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Organophosphorus Compounds. Part 144:[1] A Novel Approach to 1,3-Oxaphospholes from Phosphaalkynes and Isomünchnones

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Dedicated to Professor Manfred Meisel on the occasion of his 60th birthday

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Abstract—Phosphaalkynes **5** react with the isomünchnones **12** in a regiospecific process to furnish the 1,3-oxaphospholes **14**. In contrast to other cycloadditions to isomünchnones, the bicyclic intermediate **13** cannot be detected in these reactions. It is not necessary to use isolated isomünchnones **12** for the synthesis of the 1,3-oxaphospholes. The reaction sequence is also successful by use of the diazocarbonyl compounds **11** and in situ generation of the isomünchnones therefrom.

Introduction

The 1,3-oxaphospholes represent a rather poorly investigated class of compounds at present. Only three different approaches to the 1,3-oxaphospholes have as yet been described. The first synthesis of benzo-condensed 1,3-oxaphospholes was reported by Heinicke and Tzschach[2] in 1985 and involved the reaction of the 2-hydroxyphenylphosphane **1** with the imidoyl chlorides **2**.

In 1993 Dötz described a synthesis for the 1,3-oxaphospholes **6** without a condensed benzene ring in which the phosphaalkyne **5** was allowed to react with various chromium-carbene complexes such as **4**.[3,4] In most cases the reaction did not furnish the 1,3-oxaphospholes selectively and the yields were accordingly relatively poor (up to 35%).

Just recently, Mack and Ruf obtained the bicyclic 1,3-oxaphospholes **8** by catalytic elimination of nitrogen from the diazo compounds **7** in the presence of the phosphaalkyne **5**.[5] The mechanism of this reaction can be explained in terms of a rearrangement of a phosphirene formed as an intermediate.[6] (Scheme 1)

When we consider the well-investigated reactivity of the phosphaalkyne **5** towards various mesoionic compounds such as münchnones and sydnones,[7] it is reasonable to assume that the isomünchnones **12**, which have a carbonyl ylide dipole form in their mesoionic system, will also undergo a [3+2] cycloaddition reaction (**→13**) with subsequent cleavage of isocyanate (**→14**) in the presence of **5**.

Synthesis of Isomünchnones 12

The 2-diazomalonic ester chlorides **10** play a key role in our newly developed synthesis of isomünchnones, their synthesis was first described by Padwa.[8] The reaction of **10** with the *N*-phenylcarboxamides **9**—in deprotonated form after treatment with a strong base such as *n*-BuLi—at −78°C in THF as solvent leads to the diazocarbonyl compounds **11** which can be isolated in yields of up to 36% by aqueous work-up of the reaction mixture. However, since most of the products **11** are oily substances that cannot be purified by crystallization and decompose readily on chromatographic work-up, they are used in the next steps without further purification. (Scheme 2)

When the diazocarbonyl compounds **11d**–**h** are heated with a small amount of rhodium acetate—which acts as a catalyst—in toluene at 100°C the isomünchnones **12d**–**h** can be isolated in yields of up to 49% after a reaction time of 30 m. Completion of the reaction can be determined precisely by IR spectroscopic monitoring of the reaction mixture. The isomünchnones are obtained as light yellow, crystalline solids simply by evaporating the reaction mixture. Some of them are obtained in analytically pure form by repeated washings with *n*-pentane and ether. With regard to yields and reaction times, this catalytic synthesis of isomünchnones is clearly superior to the synthesis of **12f** previously described by Grub, which involved the thermolysis of **11f** for several hours.[9] From the point of view of the mechanism, the formation of the isomünchnones **12** proceeds in two steps: after catalytic cleavage of nitrogen

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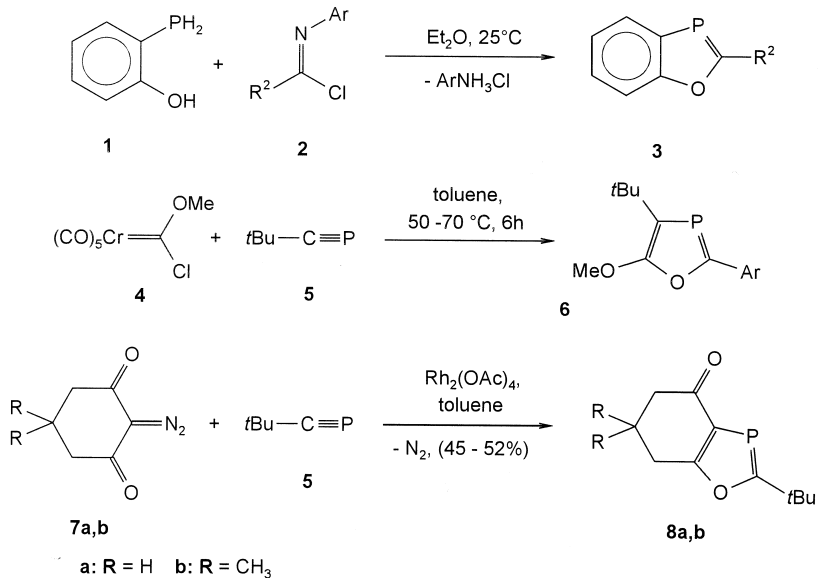
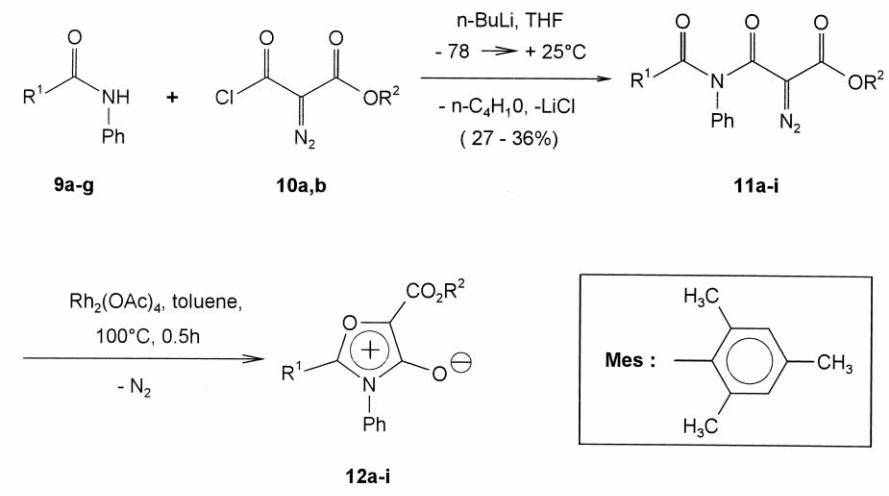


Scheme 1.

