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*ASN, Vol 4, No 1, Pages 6-12*, 2017

**Acta Scientifica Naturalis**
Former Annual of Konstantin Preslavsky University – Chemistry, Physics, Biology, Geography
Journal homepage: http://www.shu.bg

Received: 30.10.2016
Accepted: 11.01.2017

# Synthesis and properties of N-alkyl(phenyl)amido-O-methyl-1,2-alkadienephosphonates

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**Abstract***: The synthesis of the titled compounds has been described. Their reactivity towards electrophilic and nucleophilic reagents has been investigated.*

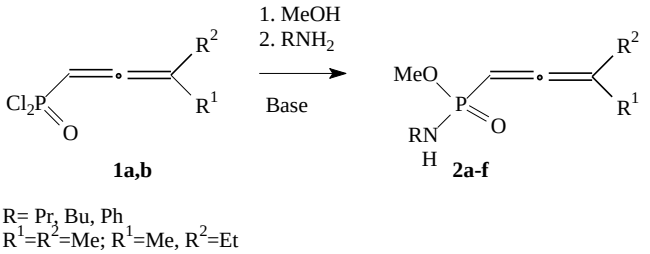
**Keywords:** 1,2-alkadienephosphonates, 2,5-dihydro-1,2-oxaphospholes, □-ketophosphonates

## Introduction

It is well known that 1,2-alkadienephosphonates react with different kinds of reagents due to their unique structure which allowed activation of different reaction centers in their molecules, i.e. 1,2- and 2,3-duble bonds or phosphoryl group, via variation of kind and number of the substituents at P, C1 and C3 atoms of the 1,2-alkadienephosphonate system of double bonds[1].
Continuing our investigations in the area of the chemistry of N-containing-1,2-alkadiene-phosphonates[2-8] , we would like to report our results on the synthesis and chemical behavior of the titled compounds.

## Results and Discussion

The methyl-N-alkyl(phenyl)-(3-methylalka-1,2-dienyl)phosphonamidates **2a-f** were synthesized via procedure described[2-8] , i.e. via nucleophilic displacement of the two chlorine atoms at phosphorus in the 1,2-alkadienephosphonic dichlorides **1a,b** with metoxy- and alkyl(phenyl)amino groups(Scheme 1):




**Scheme1.** Synthesis of methyl-N-alkyl(phenyl)-(3-methylalka-1,2-dienyl)phosphonamidates **2a-f**

The obtained methyl-N-alkyl(phenyl)-(3-methylalka-1,2-dienyl)phosphonamidates **2a-f** were investigated in the reactions with sulfenyl- and selenenylbromides. In all cases regardless of the kind of the electrophile 2,5-dihydro-1,2-oxaphosphole-2-oxide derivatives **3a-l** were obtained(Scheme 2.):



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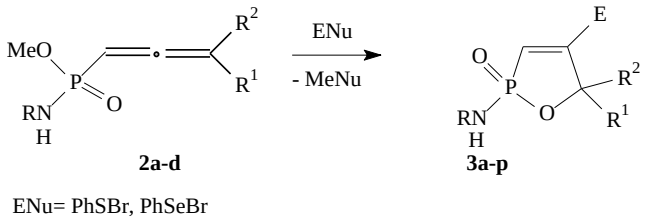
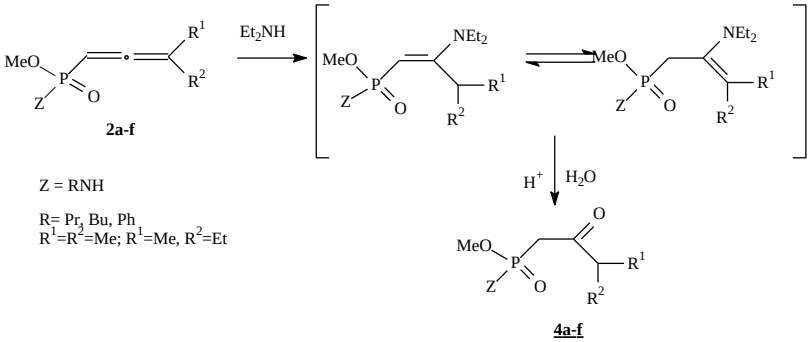
DOI: 10.1515/asn-2017-0002




**Scheme 2.** Synthesis of 2,5-dihydro-1,2-oxaphosphole-2-oxide derivatives **3a-l**

All spectral data confirm the obtaining of the products **3a-l**. Thus the characteristic band for allenic system in the IR spectra of **2a-f** at 1980-1990cm$^{-1}$, disappears in the IR spectra of the **3a-l** and new characteristic band for endocyclic carbon-carbon double bond appears at 1590-1580cm$^{-1}$. The signal for metoxy-group in the $^{1}$H NMR spectra of **2a-f** disappears in the $^{1}$H NMR spectra of **3a-l**. The multiplet signal for olephinic proton in the $^{1}$H NMR spectra of **2a-f** disappears in the $^{1}$H NMR spectra of **3a-l** while two doublets for the proton at position 3 of the oxaphosphole ring appear. The signal for $^{31}$P in the $^{31}$P NMR spectra of **2a-f** is at 16.8-17.3ppm while the signal for $^{31}$P for compounds **3a-l** is at 27.9-32.0ppm. The obtaining of 3a-**l** was also confirmed by the elemental analysis data.

