108.9(3)
N(3)-C(4)-P(14)	122.2(4)	C(15)-P(14)-C(27)	111.7(3)
C(5)-C(4)-P(14)	128.5(5)	C(21)-P(14)-C(27)	109.5(3)

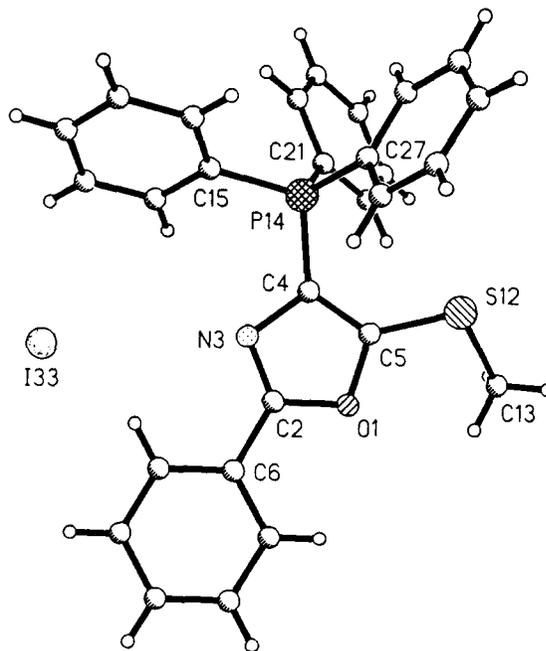


Fig. 3. Molecular Structure of Phosphonium salt 7

EXPERIMENTAL SECTION

*X-ray Structural Analyses of 2, 3 and 7:*⁹

The cell constants and the reflections were measured with a Siemens P4-PC four-circle diffractometer (graphite monochromator, $\lambda(\text{Cu-K}\alpha)=1.541781\text{\AA}$). Lattice parameters were obtained from least-squares of 20 (for **2** and **7**) or 31 (for **3**) reflections with $10.8 < \theta < 18.3^\circ$ (for **2**) and $10.8 < \theta < 17.0^\circ$ (for **3** and **7**). The structures were solved by direct (for **2** and **3**) or Patterson methods (for **7**) and refined by full-matrix least-squares¹⁰ to a final $R=0.0517$ (for **2**), $R=0.0366$ (for **3**) and $R=0.0630$ (for **7**). (H atoms refined with isotropic thermal parameters). The program package SHELXTL PC was used for other calculations and drawings.¹¹

(**2**): $\text{C}_{27}\text{H}_{20}\text{NO}_2\text{P}\cdot 3/2\text{C}_6\text{H}_6$, $\text{MW}=538.61$, a yellow crystal of $0.42 \times 0.28 \times 0.22$ mm size, space group $\text{P}2_1/\text{c}$, $Z=4$, monoclinic, $a=9.587(1)$, $b=14.289(1)$, $c=21.496(2)\text{\AA}$, $\beta=100.38(1)^\circ$, $V=2896.5(5)\text{\AA}^3$, $d_{\text{calc}}=1.235 \text{ g cm}^{-3}$, $F(000)=1132$, $T=289\text{K}$, ω -scan, $\Delta\omega=0.60^\circ$, $2.0 < \omega < 60.0^\circ \text{ min}^{-1}$, $7.5 < 2\theta < 100.9^\circ$, 4246 collected reflections ($(\sin\theta/\lambda)_{\text{max}}=0.50$), 3028 independent reflections ($R_{\text{int}}=0.04\%$), 2491 observed reflections ($F > 4.0\sigma(F)$). Semi-empirical absorption correction used ($\mu=1.093 \text{ mm}^{-1}$).

(**3**): $\text{C}_{27}\text{H}_{20}\text{NOPS}$, $\text{MW}=437.50$, a yellow crystal of $0.35 \times 0.25 \times 0.10$ mm size, space group Pn , $Z=4$, monoclinic, $a=10.877(2)$, $b=13.051(3)$, $c=16.555(3)\text{\AA}$, $\beta=102.73(3)^\circ$, $V=2292.3(8)\text{\AA}^3$, $d_{\text{calc}}=1.268 \text{ g cm}^{-3}$, $F(000)=912$, $T=289\text{K}$, ω -scan, $\Delta\omega=0.60^\circ$, $2.0 < \omega < 60.0^\circ \text{ min}^{-1}$, $6.8 < 2\theta < 100.9^\circ$, 3463 collected reflections ($(\sin\theta/\lambda)_{\text{max}}=0.50$), 2865 independent reflections ($R_{\text{int}}=2.91\%$), 2767 observed reflections ($F > 4.0\sigma(F)$). Semi-empirical absorption correction used ($\mu=2.053 \text{ mm}^{-1}$).