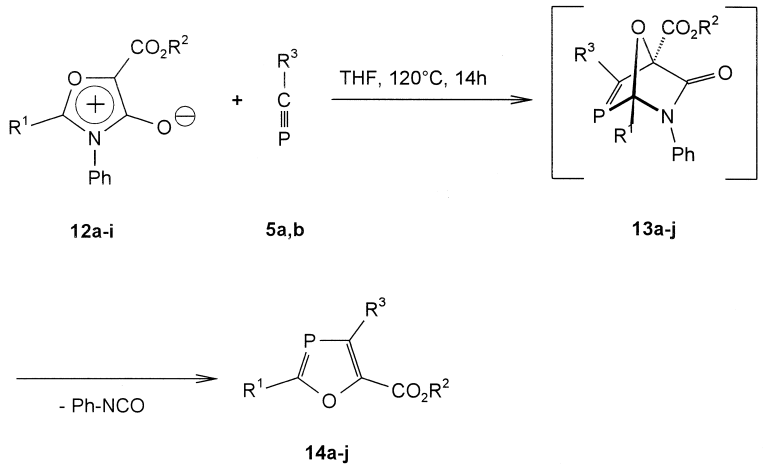


9 **a:** R^1 = Ph **b:** R^1 = C_6H_4-OCH_3-*p* **c:** R^1 = C_6H_4-C_2H_5-*p*
d: R^1 = 1-$C_{10}H_7$ **e:** R^1 = 2-$C_{10}H_7$ **f:** R^1 = Mes
g: R^1 = C_6H_4-CH_3-*p*

10 **a:** R^2 = Me **b:** R^2 = Et

11,12	**a:**	R^1 = Ph	R^2 = Me	**b:**	R^1 = C_6H_4-OCH_3-*p*	R^2 = Me
	c:	R^1 = C_6H_4-C_2H_5-*p*	R^2 = Me	**d:**	R^1 = 1-$C_{10}H_7$	R^2 = Me
	e:	R^1 = 2-$C_{10}H_7$	R^2 = Me	**f:**	R^1 = Ph	R^2 = Et
	g:	R^1 = Mes	R^2 = Et	**h:**	R^1 = C_6H_4-OCH_3-*p*	R^2 = Et
	i:	R^1 = C_6H_4-CH_3-*p*	R^2 = Et			

Scheme 2.



12a-i 5a,b 13a-j

14a-j

5	**a:**	$\mathbf{R^3}$=*t*Bu	**b:**	$\mathbf{R^3}$=*t*Pen
13,14	**a:**	$\mathbf{R^1}$=Ph	$\mathbf{R^2}$=Me	$\mathbf{R^3}$=*t*Bu
	b:	$\mathbf{R^1}$=C_6H_4-OCH_3-*p*	$\mathbf{R^2}$=Me	$\mathbf{R^3}$=*t*Bu
	c:	$\mathbf{R^1}$=C_6H_4-C_2H_5-*p*	$\mathbf{R^2}$=Me	$\mathbf{R^3}$=*t*Bu
	d:	$\mathbf{R^1}$=1-$C_{10}H_7$	$\mathbf{R^2}$=Me	$\mathbf{R^3}$=*t*Bu
	e:	$\mathbf{R^1}$=2-$C_{10}H_7$	$\mathbf{R^2}$=Me	$\mathbf{R^3}$=*t*Bu
	f:	$\mathbf{R^1}$=Ph	$\mathbf{R^2}$=Et	$\mathbf{R^3}$=*t*Bu
	g:	$\mathbf{R^1}$=Mes	$\mathbf{R^2}$=Et	$\mathbf{R^3}$=*t*Bu
	h:	$\mathbf{R^1}$=C_6H_4-OCH_3-*p*	$\mathbf{R^2}$=Et	$\mathbf{R^3}$=*t*Bu
	i:	$\mathbf{R^1}$=C_6H_4-CH_3-*p*	$\mathbf{R^2}$=Et	$\mathbf{R^3}$=*t*Bu
	j:	$\mathbf{R^1}$=Ph	$\mathbf{R^2}$=Et	$\mathbf{R^3}$=*t*Pen

Scheme 3.

from the diazo group, an intermediate rhodium carbenoid is formed and is nucleophilically attacked by the carbonyl oxygen of the benzoyl group with formation of the mesoionic five-membered ring system.[10] The isomünchnones **12** are uniquely characterized by the ^{13}C NMR signals for the three carbon atoms of the mesoionic five-membered ring which appear in the regions between δ=150 to 160 (C2, C4) and δ=116 to 120 (C5). In addition, the constitutions of products **12** were confirmed by mass spectrometry.

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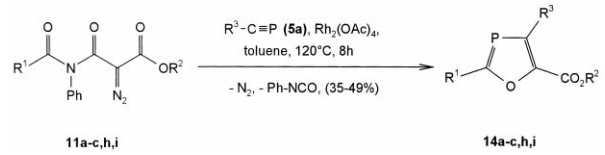
Isomünchnones as starting materials

When the thus prepared isomünchnones **12d–h** are heated with the phosphaalkynes **5a,b** in a pressure-Schlenk tube for 14 h at 120°C under an argon overpressure of 5 bar, the 1,3-oxaphospholes **14d–h,j** are formed regiospecifically and in very good yields. The bicyclic intermediates **13d–h,j** are presumably formed in the first step of this 1,3-dipolar cycloaddition process but cannot be detected by NMR spectroscopy. They apparently decompose immediately in a *retro-Diels-Alder reaction* with cleavage of phenyl isocyanate to furnish the 1,3-oxaphospholes **14d–h,j**. Separation of the 1,3-oxaphospholes from the also formed phenyl isocyanate is easily achieved by washing the residue obtained after evaporation of the reaction mixture with *n*-pentane, since the phenyl isocyanate forms a dimer that is poorly soluble in pentane under the prevailing reaction conditions.[11] The constitutions of the 1,3-oxaphospholes **14** were confirmed by NMR and mass spectrometry as well as by elemental analyses. Thus, for example, the respective ^{31}P NMR signals appear between δ=106 and 127, the region typical for monocyclic 1,3-oxaphospholes.[4] The structures of the 1,3-oxaphospholes were elucidated by ^{13}C NMR spectroscopy: accordingly, the ^{13}C NMR spectrum of compound **14f** contains three characteristic signals for the carbon atoms of the five-membered oxaphosphole ring at δ=192.2, 163.3, and 144.3. The first two signals exhibit couplings of phosphorus of 55.6 and 53.4 Hz, i.e. with a magnitude typical for $^1J_{C,P}$ couplings; thus the respective carbon atoms must be directly bound to the phosphorus atom. On account of the chemical environment the ^{13}C NMR signal at δ=192.2 can be unequivocally assigned to C2. In the proton-coupled ^{13}C NMR spectrum of **14f** the doublet signal at δ=192.2 reveals a further triplet structure with a coupling constant of 4.6 Hz resulting from long-range couplings with the *ortho*-protons of the aromatic substituent