The interaction of the titled compounds with diethylamine leads to obtaining of β-ketophosphonates **4a-f** (Scheme 3):




**Scheme 3.** Synthesis of methyl-P-(3-methyl-2-oxoalkyl)-N-alkylphosphoamidates **4a-f**

The obtaining of the products **4a-f** was confirmed by their spectral data. Thus the characteristic band for allenic system in the IR spectra of **2a-f** at 1980-1990cm$^{-1}$, disappears in the IR spectra of the **4a-f** and new characteristic band for carbonyl group appear at 1690-1700cm$^{-1}$. The signal for metoxy-group in the $^{1}$H NMR spectra of **2a-f** present also in the spectra of **4a-f**. The multiplet signal for olephinic proton in the $^{1}$H NMR spectra of **2a-f** disappears in the $^{1}$H NMR spectra of **3a-l** while two doublets for the proton at position 3 of the oxaphosphole ring appear. The signal for $^{31}$P in the $^{31}$P NMR spectra of **2a-f** is at 16.8-17.3ppm while the signal for $^{31}$P for compounds **4a-f** is at 27.9-32.0ppm. The obtaining of **4a-f** was also confirmed by the elemental analysis data.

## Experimental

### Analytical Methods

The $^{1}$H NMR spectra were measured at normal probe temperature on a spectrometer Bruker Avance DRX 250MHz using TMS as internal reference in $CDCl_3$ solution. Chemical shifts are given in *ppm* and are positively



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DOI: 10.1515/asn-2017-0002

downfield from the internal standard. The IR spectra were run on a Shimadzu FTR spectrophotometer. Elemental analyses were carried out by the University of Shumen Microanalytical Service Laboratory.

**Starting Materials**

The dichlorides **1a,b** were prepared according to the procedure described[10].
Phenylselenenylbromide is commercially available. Phenylsulfenylbromide was synthesized according to the procedure described [9].
The solvents were purified by standard methods. All reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for their purity on TLC plates.

**Synthesis of the compounds 2a-f**

**General Procedure:**

To a solution of 5*mmol* of the appropriate dichloride **1a,b** in dry diethyl ether at 0 to -5$^{o}$C and stirring a solution of 5*mmol* of methanol and 5mmol of pyridine was added, followed by addition of the mixture of 5*mmol* from the appropriate amine and 5 *mmol* of pyridine, dissolved in the same solvent. After one hour of stirring reaction mixture rest for a night, the precipitate was filtered off, the solvent was removed under low pressure and the residue was distilled *in vacuum*.

*Methyl-N-propyl-P-(3-methylbuta-1,2-dienyl)phosphonamidate* **2a**. $C_9H_{18}NO_2P$; Calcd.: P 15.24, N 6.89 %; Found: P 15.19, N 6.82 %; IR: ν($cm^{-1}$) 1986 $_{(C=C=C)}$, 1256 $_{(P=O)}$, 980 $_{(P-O-C)}$, $^{1}$H NMR ($CDCl_3$): δ/ppm 5.05-4.95(m, 1H, (HC=)); 3.39(d, $^{3}J_{HP}$ 11.25Hz, 3H, (OMe)); 2.67-2.54(m, 2H, ($CH_3CH_2CH_2N$)); 1.46(s, 3H, =C$CH_3$)); 1.51(s, 3H, (=C$CH_3$)); 2.00(d, $^{2}J_{HP}$ 10.00Hz, 1H, (NH)); 1.28-1.19(m, 2H, ($CH_3CH_2CH_2N$)); 0.91(t, 3H, ($CH_3CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 17.1; yellow-red liquid, b.p.( $^{o}$C/0.5mmHg) uncorrected 136-138; Yield (%) 85.

*Methyl-N-butyl-P-(3-methylbuta-1,2-dienyl)phosphonamidate* **2b**. $C_{10}H_{20}NO_2P$; Calcd.: P 14.26, N 6.44 %; Found: P 14.21, N 6.40 %; IR: ν($cm^{-1}$) 1988 $_{(C=C=C)}$, 1260 $_{(P=O)}$, 980 $_{(P-O-C)}$, $^{1}$H NMR ($CDCl_3$): δ/ppm 5.04-4.97(m, 1H, (HC=)); 3.38(d, $^{2}J_{HP}$ 11.25Hz, 3H, (OMe)); 2.66-2.53(m, 2H, (CH3CH2CH2CH2N)); 1.46(s, 3H, =C$CH_3$)); 1.51(s, 3H, (=C$CH_3$)); 2.00(d, $^{2}J_{HP}$ 10.00Hz, 1H, (NH)); 1.27-1.18(m, 2H, ($CH_3CH_2CH_2CH_2N$)); 1.16-0.99(m, 2H, ($CH_3CH_2CH_2CH_2N$)); 0.63(t, 3H, ($CH_3CH_2CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 16.8; yellow-red liquid, b.p. ($^{o}$C/0.5mmHg) uncorrected 138-140; Yield (%) 82.