(**7**): $\text{C}_{28}\text{H}_{23}\text{NOPS}^+\text{I}^-$, $\text{MW}=579.44$, a yellow crystal of $0.50 \times 0.40 \times 0.30$ mm size, space group $\text{P}2_1/\text{c}$, $Z=4$, monoclinic, $a=9.705(2)$, $b=13.544(3)$, $c=20.737(4)\text{\AA}$, $\beta=92.53(3)^\circ$, $V=2723.1(1)\text{\AA}^3$, $d_{\text{calc}}=1.429 \text{ g cm}^{-3}$, $F(000)=1173$, $T=289\text{K}$, ω -scan, $\Delta\omega=0.60^\circ$, $2.0 < \omega < 60.0^\circ \text{ min}^{-1}$, $7.8 < 2\theta < 100.9^\circ$, 2857 collected reflections ($(\sin\theta/\lambda)_{\text{max}}=0.50$), 2857 independent reflections, 2646 observed reflections ($F > 4.0\sigma(F)$). Semi-empirical absorption correction used ($\mu=10.66 \text{ mm}^{-1}$).

IR spectra: Specord M-80; KBr tablets. *UV spectra:* Specord UV-Vis. *¹H NMR spectra:* Varian Gemini (200 MHz); δ -scale; internal reference hexamethyldisiloxane, coupling constants J in Hz. *Dipole moments:* E 9-5 device, calculated by Yu.Ya. Borovikov using the Onsager formula taking into account the perturbational effect of the concentration fluctuations.

2-Phenyl-5-oxo-4,5-dihydrooxazol-4-idenetriphenylphosphorane (2):

To a solution of ylide **3²** (0.015 mol) in methylene chloride (10 ml) is added a solution of phenacyl bromide (0.015 mol) in methylene chloride (5 ml); the mixture is left at $20\text{--}25^\circ\text{C}$ for 72h, then the solvent is removed in vacuum, the residue is dissolved in methanol (10 ml), and the saturated sodium perchlorate

solution (5 ml) is added. The phosphonium salt **5** is filtered off, washed with water, dried in a vacuum desiccator over phosphoric anhydride and dissolved at 50 °C in absolute methanol (900 ml). Then the sodium methoxide solution (0.015 mol) in absolute methanol (15 ml) is added, the mixture is left at 20-25 °C for 24h, the residue is filtered off, methanol is removed in vacuum, the residue is purified by threefold crystallization from benzene and dried in vacuum (10-15 mm Torr) at 20 °C. $C_{27}H_{20}NO_2P \cdot 3/2 C_6H_6$ solvate, yield 35-40%, mp 176-178 °C. IR: 1690 (C=O) cm^{-1} . (Found: C, 79.87; H, 5.60; N, 2.64; P, 5.80. Calc for $C_{27}H_{20}NO_2P \cdot 3/2 C_6H_6$ (MW=538.61): C, 80.28; H, 5.43; N, 2.60; P, 5.75%). This solvate loses benzene completely at heating to 80-100 °C in vacuum (0.1 mm Torr); as a result, crystals of ylide **2** are obtained, however, they are not suitable for X-ray structural analysis.

2-Phenyl-5-thioxo(selenoxo)-4,5-dihydrooxazol-4-idenetriphenylphosphoranes (3, 4):

Prepared as was described previously^{2,3}. Compound **3** is twice crystallized from methanol for the X-ray structural analysis.

4-Methyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-idenetriphenylphosphonium iodide (6):

The mixture of ylide **2** (0.002 mol) and methyl iodide (5 ml) is boiled for 10-15 min to the complete dissolution of the precipitate, the solution is left at 20-25 °C for 7 days, the precipitate is filtered off and purified by reprecipitation from methanol with diethyl ether, yield 40%, mp 162-164 °C (decomp). IR: 1820 (C=O), 1640 (C=N) cm^{-1} . ¹H NMR (CDCl₃): 2.17 (d, CH₃, ³J_{HP} 16), 7.40-7.90 (m, 4C₆H₅). (Found: C, 59.28; H 4.27; I, 22.74; P, 5.40. Calc for C₂₈H₂₃INO₂P (MW=563.38): C, 59.70; H, 4.12; I, 22.53; P, 5.50%).