Scheme 4.

at C2. These results confirm the 1,3-oxaphosphole structures of products **14**. (Scheme 3)

The regiochemistry of this 1,3-dipolar cycloaddition is rather surprising. On consideration of the charge distribution in the isomünchnone system and the polarity of the P/C triple bond it is clear that this 1,3-dipolar cycloaddition does not proceed under charge control. However, when the reactivity of the isomünchnones **12** with the phosphaalkynes **5** is considered in comparison with the corresponding reactions of sydnones and münchnones,[7] clear parallels can be seen with regard to the reaction conditions.

In situ generation of the isomünchnones 12

In the chemistry of mesoionic compounds many synthetic methods are based on the in situ generation of the mesoionic dipole.[12] Thus, the question arises as to whether such a procedure can be applied in the synthesis of the 1,3-oxaphospholes **14**.

When the diazocarbonyl compounds **11a**–**c,h,i** are heated at 120°C for 8 h in the presence of the phosphaalkyne **5a** and $Rh_2(OAc)_4$ as catalyst the 1,3-oxaphospholes **14a**–**c,h,i** are the sole products that can be isolated. The products obtained by the two synthetic routes are identical in all respects, as was demonstrated for compound **14h**. The yields in this process reach about 49% and thus are comparable with the total yields of the 1,3-oxaphospholes obtained in the syntheses involving the isolated isomünchnones **12d**–**h**. It would seem in both cases that the yield-determining step is the formation of the isomünchnones **12**. It is also worthy of note that the direct synthesis of the 1,3-oxaphosphole from the diazocarbonyl compounds **11** requires appreciably shorter reaction times.

The 1,3-oxaphospholes **14a**–**c,h,i** prepared in this way were isolated by column chromatography using an *n*-pentane/ether mixture as eluant. (Scheme 4)

The catalytic elimination of nitrogen from the diazo group and the resulting formation of the isomünchnone systems **12a**–**c,h,i** proceeds markedly more rapidly than the feasible competing reaction of 1,3-dipolar cycloaddition of the diazo group to the phosphaalkyne **5**. This result is in complete harmony with previously performed reactivity studies on the 1,3-dipolar cycloaddition of diazocarbonyl compounds to phosphaalkynes.[13]

The structures postulated above for the 1,3-oxaphospholes **14** on the basis of their ^{13}C NMR data were irrevocably confirmed by an X-ray crystallographic analysis of product **14b** (see Fig. 1).

In the crystal state the heterocyclic compound **14b** is characterized by a completely planar structure. Thus, the five-membered ring skeleton together with the aromatic substituents lies in one plane. Not only this planar structure but also the measured bond lengths are indicative of a delocalized π-electron system (see Table 1). The measured bond length of the phosphaalkene increment between P1 and C1 of 1.718(3) Å is somewhat stretched in comparison to typical P/C double bond lengths.[15] On the other hand, the P/C single bond length between P1 and C1 of merely 1.785(2) Å is markedly shortened. The value given in the literature for a P/C single bond not incorporated in a delocalized system is 1.86 Å.[15]

Table 1. Selected bond distances [Å] and angles [°] of **14b**

P(1)-C(1)	1.785(2)	C(3)-P(1)-C(1)	88.97(11)
P(1)-C(3)	1.718(3)	C(3)-O(1)-C(2)	112.0(2)
O1-C2	1.372(3)	C(2)-C(1)-P(1)	121.6(2)
O(1)-C(3)	1.352(3)	C(1)-C(2)-O(1)	114.9(2)
C(1)-C(2)	1.371(3)	O(1)-C(C3)-P(1)	114.4(2)

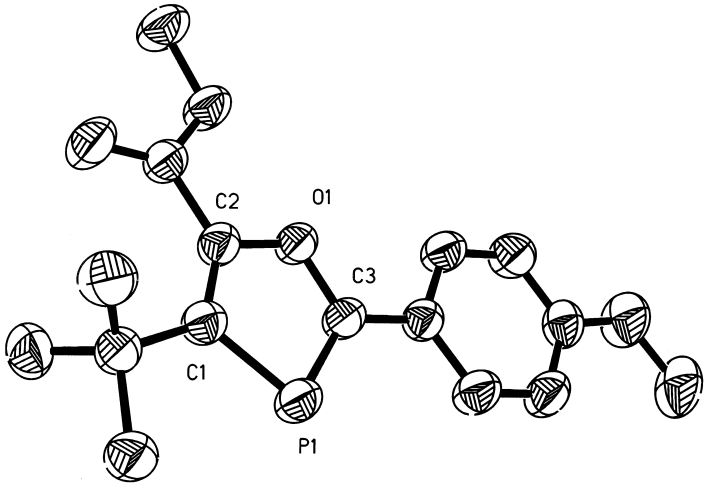


Figure 1. X-ray plot and numbering of atoms of **14b**. (Molecular Graphics from SHELXTL-Plus[14] software package; thermal ellipsoids were drawn at the 33% probability level. Hydrogen atoms were omitted for reasons of clarity.)

The double bond length between the carbon atoms C1 and C2 amounts to 1.371(0) Å and is also somewhat stretched. However, this value is still clearly smaller than the length of 1.40 Å reported for C/C single bonds in phosphabenzenes.[16]

The results of our X-ray crystallographic analysis of the 1,3-oxaphosphole **14b** are in good agreement with the values for other 1,3-oxaphosphole systems reported in the literature.[4]

Conclusion

The 1,3-dipolar cycloaddition reactions of isomünchnones **12** with phosphaalkynes **5** described here open a new, simple, and selective access to the monocyclic 1,3-oxaphospholes **14**. It is not necessary to isolate the isomünchnones **12** since the reaction sequence starting from the diazocarbonyl compounds **11** incorporates the in situ generation of compounds **12** and is equally successful. Since the reactions of 1,3-oxaphospholes without a condensed ring have not been reported in the literature, the present method provides the starting point for further studies on the reactivity of such 1,3-oxaphospholes.