*Methyl-P-3-methylbuta-1,2-dienyl-N-phenylphosphonamidate* **2c**. $C_{12}H_{16}NO_2P$; Calcd.: P 13.06, N 5.90 %; Found: P 13.00, N 5.88 %; IR: ν($cm^{-1}$) 1987 $_{(C=C=C)}$, 1264 $_{(P=O)}$, 980 $_{(P-O-C)}$, $^{1}$H NMR ($CDCl_3$): δ/ppm 7.29-7.17(m, 2H, (Ph)); 7.05(d, $^{2}J_{HH}$ 7.75Hz, 1H, (Ph)); 6.89(t, $^{2}J_{HH}$ 7.25Hz, 2H, (Ph)); 5.45-5.35(m, 1H, (HC=)); 4.03(d, $^{2}J_{HP}$ 11.5Hz, 1H, (NH)); 3.74(d, $^{3}J_{HP}$ 11.5Hz, 3H, OMe)); 1.46(s, 3H, =C$CH_3$)); 1.51(s, 3H, (=C$CH_3$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 17.0; cryst., m.p. ($^{o}$C) uncorrected 143-146, Yield (%) 80.

*Methyl-N-propyl-P-(3-methylpenta-1,2-dienyl)phosphonamidate* **2d**. $C_{10}H_{20}NO_2P$; Calcd.: P 14.26, N 6.44 %; Found: P 14.21, N 6.40 %; IR: ν ($cm^{-1}$) 1990 $_{(C=C=C)}$, 1258 $_{(P=O)}$, 980 $_{(P-O-C)}$, $^{1}$H NMR ($CDCl_3$): δ/ppm 5.04-4.97(m, 1H, (HC=)); 3.38(d, $^{2}J_{HP}$ 11.25Hz, 3H, (OMe)); 2.67-2.54(m, 2H, ($CH_3CH_2CH_2N$)); 1.82-1.68(m, 3H, (NH), ($CH_3CH_2$)); 1.49(dd, $^{3}J_{HH}$ 10,00Hz, $^{4}J_{HH}$ 3.53Hz, 3H, (=C$CH_3$)); 1.28-1.19(m, 2H, ($CH_3CH_2CH_2N$)); 0.77(dt, $^{2}J_{HH}$ 1.25Hz, 3H, ($CH_3CH_2$)); 0.91(t, 3H, ($CH_3CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 16.8; yellow-red liquid, b.p. ($^{o}$C /0.5 mmHg) uncorrected 137-139; Yield (% ) 87.

*Methyl-N-butyl-P-(3-methylpenta-1,2-dienyl)phosphonamidate* **2e**. $C_{11}H_{22}NO_2P$; Calcd.: P 13.39, N 6.05 %; Found: P 13.34, N 6.00 %; IR: ν ($cm^{-1}$) 1989 $_{(C=C=C)}$, 1260 $_{(P=O)}$, 980 $_{(P-O-C)}$, $^{1}$H NMR ($CDCl_3$): δ/ppm 5.04-4.97(m, 1H, (HC=)); 3.38(d, $^{2}J_{HP}$ 11.25Hz, 3H, (OMe)); 2.66-2.53(m, 2H, ($CH_3CH_2CH_2CH_2N$)); 1.82-1.68(m, 3H, (NH), ($CH_3CH_2$)); 1.49(dd, $^{3}J_{HH}$ 10,00Hz, $^{4}J_{HH}$ 3.53Hz, 3H, (=C$CH_3$)); 1.27-1.18(m, 2H, ($CH_3CH_2CH_2CH_2N$)); 1.16-0.99(m, 2H, ($CH_3CH_2CH_2CH_2N$)); 0.77(dt, $^{2}J_{HH}$ 1.25Hz, 3H, ($CH_3CH_2$)); 0.63(t, 3H, ($CH_3CH_2CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 17.3; yellow-red liquid, b.p. ($^{o}$C/0.5mmHg) uncorrected 142-145; Yield (%) 81.



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DOI: 10.1515/asn-2017-0002

*Methyl-P-3-methylpenta-1,2-dienyl-N-phenylphosphonamidate* **2f**. $C_{13}H_{18}NO_2P$; Calcd.: P 12.33, N 5.57 %; Found: P 12.29, N 5.52 %; IR: ν ($cm^{-1}$) 1992 $_{(C=C=C)}$, 1259 $_{(P=O)}$, 980 $_{(P-O-C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.29-7.17(m, 2H, (Ph)); 7.05(d, $^2J_{HH}$ 7.75Hz, 1H, (Ph)); 6.89(t, $^2J_{HH}$ 7.25Hz, 2H, (Ph)); 5.45-5.35(m, 1H, (HC=)); 4.03(d, $^2J_{HP}$ 11.5Hz, 1H, (NH)); 3.74(d, $^3J_{HP}$ 11.5Hz, 3H, OMe)); 1.98-1.75(m, 2H, ($CH_3CH_2$)); 1.64(dd, $^3J_{HH}$ 8.5Hz, $^4J_{HH}$ 3.25Hz, 3H, (=C$CH_3$)); 0.85(t, 3H, ($CH_3CH_2$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 16.9; cryst., m.p. ($^o$C) uncorrected 145-147, Yield (%) 81.