5-Methylthio-2-phenyloxazol-4-yltriphenylphosphonium iodide (7):

To a solution of ylide **3** (0.001 mol) in methanol (20 ml) is added methyl iodide (0.003 mol), the solution is left at 20-25 °C for 30h. Methanol and excess of methyl iodide are removed in vacuum, the residue is crystallized from ethanol, yield 85%, mp 223-225 °C. ¹H NMR (CF₃COOH): 2.28 (s, CH₃S). (Found: I, 21.64; P, 5.30; S, 5.55. Calc for C₂₈H₂₃INOPS (MW=579.44): I, 21.90; P, 5.35; S, 5.53%).

5-Methylseleno-2-phenyloxazol-4-yltriphenylphosphonium iodide (8):

Prepared as compound **7**, converted into perchlorate for analysis, yield 66%, mp 208-210 °C (decomp). (Found: Cl, 5.93; Se, 13.18. Calc for C₂₈H₂₃ClNO₅PSe (MW=598.82): Cl, 5.92; Se, 13.19%).

Z-4-Benzylidene-2-phenyl-2-oxazolin-5-one (9):

To a solution of ylide **2** (0.002 mol) in chlorobenzene (15 ml) is added freshly distilled benzaldehyde (0.002 mol) and boiled for 40h. Chlorobenzene is removed in vacuum, the residue is crystallized from methanol, yield 51%, mp 163-164 °C. (Found: C, 76.96; H, 4.65; N, 5.65. Calc for C₁₆H₁₁NO₂ (MW=249.27): C, 77.10; H, 4.45; N, 5.62%). The mixed sample of this preparate and Z-4-benzylidene-2-phenyl-2-oxazolin-5-one prepared by the Plochl-Erlenmeyer method⁶, shows no melting point depression. The IR spectra of 0.1 M solutions of these samples in methylene chloride were identical.

5-Methylthio-2-phenyloxazole (10):

To a suspension of the phosphonium salt **7** (0.01 mol) in methanol (50 ml) is added the solution of sodium

hydroxide (5 g) in water (10 ml). The mixture stands at 20-25°C for 3h, methanol is removed at atmospheric pressure, the residue is distilled with steam. After the collection of 1 l of distillate, compound 10 is extracted with diethyl ether (3 x 75 ml), the solution is dried over anhydrous sodium sulfate, ether is removed at atmospheric pressure, the residue is distilled in vacuum, yield 83%, bp 80-82°C (0.06 mm Torr), d_4^{20} 1.1904, n_D^{20} 1.6208. ^1H NMR (CCl_4): 2.72 (s, CH_3S), 7.72 (s, $\text{C}^4\text{-H}$), 7.82-8.12, (m, C_6H_5). (Found: N, 7.16; S 16.57. Calc for $\text{C}_{10}\text{H}_9\text{NOS}$ (MW=191.25): N, 7.32; S, 16.77%).

5-Methylseleno-2-phenyloxazole (11):

To a solution of sodium hydroselenide (0.03 mol) in absolute ethanol (50 ml) is added the solution of the phosphonium salt 1 (0.01 mol) in absolute ethanol (40 ml). The mixture stands at 20-25°C for 24h, ethanol is removed in vacuum, the betaine 4 is washed with water and dried in a vacuum desiccator over phosphoric anhydride. Then methyl iodide (25 ml) is added. The mixture is left for 24h on stirring, diethyl ether (75 ml) is added, compound 8 is filtered off, and a solution of sodium hydroxide (4 g) in water (20 ml) is added. The mixture is heated at 80-90°C for 5-10 min and is distilled with steam. The isolation of compound 11 is performed similarly to compound 10. Yield 60%, bp 79-83°C (0.03 mm Torr), d_4^{20} 1.4444, n_D^{20} 1.6348. ^1H NMR (CCl_4): 2.65 (s, CH_3Se), 7.88 (s, $\text{C}^4\text{-H}$), 7.98-8.85, (m, C_6H_5). (Found: N, 6.00; Se 33.10. Calc for $\text{C}_{10}\text{H}_9\text{NOSe}$ (MW=238.15): N, 5.88; S, 33.16%).

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