Experimental

All reactions were carried out under argon (purity >99.998%) atmosphere using Schlenk techniques. The solvents were dried by standard procedures, distilled, and stored under argon prior to use. Compounds **9** and **10** were prepared by published methods.[8,17] Column chromatography was performed in water-cooled glass tubes under argon. Silica gel was heated for 3 h in vacuo and then deactivated with 4% water (Brockmann activity II). Melting points were determined on a Mettler FP61 apparatus (heating rate 2°C/min) and are uncorrected. Microanalyses were performed with a Perkin-Elmer Analyzer 2400. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AC 200 and Bruker AMX 400 spectrometers and referenced to the solvent as internal standard. ^{31}P NMR spectra were measured on a Bruker AC 200 (80.8 MHz) spectrometer with 85% H_3PO_4 as external standard. MS and HRMS were recorded on a Finnigan MAT 90 spectrometer at 70 eV ionization voltage. IR spectra were measured on a Perkin-Elmer 16 PC FT-IR spectrophotometer.

Alkyl 3-(*N*-aroyl-*N*-phenylamino)-2-diazo-3-oxopropanoates (11a–i)—general procedure. The appropriate aromatic *N*-phenylcarboxamides **9** (20 mmol) were dissolved in 50 ml of THF, the solutions were cooled to −78°C), and treated dropwise with 12.5 ml of a 1.6 M solution of *n*-BuLi in *n*-hexane during 1 h. Stirring was continued for 30 m more at −78°C and then the 2-diazomalonyl chloride ester **10** (20 mmol) was added dropwise to the mixture. The reaction mixture was allowed to warm to RT over a period of 24 h. Then the solvent was removed in vacuo and the residue was dissolved in ether. The organic layer was washed twice with a saturated NH_4Cl solution and then with water. The organic layer was separated, dried over $MgSO_4$, and the solvent removed. The thus isolated products were used without further purification.

Methyl 3-(*N*-benzoyl-*N*-phenylamino)-2-diazo-3-oxopropanoate (11a). Yield: 2.26 g (35%); IR ($CHCl_3$) ν 1664 (vs, CO), 2131 (vs, CN_2) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 3H, $-CO_2CH_3$), 7.10–7.95 (m, 10H, aryl-H); $C_{17}H_{13}N_3O_4$ (323.30).

Methyl 2-diazo-3-[*N*-(4-methoxybenzoyl)-*N*-phenylamino]-3-oxopropanoate (11b). Yield: 2.50 g (36%); IR ($CHCl_3$) ν 1669 (vs, CO), 2131 (vs, CN_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.77, 3.92 (each s, 3H, $-OCH_3$, $-CO_2CH_3$) 6.95–8.0 (m, 9H, aryl-H); $C_{18}H_{15}N_3O_5$ (353.33).

Methyl 2-diazo-3-[*N*-(4-ethylbenzoyl)-*N*-phenylamino]-3-oxopropanoate (11c). Yield: 2.16 g (31%); IR ($CHCl_3$) ν 1672 (vs, CO), 2128 (vs, CN_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1,24 (t, 3H, $^{3}J_{H,H}$=7.2 Hz, $-CH_2CH_3$), 2.59 (q, 2H, $^{3}J_{H,H}$=7.2 Hz, $-CH_2CH_3$), 3.70 (s, 3H, $-CO_2CH_3$), 7.00–7.90 (m, 9H, aryl-H); $C_{19}H_{15}N_3O_4$ (349.34).

Methyl 2-diazo-3-[*N*-(1-naphthoyl)-*N*-phenylamino]-3-oxopropanoate (11d). Yield: 2.46 g (33%); IR ($CHCl_3$) ν 1676 (vs, CO), 2136 (vs, CN_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 3H, $-CO_2CH_3$), 6.95–8.15 (m, 12H, aryl-H); $C_{21}H_{15}N_3O_4$ (373.36).

Methyl 2-diazo-3-[*N*-(2-naphthoyl)-*N*-phenylamino]-3-oxopropanoate (11e). Yield: 2.54 g (34%); IR ($CHCl_3$) ν 1674 (vs, CO), 2134 (vs, CN_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 3H, $-CO_2CH_3$), 7.00–8.36 (m, 12H, aryl-H); $C_{21}H_{15}N_3O_4$ (373.36).

Ethyl 3-(*N*-benzoyl-*N*-phenylamino)-2-diazo-3-oxopropanoate (11f). Yield: 2.26 g (35%); $C_{18}H_{17}N_3O_4$ (337.33); Analytical data are identical to those given in the literature.[9]

Ethyl 2-diazo-3-oxo-3-[*N*-(2,4,6-trimethylbenzoyl)-*N*-phenylamino]-propanoate (11g). Yield: 2.26 g (35%); IR ($CHCl_3$) ν 1672 (vs, CO), 2130 (vs, CN_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (t, 3H, $^{3}J_{H,H}$=7.2 Hz, $-CH_2-CH_3$), 2.15 (s, 3H, *p*-CH_3), 2.26 (s, 6H, *o*-CH_3), 4.20 (q, 2H, $^{3}J_{H,H}$=7.2 Hz, $-CH_2-CH_3$), 6.85 (s, 2H, aryl-H, Mes), 7.01–7.65 (m, 5H, aryl-H); $C_{21}H_{17}N_3O_4$ (379.41).

Ethyl 2-diazo-3-[*N*-(4-methoxybenzoyl)-*N*-phenylamino]-3-oxopropanoate (11h). Yield: 2.13 g (29%); IR ($CHCl_3$) ν 1678 (vs, CO), 2133 (vs, CN_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3H, $^{3}J_{H,H}$=7.0 Hz, $-CH_2-CH_3$), 3.75 (s, 3H, $-OCH_3$), 4.27 (q, 2H, $^{3}J_{H,H}$=7.0 Hz, $-CH_2-CH_3$), 6.95–7.91 (m, 9H, aryl-H); $C_{19}H_{17}N_3O_4$ (351.36).