**Synthesis of compounds 3a-l**

**General Procedure:**

To a solution of 5*mmol* of the appropriate methyl-N-alkyl(phenyl)-(3-methylalk-1,2-dienyl)phosphonamidates (**2a-f**) in methylene chloride a solution of 5*mmol* of the appropriate electrophile ( PhSBr, PhSeBr) was added at low temperature (-12 to -10$^o$C). The solvent was then removed *in vacuo* and the residue was purified by chromatography (50*g* silicagel, hexane/ethylacetate 1:1.

*(5,5-Dimethyl-2-oxo-4-phenylsulfenyl-2,5-dihydro-2$^5$-[1,2]oxaphosphol-2-yl)-propylamine* **3a**. $C_{14}H_{20}NO_2PS$, Calcd.: P 10.42, N 4.71, S 10.78%, Found: P 10.40, N 4.68, S 10.72%; IR: ν ($cm^{-1}$) 1592 $_{(C=C)}$, 1259 $_{(P=O)}$, 1000 $_{(P-O-C)}$, $^1$H NMR ($CDCl_3$) δ/ppm: 7.56-7.46(m, 2H, (Ph)); 7.29-7.23(m, 3H, (Ph)); 5.35(dd, $^2J_{HP}$ 27.75Hz, $^3J_{HH}$ 3.75Hz, 1H, (HC=)); 2.54(m, 2H, ($CH_3CH_2CH_2N$)); 1.46(s, 3H, =C$CH_3$)); 1.51(s, 3H, (=C$CH_3$)); 2.00(d, $^2J_{HP}$ 10.00Hz, 1H, (NH)); 1.28-1.19(m, 2H, ($CH_3CH_2CH_2N$)); 0.91(t, 3H, ($CH_3CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 29.0; cryst., m.p. ($^o$C) uncorrected 113-116, Yield (%) 85.

*(5,5-Dimethyl-2-oxo-4-phenylsulfenyl-2,5-dihydro-2λ$^5$-[1,2]oxaphosphol-2-yl)-butylamine* **3b**. $C_{15}H_{22}NO_2PS$, Calcd.: P 9.95, N 4.50, S 10.30%, Found: P 9.91, N 4.48, S 10.28%; IR: ν ($cm^{-1}$) 1590 $_{(C=C)}$, 1260 $_{(P=O)}$, 1000 $_{(P-O-C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.64-7.60(m, 5H, (Ph)); 5.35(dd, $^2J_{HP}$ 27.75Hz, $^3J_{HH}$ 3.75Hz, 1H, (HC=)); 2.66-2.53(m, 2H, ($CH_3CH_2CH_2CH_2N$)); 2.00(d, $^2J_{HP}$ 10.00Hz, 1H, (NH)); 1.46(s, 3H, =C$CH_3$)); 1.51(s, 3H, (=C$CH_3$)); 1.27-1.18(m, 2H, ($CH_3CH_2CH_2CH_2N$)); 1.16-0.99(m, 2H, ($CH_3CH_2CH_2CH_2N$));0.63(t, 3H,($CH_3CH_2CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 28.9; cryst., m.p. ($^o$C) uncorrected 115-118, Yield (%) 84.

*(5,5-Dimethyl-2-oxo-4-phenylsulfenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-phenylylamine* **3c**. $C_{17}H_{18}NO_2PS$, Calcd.: P 9.35, N 4.22, S 9.68%, Found: P 9.33, N 4.19, S 9.65%; IR: ν ($cm^{-1}$) 1589 $_{(C=C)}$, 1257 $_{(P=O)}$, 1000 $_{(P-O-C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.63-7.59(m, 2H, (Ph)); 7.49-7.37(m, 3H, (Ph)); 7.26-7.18(m, 2H, (Ph)); 7.07-6. 95(m, 3H, (Ph)); 5.44(dd, $^2J_{HP}$ 28.05, $^3J_{HH}$ 5.00Hz, 1H, (HC=)); 1.46(s, 3H, =C$CH_3$)); 1.51(s, 3H, (=C$CH_3$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 30.0; cryst., m.p. ($^o$C) uncorrected 123-126, Yield (%) 82.

*(5-Ethyl-5-methyl-2-oxo-4-phenylsulfenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-propylamine* **3d**. $C_{15}H_{22}NO_2PS$, Calcd.: P 9.95, N 4.50, S 10.30%, Found: P 9.91, N 4.48, S 10.28%; IR: ν ($cm^{-1}$) 1592 $_{(C=C)}$, 1259 $_{(P=O)}$, 1000 $_{(P-O-C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.56-7.46(m, 2H, (Ph)); 7.29-7.23(m, 3H, (Ph)); 5.35(dd, $^2J_{HP}$ 27.75Hz, $^3J_{HH}$ 3.75Hz, 1H, (HC=)); 2.67-2.54(m, 2H, ($CH_3CH_2CH_2N$)); 1.82-1.68(m, 3H, (NH), ($CH_3CH_2$)); 1.49(dd, $^3J_{HH}$ 10,00Hz, $^4J_{HH}$ 3.53Hz, 3H, (=C$CH_3$)); 1.28-1.19(m, 2H, ($CH_3CH_2CH_2N$)); 0.77(dt, $^2J_{HH}$ 1.25Hz, 3H, ($CH_3CH_2$)); 0.91(t, 3H, ($CH_3CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 29.8; cryst., m.p. ($^o$C) uncorrected 114-116, Yield (%) 84.