Ethyl 2-diazo-3-[*N*-(4-methylbenzoyl)-*N*-phenylamino]-3-oxo-propanoate (11i). Yield: 1.89 g (27%); IR ($CHCl_3$) ν 1668 (vs, CO), 2134 (vs, CN_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (t, 3H, $^{3}J_{H,H}$=6.9 Hz, $-CH_2-CH_3$), 2.35 (s, 3H, *p*-CH_3), 4.27 (q, 2H, $^{3}J_{H,H}$=6.9 Hz, $-CH_2-CH_3$), 7.0–7.91 (m, 9H, aryl-H); $C_{19}H_{17}N_3O_5$ (367.36).

5-Alkoxycarbonyl-2-aryl-3-phenyl-1,3-oxazolium-4-olates (12d–h)—general procedure. The diazocarbonyl

compounds **11d**–**h** were dissolved in 50 ml toluene and $Rh_2(OAc)_4$ (1 mol%) as catalyst was added. The reaction flask was placed in an oil bath preheated to 100°C. The evolution of nitrogen was usually finished after 0.5 h, the end of the reaction is easily recognized by monitoring the reaction mixture with IR (disappearance of the diazo-band). After evaporation of the solvent and washing the residue three times with pentane and ether (10 ml) the isomünchnones **12d**–**i** were isolated as yellow solids.

5-Methoxycarbonyl-2-(1-naphthyl)-3-phenyl-1,3-oxazolium-4-olate (12d). Yield: 400 mg (43%); mp 178°C; IR ($CHCl_3$) ν 1686 (vs, CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.92 (s, 3H, $-CH_3$), 7.22–8.03 (m, 12H, aryl-H); ^{13}C NMR ($CDCl_3$) δ 51.3 (s, $-CH_3$), 118.7 (s, C5), 118.9, 124.1, 124.5, 126.2, 127.4, 128.9, 129.0, 129.7, 129.9, 130.0, 130.5, 131.2, 133.5, 134.2 (each s, aryl-C), 152.7, 155.9 (each s, C2, C4), 159.8 (s, $-CO_2Et$); MS: (EI, 70 eV) *m/z* 345 (11.6) $[M]^+$, 230 (50.5) $[C_{17}H_{12}N]^+$, 155 (100) [2-Naph-CO]$^+$, 127 (44.6) $[C_{10}H_7]^+$, 77 (16.4) $[C_6H_5]^+$, 51 (3.8) $[C_4H_3]^+$; $C_{21}H_{15}NO_4$ (345.36).

5-Methoxycarbonyl-2-(2-naphthyl-)-3-phenyl-1,3-oxazolium-4-olate (12e). Yield: 370 mg (43%), mp 185°C; IR ($CHCl_3$) ν 1687 (vs, CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.86 (s, 3H, $-CH_3$), 7.31–7.89 (m, 12H, aryl-H); ^{13}C NMR ($CDCl_3$) δ 51.3 (s, $-CH_3$), 118.3 (s, C5), 120.1, 122.6, 127.1, 127.8, 127.9, 129.0, 129.2, 129.4, 129.9, 130.4, 130.7, 131.2, 132.2, 135.2 (each s, aryl-C), 153.5, 161.2 (each s, C2, C4), 166.5 (s, $-CO_2Et$); MS (EI, 70 eV) *m/z* 345 (31.6) $[M]^+$, 230 (100) $[C_{17}H_{12}N]^+$, 155 (68.5) [2-Naph-CO]$^+$, 127 (37.2) $[C_{10}H_7]^+$, 77 (30.7) $[C_6H_5]^+$, 51 (5.9) $[C_4H_3]^+$; $C_{21}H_{15}NO_4$ (345.36).

5-Ethoxycarbonyl-2,3-diphenyl-1,3-oxazolium-4-olate (12f). Yield: 410 mg (44%); mp 153°C; Analytical data are identical to those reported in the literature.[9]

5-Ethoxycarbonyl-2-(2,4,6-trimethylphenyl)-3-phenyl-1,3-oxazolium-4-olate (12g). Yield: 550 mg (49%); mp 207°C; IR ($CHCl_3$) ν 1686 (vs, CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, 3H, $^3J_{H,H}$=7.0 Hz, $-CH_2-CH_3$), 1.96 (s, 3H, *p*-CH_3), 2.14 (s, 6H, *p*-CH_3), 4.25 (q, 2H, $^3J_{H,H}$=7.0 Hz, $-CH_2-CH_3$), 6.75 (s, 2H, aryl-H, Mes), 7.10–7.24 (m, 5H, aryl-H, Ph); ^{13}C NMR ($CDCl_3$): δ=14.3 (s, $-CH_2-CH_3$), 19.2 (s, *o*-CH_3), 20.9 (s, *p*-CH_3), 59.5 (s, $-CH_2-CH_3$), 118.5 (s, C5), 119.1, 124.9, 128.6, 129.1, 129.5, 130.2, 137.6, 142.8 (each s, aryl-C), 151.9, 157.3 (each s, C2, C4), 158.9 (s, $-CO_2Et$); MS: (EI, 70 eV) *m/z* 351 (18.9) $[M]^+$, 305 (2.4) $[M-C_2H_4-H_2O]^+$, 279 (13.6) $[M-C_2H_4-CO_2]^+$, 222 (100) $[C_{16}H_{16}N]^+$, 147 (44.4) $[C_{10}H_{11}O]^+$, 119 (6.3) $[C_9H_{11}]^+$, 77 (22.2) $[C_6H_5]^+$; Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.79; H, 5.98; N, 3.99. Found: C, 71.30; H, 6.30; N, 3.90.

5-Ethoxycarbonyl-2-(4-methoxyphenyl)-3-phenyl-1,3-oxazolium-4-olate (12h). Yield: 388 mg (42%), mp 158°C; IR ($CHCl_3$): ν 1690 (vs, CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.49 (t, 3H, $^3J_{H,H}$=7.1 Hz, $-CH_2-CH_3$), 3.95 (s, 3H, $-OCH_3$), 4.80 (q, 2H, $^3J_{H,H}$=7.1 Hz, $-CH_2-CH_3$), 6.98, 7.62 (each d, 2H, aryl-H), 7.49–7.69 (m, 5H, aryl-H, Ph); ^{13}C NMR ($CDCl_3$): δ 14.6 (s, $-CH_2-CH_3$), 55.6 (s, $-OCH_3$), 59.7 (s, $-CH_2-CH_3$), 116.9 (s, C5), 113.2, 114.7, 127.0, 130.2, 130.4, 130.8, 131.6, 154.0 (each s, aryl-C), 153.4, 159.4 (each s, C2, C4), 163.9 (s, $-CO_2Et$); MS: (EI, 70 eV) *m/z* 339 (30.7) $[M]^+$, 294 (3.8) $[M-C_2H_5O]^+$, 267 (8.8) $[M-C_2H_4-CO_2]^+$, 210 (100) $[C_{14}H_{12}NO]^+$, 135 (48.7) $[C_8H_7O]^+$, 92 (3.5) $[C_6H_4O]^+$, 77 (21.5) $[C_6H_5]^+$; Anal. Calcd for $C_{21}H_{21}NO_4$: C, 67.26; H, 5.02; N, 4.13. Found: C, 66.40; H, 5.10; N, 4.00.