*(5-Ethyl-5-methyl-2-oxo-4-phenylsulfenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-butylamine* **3e**. $C_{16}H_{24}NO_2PS$, Calcd.: P 9.52, N 4.30, S 9.85%, Found: P 9.50, N 4.28, S 9.81%; IR: ν ($cm^{-1}$) 1590 $_{(C=C)}$, 1260 $_{(P=O)}$, 1000 $_{(P-O-C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.64-7.60(m, 5H, (Ph)); 5.35(dd, $^2J_{HP}$ 27.75Hz, $^3J_{HH}$ 3.75Hz, 1H, (HC=)); 2.66-2.53(m, 2H,($CH_3CH_2CH_2CH_2N$)); 1.82-1.68(m, 3H, (NH), ($CH_3CH_2$)); 1.49(dd, $^3J_{HH}$ 10,00Hz, $^4J_{HH}$



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DOI: 10.1515/asn-2017-0002

3.53Hz, 3H, (=C$\underline{CH_3}$)); 1.27-1.18(m, 2H, ($CH_3CH_2\underline{CH_2}CH_2N$)); 1.16-0.99(m, 2H, ($CH_3\underline{CH_2}CH_2CH_2N$)); 0.77(dt, $^2J_{HH}$ 1.25Hz, 3H, ($\underline{CH_3}CH_2$)); 0.63(t, 3H, ($\underline{CH_3}CH_2CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 32.0; cryst., m.p. ($^o$C) uncorrected 116-118, Yield (%) 82.

*(5-Ethyl-5-methyl-2-oxo-4-phenylsulfenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-phenylylamine* **3f**. $C_{18}H_{20}NO_2PS$, Calcd.: P 8.97, N 4.05, S 9.22%, Found: P 8.94, N 4.00, S 9.22%; IR: ν ($cm^{-1}$) 1589 $_{(C=C)}$, 1257 $_{(P=O)}$, 1000 $_{(P\text{-}O\text{-}C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.63-7.59(m, 2H, (Ph)); 7.49-7.37(m, 3H, (Ph)); 7.26-7.18(m, 2H, (Ph)); 7.07-6. 95(m, 3H, (Ph)); 5.44(dd, $^2J_{HP}$ 28.05, $^3J_{HH}$ 5.00Hz, 1H, (HC=)); 1.98-1.75(m, 2H, ($CH_3\underline{CH_2}$)); 1.64(dd, $^3J_{HH}$ 8.5Hz, $^4J_{HH}$ 3.25Hz, 3H, (=C$\underline{CH_3}$)); 0.85(t, 3H, ($\underline{CH_3}CH_2$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 27.9; cryst., m.p. ($^o$C) uncorrected 125-127, Yield (%) 80.

*(5,5-Dimethyl-2-oxo-4-phenylselenenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-propylamine* **3g**. $C_{14}H_{20}NO_2PSe$, Calcd.: P 9.92, N 4.48%, Found: P 9.90, N 4.43%; IR: ν ($cm^{-1}$) 1592 $_{(C=C)}$, 1259 $_{(P=O)}$, 1000 $_{(P\text{-}O\text{-}C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.56-7.46(m, 2H, (Ph)); 7.29-7.23(m, 3H, (Ph)); 5.35(dd, $^2J_{HP}$ 27.75Hz, $^3J_{HH}$ 3.75Hz, 1H, (HC=)); 2.54(m, 2H, ($CH_3CH_2\underline{CH_2}N$)); 1.46(s, 3H, =C$\underline{CH_3}$)); 1.51(s, 3H, (=C$\underline{CH_3}$)); 2.00(d, $^2J_{HP}$ 10.00Hz, 1H, (N$\underline{H}$)); 1.28-1.19(m, 2H, ($CH_3\underline{CH_2}CH_2N$)); 0.91(t, 3H, ($\underline{CH_3}CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 29.7; cryst., m.p. ($^o$C) uncorrected 114-116, Yield (%) 84.

*(5,5-Dimethyl-2-oxo-4-phenylselenenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-butylamine* **3h**. $C_{15}H_{22}NO_2PSe$, Calcd.: P 9.49, N 4.29%, Found: P 9.45, N 4.23%; IR: ν ($cm^{-1}$) 1590 $_{(C=C)}$, 1260 $_{(P=O)}$, 1000 $_{(P\text{-}O\text{-}C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.64-7.60(m, 5H, (Ph)); 5.35(dd, $^2J_{HP}$ 27.75Hz, $^3J_{HH}$ 3.75Hz, 1H, (HC=)); 2.66-2.53(m, 2H, ($CH_3CH_2CH_2\underline{CH_2}N$)); 2.00(d, $^2J_{HP}$ 10.00Hz, 1H, (N$\underline{H}$)); 1.46(s, 3H, =C$\underline{CH_3}$)); 1.51(s, 3H, (=C$\underline{CH_3}$)); 1.27-1.18(m, 2H, ($CH_3CH_2\underline{CH_2}CH_2N$)); 1.16-0.99(m, 2H, ($CH_3\underline{CH_2}CH_2CH_2N$));0.63(t, 3H, ($\underline{CH_3}CH_2CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 30.5; cryst., m.p. ($^o$C ) uncorrected 119-120, Yield (%) 86.

*(5,5-Dimethyl-2-oxo-4-phenylselenenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-phenylylamine* **3i**. $C_{17}H_{18}NO_2PSe$, Calcd.: P 8.94, N 4.04%, Found: P 8.90, N 4.00%; IR: ν ($cm^{-1}$) 1589 $_{(C=C)}$, 1257 $_{(P=O)}$, 1000 $_{(P\text{-}O\text{-}C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.63-7.59(m, 2H, (Ph)); 7.49-7.37(m, 3H, (Ph)); 7.26-7.18(m, 2H, (Ph)); 7.07-6. 95(m, 3H, (Ph)); 5.44(dd, $^2J_{HP}$ 28.05, $^3J_{HH}$ 5.00Hz, 1H, (HC=)); 1.46(s, 3H, =C$\underline{CH_3}$)); 1.51(s, 3H, (=C$\underline{CH_3}$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 28.8; cryst., m.p. ($^o$C) uncorrected 124-126, Yield (%) 82.

*(5-Ethyl-5-methyl-2-oxo-4-phenylselenenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-propylamine* **3j**. $C_{15}H_{22}NO_2PSe$, Calcd.: P 9.49, N 4.29%, Found: P 9.45, N 4.23%; IR: ν ($cm^{-1}$) 1592 $_{(C=C)}$, 1259 $_{(P=O)}$, 1000 $_{(P\text{-}O\text{-}C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.56-7.46(m, 2H, (Ph)); 7.29-7.23(m, 3H, (Ph)); 5.35(dd, $^2J_{HP}$ 27.75Hz, $^3J_{HH}$ 3.75Hz, 1H, (HC=)); 2.67-2.54(m, 2H, ($CH_3CH_2\underline{CH_2}N$)); 1.82-1.68(m, 3H, ($\underline{NH}$), ($CH_3\underline{CH_2}$)); 1.49(dd, $^3J_{HH}$ 10,00Hz, $^4J_{HH}$ 3.53Hz, 3H, (=C$\underline{CH_3}$)); 1.28-1.19(m, 2H, ($CH_3\underline{CH_2}CH_2N$)); 0.77(dt, $^2J_{HH}$ 1.25Hz, 3H, ($\underline{CH_3}CH_2$)); 0.91(t, 3H, ($\underline{CH_3}CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 29.8; cryst., m.p. ($^o$C) uncorrected 115-117, Yield (%) 83.

*(5-Ethyl-5-methyl-2-oxo-4-phenylselenenyl-2,5-dihydro-2 λ$^5$-[1,2]oxaphosphol-2-yl)-butylamine* **3k**. $C_{16}H_{24}NO_2PSe$, Calcd.: P 9.10, N 4.11%, Found: P 9.06, N 4.08%; IR: ν ($cm^{-1}$) 1590 $_{(C=C)}$, 1260 $_{(P=O)}$, 1000 $_{(P\text{-}O\text{-}C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.64-7.60(m, 5H, (Ph)); 5.35(dd, $^2J_{HP}$ 27.75Hz, $^3J_{HH}$ 3.75Hz, 1H, (HC=)); 2.66-2.53(m, 2H,($CH_3CH_2CH_2\underline{CH_2}N$)) ; 1.82-1.68(m, 3H, ($\underline{NH}$), ($CH_3\underline{CH_2}$)); 1.49(dd, $^3J_{HH}$ 10,00Hz, $^4J_{HH}$ 3.53Hz, 3H, (=C$\underline{CH_3}$)); 1.27-1.18(m, 2H, ($CH_3CH_2\underline{CH_2}CH_2N$)); 1.16-0.99(m, 2H, ($CH_3\underline{CH_2}CH_2CH_2N$)); 0.77(dt, $^2J_{HH}$ 1.25Hz, 3H, ($\underline{CH_3}CH_2$)); 0.63(t, 3H, ($\underline{CH_3}CH_2CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 30.9; cryst., m.p. ($^o$C) uncorrected 120-122, Yield (%) 82.



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DOI: 10.1515/asn-2017-0002

*(5-Ethyl-5-methyl-2-oxo-4-phenylselenenyl-2,5-dihydro-2 $\lambda^5$-[1,2]oxaphosphol-2-yl)-phenylylamine* **3l**. $C_{18}H_{20}NO_2PSe$, Calcd.: P 8.59, N 3.88%, Found: P 8.55, N 3.85%; IR: ν ($cm^{-1}$) 1589 $_{(C=C)}$, 1257 $_{(P=O)}$, 1000 $_{(P-O-C)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.63-7.59(m, 2H, (Ph)); 7.49-7.37(m, 3H, (Ph)); 7.26-7.18(m, 2H, (Ph)); 7.07-6. 95(m, 3H, (Ph)); 5.44(dd, $^2J_{HP}$ 28.05, $^3J_{HH}$ 5.00Hz, 1H, (HC=)); 1.98-1.75(m, 2H, ($CH_3\underline{CH_2}$)); 1.64(dd, $^3J_{HH}$ 8.5Hz, $^4J_{HH}$ 3.25Hz, 3H, (=C$\underline{CH_3}$)); 0.85(t, 3H, ($\underline{CH_3}CH_2$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 31.7; cryst., m.p. ($^o$C) uncorrected 127-129, Yield (%) 81.