Alkyl 4-tert-alkyl-2-aryl-1,3-oxaphosphole-5-carboxylates (14)—general procedures

Method A. A solution of equimolar amounts of diazocarbonyl compound **11** and phosphaalkyne **5** with a catalytic amount of $Rh_2(OAc)_4$ in 10 ml of toluene was heated for 8 h at 120°C in a Schlenk pressure tube under 5 bar Ar-pressure. The reaction progress was monitored by ^{31}P NMR spectroscopy. After evaporation of volatile components a brown residue was obtained. Further purification was achieved by column chromatography on silica gel with an *n*-pentane/diethyl ether mixture (10:1) as eluant.

Method B. The isolated isomünchnones **12** were heated together with an equimolar amount of phosphaalkyne **5** in 10 ml of THF as solvent in a Schlenk pressure tube for 14 h at 120°C under 5 bar Ar-pressure. Monitoring of the reaction mixture with ^{31}P NMR spectroscopy indicated the exact end of the reaction. After evaporation of the solvent under vacuum (20°C/0.001 mbar) the residue was extracted three times with pentane (15 ml). The extract was separated from insoluble material by filtration through a D3 glass sinter covered with Celite. Final removal of the solvent furnished the 1,3-oxaphospholes **14**.

Methyl 4-tert-butyl-2-phenyl-1,3-oxaphosphole-5-carboxylate (14a). Yield: 140 mg (48%), (**Method A**); IR ($CHCl_3$) ν 1728 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 114.9 (s); ^1H NMR ($CDCl_3$) δ 1.76 (d, 9H, $^4J_{H,P}$=1.9 Hz, $-C(CH_3)_3$), 4.18 (s, 3H, $-CO_2CH_3$), 7.59–8.11 (m, 5H, aryl-H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.3 [d, $^3J_{C,P}$=11.2 Hz, $-C(CH_3)_3$], 33.9 [d, $^2J_{C,P}$=15.2 Hz, $-C(CH_3)_3$], 52.2 (s, $-CO_2CH_3$), 124.6 (d, $^3J_{C,P}$=12.9 Hz, *o*-C, Ph), 128.8 (s, *m*-C, Ph), 129.7 (d, $^5J_{C,P}$=4.0 Hz, *p*-C, Ph), 133.7 (d, $^2J_{C,P}$=12.9 Hz, *ipso*-C, Ph), 143.9 (d, $^2J_{C,P}$=5.6 Hz, C5), 159.4 (s, $-CO_2CH_3$), 164.2 (d, $^1J_{C,P}$=53.0 Hz, C4), 192.2 (d, $^1J_{C,P}$=55.4 Hz, C2); MS (EI, 70 eV): *m/z* 276 (100.0) $[M]^+$, 245 (5.9) $[M-CH_3O]^+$, 229 (97.5) $[M-CH_3O_2]^+$, 171 (5.0) $[C_8H_{12}O_2P]^+$, 105 (61.1) $[C_7H_5O]^+$, 77 (39.3) $[C_6H_5]^+$, 51 (7.8) $[C_4H_3]^+$; HRMS for $C_{15}H_{17}O_3P$ Calcd: 276.0915. Found: 276.0914.

Methyl 4-tert-butyl-2-(4-methoxyphenyl)-1,3-oxaphosphole-5-carboxylate (14b). Yield: 251 mg (36%), (**Method A**); IR ($CHCl_3$): ν 1720 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$): δ 108.2 (s); ^1H NMR ($CDCl_3$): δ 1.51 [d, 9H, $^4J_{H,P}$=2.0 Hz, $-C(CH_3)_3$], 3.82, 3.92 (each s, 3H, $-OCH_3$, $-CO_2CH_3$), 6.88, 7.80 (2d, 4H, aryl-H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.1 [d, $^3J_{C,P}$=11.3 Hz, $-C(CH_3)_3$], 33.7 [d, $^2J_{C,P}$=14.5 Hz, $-C(CH_3)_3$] 52.0, 55.2 (each s, $-OCH_3$, $-CO_2CH_3$), 114.1 (s, *m*-C), 126.2 (d, $^3J_{C,P}$=12.1 Hz, *o*-C), 126.8 (d, $^2J_{C,P}$=12.9 Hz, *ipso*-C), 143.1 (d, $^2J_{C,P}$=5.6 Hz, C5), 159.2 (s, $-CO_2CH_3$), 160.8 (d, $^5J_{C,P}$=4.0 Hz, *p*-C), 164.2

(d, $^{1}J_{C,P}$=53.0 Hz, C4), 192.2 (d, $^{1}J_{C,P}$=56.2 Hz, C2); MS (EI, 70 eV): *m/z* 306 (100.0) [M^+], 275 (3.75) [M^+–CH_3O], 259 (28.7) [M^+–CH_3O_2], 171 (1.2) [$C_8H_{12}O_2P^+$], 135 (30.7) [$C_8H_7O_2^+$], 57 (12.8) [$C_4H_9^+$]; Anal. Calcd for $C_{16}H_{19}O_4P$: C, 62.75; H, 6.21. Found: C, 62.99; H, 6.04.

Methyl 4-tert-butyl-2-(4-ethylphenyl)-1,3-oxaphosphole-5-carboxylate (14c). Yield: 130 mg (38%), (**Method A**); IR ($CHCl_3$) ν 1728 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 112.1 (s); ^{1}H NMR ($CDCl_3$) δ 1.16 (t, 3H, $^{3}J_{H,H}$=7.6 Hz, –CH_2CH_3), 1.48 [d, 9H, $^{4}J_{H,P}$=1.9 Hz, –$C(CH_3)_3$], 2.57 (q, 2H, $^{3}J_{H,H}$=7.6 Hz, –CH_2CH_3), 3.87 (s, 3H, –CO_2CH_3), 7.14, 7.62 (each d, 4H, aryl-H, Ph); ^{13}C NMR ($CDCl_3$) δ 15.2 (s, –CH_2CH_3), 28.7 (s, –CH_2CH_3), 31.1 [d, $^{3}J_{C,P}$=10.4 Hz, –$C(CH_3)_3$], 33.7 [d, $^{2}J_{C,P}$=15.2 Hz, –$C(CH_3)_3$], 51.9 (s, –CO_2CH_3), 124.5 (d, $^{3}J_{C,P}$=12.0 Hz, *o*-C), 128.8 (s, *m*-C), 131.2 (d, $^{2}J_{C,P}$=12.0 Hz, *ipso*-C), 143.4 (d, $^{2}J_{C,P}$=4.8 Hz, C5), 146.1 (d, $^{5}J_{C,P}$=3.2 Hz, *p*-C), 159.4 (s, –CO_2CH_3), 163.9 (d, $^{1}J_{C,P}$=53.0 Hz, C4), 192.3 (d, $^{1}J_{C,P}$=56.2 Hz, C2); MS (EI, 70 eV) *m/z* 304 (100.0) [$M]^+$, 289 (6.6) [$M–CH_3]^+$, 273 (4.9) [$M–CH_3O]^+$, 257 (49.0) [$M–CH_3O_2]^+$, 171 (2.8) [$C_8H_{12}O_2P]^+$, 133 (53.2) [$C_9H_9O]^+$, 105 (7.5) [$C_6H_4C_2H_5]^+$, 77 (7.8) [$C_6H_5]^+$; HRMS Calcd for $C_{17}H_{21}O_3P$: 304.1228. Found: 304.1235.

Methyl 4-tert-butyl-2-(1-naphthyl)-1,3-oxaphosphole-5-carboxylate (14d). Yield: 201 mg (85%), (**Method B**); mp 121°C; IR ($CHCl_3$) ν 1721 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 126.8 (s); ^{1}H NMR ($CDCl_3$) δ 1.65 [d, 9H, $^{4}J_{H,P}$=2.0 Hz, –$C(CH_3)_3$], 3.99 (s, 3H, –CO_2CH_3), 7.43–8.06 (m, 7H, 1-naphthyl); ^{13}C NMR ($CDCl_3$) δ 31.4 [d, $^{3}J_{C,P}$=10.4 Hz, –$C(CH_3)_3$], 34.0 [d, $^{2}J_{C,P}$=15.3 Hz, –$C(CH_3)_3$], 52.3 (s, –CO_2CH_3), 125.6, 126.7 (each d, $^{3}J_{C,P}$=13.7 and 12.0 Hz, C2, C8a, 1-naphthyl), 125.2, 126.1, 127.3, 128.8, 129.7, 134.0, (each s, C 1-naphthyl), 130.4 (d, $^{5}J_{C,P}$=2.4 Hz, C-4, 1-naphthyl), 130.9 (d, $^{3}J_{C,P}$=9.6 Hz, C-1, 1-naphthyl), 144.2 (d, $^{2}J_{C,P}$=5.6 Hz, C-5), 159.5 (d, $^{3}J_{C,P}$=1.6 Hz, –CO_2CH_3), 163.7 (d, $^{1}J_{C,P}$= 54.6 Hz, C-4), 192.4 (d, $^{1}J_{C,P}$=57.8 Hz, C-2); MS (EI, 70 eV): *m/z* 326 (100) [$M]^+$, 295 (3.1) [$M–CH_3O]^+$, 155 (39.1) [Naph-$CO]^+$, 127 (27.6) [$C_{10}H_7]^+$; $C_{19}H_{19}O_3P$ (326.33).

Methyl 4-tert-butyl-2-(2-naphthyl)-1,3-oxaphosphole-5-carboxylate (14e). Yield: 191 mg (89%), (**Method B**); mp 122°C; IR ($CHCl_3$) ν 1720 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 126.4 (s); ^{1}H NMR ($CDCl_3$) δ 1.54 [d, 9H, $^{4}J_{H,P}$=2.0 Hz, –$C(CH_3)_3$], 3.94 (s, 3H, –CO_2CH_3), 7.41–8.32 (m, 7H, 2-naphthyl); ^{13}C NMR ($CDCl_3$) δ 31.7 [d, $^{3}J_{C,P}$=10.7 Hz, –$C(CH_3)_3$], 34.3 (d, $^{2}J_{C,P}$=14.5 Hz, –$C(CH_3)_3$], 52.6 (s, –CO_2CH_3), 123.3, 123.5 (each d, $^{3}J_{C,P}$=12.2 and 13.7 Hz, C1, C3, 2-naphthyl), 127.1, 127.2, 127.3, 128.2, 128.9, 129.1, (each s, C 2-naphthyl), 131.5 (d, $^{2}J_{C,P}$=12,2 Hz, C-2, 2-naphthyl), 134.3 (d, $^{5}J_{C,P}$=3 Hz, C-4a, 2-naphthyl), 144.5 (d, $^{2}J_{C,P}$=5.3 Hz, C-5), 159.7 (d, $^{3}J_{C,P}$=2.3 Hz, –CO_2CH_3), 164.7 (d, $^{1}J_{C,P}$=52.7 Hz, C-4), 192.5 (d, $^{1}J_{C,P}$=55.7 Hz, C-2); MS (EI, 70 eV) *m/z* 326 (100) [$M]^+$, 295 (2.5) [$M–CH_3O]^+$, 279 (12.0) [$M–CH_3O_2]^+$), 155 (39.1) [Naph-$CO]^+$, 127 (27.6) [$C_{10}H_7]^+$); $C_{19}H_{19}O_3P$ (326.33).