**Synthesis of compounds 4a-f**

**General Procedure:**

To a solution of 5*mmol* of the appropriate methyl-N-alkyl(phenyl)-(3-methylalk-1,2-dienyl)phosphonamidates (**2a-f**) in methylene chloride a solution of 5*mmol* of dialkylamine was added at -8$^o$C. After warm up to room temperature and additional stirring for an hour, 10% aqueous HCl was added. The organic phase was separated and the residue was extracted with $CHCl_3$. The organic phases were dried with $MgSO_4$, the solvent was then removed *in vacuum* and the residue was distilled.

*Methyl-P-(3-methyl-2-oxobuty)-N-propylphosphonamidate* **4a** $C_8H_{20}NO_3P$; Calcd.: P 14.66, N 6.63 %; Found: P 14.49, N 6.52 %; IR: ν ($cm^{-1}$) 1238 $_{(P=O)}$, 1700 $_{(C=O)}$, $^1$H NMR ($CDCl_3$): δ/ppm 3.78(d, $^3J_{HP}$ 10.09Hz, 3H, (O$\underline{Me}$)); 2.56(t, $^2J_{HH}$ 6.8Hz, 1H, (C$\underline{H}$)), 2.63(t, $^2J_{HH}$ 7.1Hz, 2H, ($CH_3CH_2\underline{CH_2}N$)); 2.50(d, $^2J_{HP}$ 11.9Hz, 2H ($C\underline{H_2}$)); 1.04(d, $^2J_{HH}$ 6.8Hz, 6H, =C($\underline{CH_3}$)$_2$); 3.69(m, 1H, (N$\underline{H}$)); 1.60(q, $^2J_{HH}$ 7.1Hz, $^3J_{HH}$ 8.0Hz, 2H, ($CH_3\underline{CH_2}CH_2N$)); 0.87(t, $^2J_{HH}$ 8.0Hz, 3H, ($\underline{CH_3}CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 18.1; oil; Yield (%) 85.

*Methyl-P-(3-methyl-2-oxopentyl)-N-propylphosphonamidate* **4b**. $C_9H_{21}NO_3P$; Calcd.: P 13.93, N 6.30 %; Found: P 13.81, N 6.25 %; IR: ν ($cm^{-1}$) 1260 $_{(P=O)}$, 1690 $_{(C=O)}$, $^1$H NMR ($CDCl_3$): δ/ppm 3.78(d, $^2J_{HP}$ 10.9Hz, 3H, (O$\underline{Me}$)); 3.69 (m, 1H (N$\underline{H}$)); 2.84(d, $^2J_{HP}$ 11.9Hz,2H ($C\underline{H_2}$)); 2.63(t, $^2J_{HH}$ 7.1Hz, 2H, ($CH_3CH_2C\underline{H_2}N$)); 2.36(q, $^2J_{HH}$7.0Hz, $^3J_{HH}$ 6.8Hz 1H (CH)); 1.06(q, $^2J_{HH}$ 7.0Hz, $^2J_{HH}$ 8.0Hz, 2H($CH_3C\underline{H_2}CH_2N$));1.68 (q, $^2J_{HH}$ 7.0Hz, $^2J_{HH}$ 8.0Hz, 2H ($CH_3C\underline{H_2}$)); 1.04 (d, $^2J_{HH}$ 6.8Hz, 3H ($C\underline{H_3}$)); 0.94 (t, $^2J_{HH}$ 8.0Hz, 3H ($C\underline{H_3}CH_2$)); 0.84 (t, $^2J_{HH}$ 8.0Hz, 3H ($C\underline{H_3}CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 16.8; oil; Yield (%) 82.

*Methyl -P-(3-methyl-2-oxobutyl)-N-butyl phosphonamidate* **4c**. $C_{10}H_{21}NO_3P$; Calcd.: P 13.22, N 5.98 %; Found: P 13.19, N 5.82 %; IR: ν ($cm^{-1}$) 1238 $_{(P=O)}$, 1700 $_{(C=O)}$, $^1$H NMR ($CDCl_3$): δ/ppm 3.78(d, $^3J_{HP}$ 10.09Hz, 3H, (O$\underline{Me}$)); 2.56(t, $^2J_{HH}$ 6.8Hz, 1H, (C$\underline{H}$)); 2.63(t, $^2J_{HH}$ 7.1Hz, 2H, ($CH_3CH_2CH_2C\underline{H_2}N$)); 2.50(d, $^2J_{HP}$ 11.9Hz, 2H ($C\underline{H_2}$)); 1.04(d, $^2J_{HH}$ 6.8Hz, 6H, CH($\underline{CH_3}$)$_2$); 3.69(m, 1H, (NH); 1.52(q, $^2J_{HH}$ 7.0Hz, $^2J_{HH}$ 6.8 Hz, 2H($CH_3CH_2C\underline{H_2}CH_2N$)); 1.30 (q, $^2J_{HH}$ 7.1Hz, $^2J_{HH}$ 8.0Hz, 2H ($CH_3C\underline{H_2}CH_2CH_2N$)); 0.89 (t, $^2J_{HH}$ 8.0Hz, 3H ($C\underline{H_3}CH_2CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 17.1; oil; Yield (%) 85.

*Methyl- P-(3-methyl-2-oxopentyl) -N-butylphosphonamidate* **4d**. $C_{11}H_{23}NO_3P$; Calcd.: P 12.47, N 5.63%; Found: P 12.35, N 5.44; IR: ν ($cm^{-1}$) 1259 $_{(P=O)}$, 1700 $_{(C=O)}$, $^1$H NMR ($CDCl_3$): δ/ppm 3.78(d, $^2J_{HP}$ 10.9Hz, 3H, (O$\underline{Me}$)); 3.69 (m, 1H (N$\underline{H}$)); 2.84(d, $^2J_{HP}$ 11.9Hz,2H ($C\underline{H_2}$)); 2.63(t, $^2J_{HH}$ 7.1Hz, 2H, ($CH_3CH_2CH_2C\underline{H_2}N$)); 2.36(q, $^2J_{HH}$7.0Hz, $^3J_{HH}$ 6.8Hz 1H (CH)); 1.52(q, $^2J_{HH}$ 7.0Hz, $^2J_{HH}$ 6.8 Hz, 2H($CH_3CH_2C\underline{H_2}CH_2N$));1.68 (q, $^2J_{HH}$ 7.0Hz, $^2J_{HH}$ 8.0Hz, 2H ($CH_3C\underline{H_2}$)); 1.30 (q, $^2J_{HH}$ 7.1Hz, $^2J_{HH}$ 8.0Hz, 2H ($CH_3C\underline{H_2}CH_2CH_2N$)); 1.04 (d, $^2J_{HH}$ 6.8Hz, 3H ($C\underline{H_3}$)); 0.94 (t, $^2J_{HH}$ 8.0Hz, 3H ($C\underline{H_3}CH_2$)); 0.89 (t, $^2J_{HH}$ 8.0Hz, 3H ($C\underline{H_3}CH_2CH_2CH_2N$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 16.8; oil ; Yield (%) 82.

*Methyl- P-(3-methyl-2-oxobutyl)-N-phenylphosphonamidate* **4e**. $C_{12}H_{17}NO_3P$; Calcd.: P 12.18, N 5.50 %; Found: P 12.09, N 5.43 %; IR: ν ($cm^{-1}$) 1259 $_{(P=O)}$, 1700 $_{(C=O)}$, $^1$H NMR ($CDCl_3$): δ/ppm 3.38(d, $^2J_{HP}$ 11.25Hz, 3H, (OMe)); 7.29-7.17(m, 2H, (Ph)); 7.05(d, $^2J_{HH}$ 7.75Hz, 1H, (Ph)); 6.89(t, $^2J_{HH}$ 7.25Hz, 2H, (Ph)); 6.70(m, 1H, ($\underline{NH}$); 1.49(dd, $^3J_{HH}$ 10,00Hz, $^4J_{HH}$ 3.53Hz, 6H, (CH$\underline{CH_3}$)); 2.56(t, $^2J_{HH}$ 6.8Hz, 1H, (C$\underline{H}$)); 2.84(d, $^2J_{HP}$ 11.9Hz, 2H ($C\underline{H_2}$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 17.3; oil; Yield (%) 81.



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DOI: 10.1515/asn-2017-0002

*Methyl- P-(3-methyl-2-oxopentyl)-N-phenylphosphonamidate* **4f**. $C_{13}H_{19}NO_2P$; Calcd.: P 11.54, N 5.22 %; Found: P 11.29, N 5.12 %; IR: ν ($cm^{-1}$) 1259 $_{(P=O)}$, 1700 $_{(C=O)}$, $^1$H NMR ($CDCl_3$): δ/ppm 7.29-7.17(m, 2H, (Ph)); 7.05(d, $^2J_{HH}$ 7.75Hz, 1H, (Ph)); 6.89(t, $^2J_{HH}$ 7.25Hz, 2H, (Ph)); 6.70(m, 1H, (NH); 3.74(d, $^3J_{HP}$ 11.5Hz, 3H, OMe)); 1.68 (q, $^2J_{HH}$ 7.0Hz, $^2J_{HH}$ 8.0Hz, 2H ($CH_3C\underline{H}_2$)); 1.04 (d, $^2J_{HH}$ 6.8Hz, 3H ($C\underline{H}_3$)); 0.94 (t, $^2J_{HH}$ 8.0Hz, 3H ($C\underline{H}_3CH_2$)); 2.56(t, $^2J_{HH}$ 6.8Hz, 1H, (C<u>H</u>)); 2.84(d, $^2J_{HP}$ 11.9Hz, 2H ($C\underline{H}_2$)); $^{31}$P NMR($CDCl_3$) δ/ppm: $^{31}$P 16.9; oil; Yield (%) 84.

**Acknowledgement**
The authors are indebted to Prof. S. Simova and to all the staff of the National Centre of NMR Spectroscopy, Bulgarian Academy of Sciences.

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DOI: 10.1515/asn-2017-0002