Ethyl 4-tert-butyl-2-phenyl-1,3-oxaphosphole-5-carboxylate (14f). Yield: 100 mg (89%), (**Method B**), IR ($CHCl_3$) ν 1714 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 113.1 (s); ^{1}H NMR ($CDCl_3$): δ 1.38 (t, 3H, $^{3}J_{H,H}$=7.2 Hz, –$CO_2CH_2CH_3$), 1.48 [d, 9H, $^{4}J_{P,H}$=2.2 Hz, –$C(CH_3)_3$], 4.36 (q, 2H, $^{3}J_{H,H}$=7.2 Hz, –$CO_2CH_2CH_3$), 7.30–7.82 (m, 5H, aryl-H); ^{13}C NMR ($CDCl_3$) δ 14.2 (s, –$CO_2CH_2CH_3$), 31.3 [d, $^{3}J_{C,P}$=10,9 Hz, –$C(CH_3)_3$], 33.6 [d, $^{2}J_{C,P}$=15.3 Hz, –$C(CH_3)_3$], 61.2 (s, –$CO_2CH_2CH_3$), 124.5 (d, $^{3}J_{C,P}$=12,1 Hz, *o*-C, Ph), 128.7 (s, *m*-C, Ph), 129.5 (d, $^{5}J_{C,P}$=3.0 Hz, *p*-C, Ph), 133.8 (d, $^{2}J_{C,P}$=13.1 Hz, *ipso*-C, Ph), 144.3 (d, $^{2}J_{C,P}$=5.5 Hz, C5), 158.9 (d, $^{3}J_{C,P}$=2.2 Hz, –$CO_2CH_2CH_3$), 163.3 (d, $^{1}J_{C,P}$=53.4 Hz, C4), 192.2 (d, $^{1}J_{C,P}$=55.6 Hz, C2); MS (EI, 70 eV) *m/z* 290 (100.0) [$M]^+$, 275 (2.2) [$M–CH_3]^+$, 245 (2.9) [$M–C_2H_5O]^+$, 229 (69.4) [$M–C_2H_5O_2]^+$,105 (18.8) [Ph-$CO]^+$, 77 (11.9) [$C_6H_5]^+$, 51 (2.4) [$C_4H_3]^+$; Anal. Calcd. for $C_{16}H_{19}O_3P$: C, 66.21; H, 6.57. Found: C, 65.50; H, 6.60.

Ethyl 4-tert-butyl-2-(2,4,6-trimethylphenyl)-1,3-oxaphosphole-5-carboxylate (14g). Yield: 89 mg (72%), (**Method B**), IR ($CHCl_3$) ν 1710 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 128.9 (s); ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 3H, $^{3}J_{H,H}$=7.2 Hz, –$CO_2CH_2CH_3$), 1.47 [d, 9H, $^{4}J_{H,P}$=1.7 Hz, –$C(CH_3)_3$), 2.20 (s, 6H, *o*-CH_3), 2.24 (s, 3H, *p*-CH_3), 4.28 (q, 2H, $^{3}J_{H,H}$=7.2 Hz, –$CO_2CH_2CH_3$), 6.90 (s, 2H, Mes); ^{13}C NMR ($CDCl_3$) δ 14.2 (s, –$CO_2CH_2CH_3$), 21.1 (s, *p*-CH_3), 21.2 (d, $^{4}J_{C,P}$=3.2 Hz, *o*-CH_3), 31.5 [d, $^{3}J_{C,P}$=10.4 Hz, –$C(CH_3)_3$], 33.7 [d, $^{2}J_{C,P}$=14.5 Hz, –$C(CH_3)_3$], 61.2 (s, –$CO_2CH_2CH_3$), 128.7 (s, *m*-C, Mes), 130.4 (d, $^{2}J_{C,P}$=12.0 Hz, *ipso*-C, Mes), 137.5 (d, $^{3}J_{C,P}$=4.0 Hz, *o*-C, Mes), 138.9 (s, *p*-C, Mes), 144.3 (d, $^{2}J_{C,P}$=4.8 Hz, C5), 159.3 (s, –$CO_2CH_2CH_3$), 163.0 (d, $^{1}J_{C,P}$=55.4 Hz, C4), 192.2 (d, $^{1}J_{C,P}$=54.6 Hz, C2); MS (EI, 70 eV) *m/z* 332 (100.0) [$M]^+$, 287 (2.3) [$M–C_2H_5O]^+$, 271 (7.3) [$M–C_2H_5O_2]^+$, 147 (15.7) [Mes-$CO]^+$, 119 (6.1) [$C_6H_2(CH_3)_3]^+$; HRMS Calcd. for $C_{19}H_{25}O_3P$: 332.1541. Found: 332.1542.

Ethyl 4-tert-butyl-2-(4-methoxyphenyl)-1,3-oxaphosphole-5-carboxylate (14h). Yield: 77 mg (45%), (**Method A**). Yield: 98 mg (81%), (**Method B**); IR ($CHCl_3$) ν 1718 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 107.4 (s); ^{1}H NMR ($CDCl_3$) δ 1.37 (t, 3H, $^{3}J_{H,H}$=7.2 Hz, –$CO_2CH_2CH_3$), 1.45 [d, 9H, $^{4}J_{H,P}$=2.0 Hz, –$C(CH_3)_3$], 3.77 (s, 3H, –C_6H_4–OCH_3), 4.34 (q, 2H, $^{3}J_{H,H}$=7.2 Hz, –$CO_2CH_2CH_3$), 6.84, 7.76 (each d, 4H, aryl-H); ^{13}C NMR ($CDCl_3$) δ 14.2 (s, –$CO_2CH_2CH_3$), 31.3 [d, $^{3}J_{C,P}$=10.2 Hz, –$C(CH_3)_3$], 33.7 [d, $^{2}J_{C,P}$=15.3 Hz, –$C(CH_3)_3$], 55.3 (s, –C_6H_4–OCH_3), 61.1 (s, –$CO_2CH_2CH_3$), 114.1 (s, *m*-C, aryl), 126.3 (d, $^{3}J_{C,P}$=11.9 Hz, *o*-C, aryl), 127.0 (d, $^{2}J_{C,P}$=12.7 Hz, *ipso*-C, aryl), 143.6 (d, $^{2}J_{C,P}$=5.1 Hz, C5), 158.9 (d, $^{3}J_{C,P}$=2.6 Hz, –$CO_2CH_2CH_3$), 160.9 (d, $^{5}J_{C,P}$ =3.4 Hz, *p*-C, aryl), 163.7 (d, $^{1}J_{C,P}$=53.4 Hz, C4), 192.3 (d, $^{1}J_{C,P}$=55.1 Hz, C2); MS (EI, 70 eV) *m/z* 320 (100.0) [$M]^+$, 275 (2.9) [$M–C_2H_5O]^+$, 259 (26.5) [$M–C_2H_5O_2]^+$, 77 (3.9) [$C_6H_5]^+$; Anal. Calcd. for $C_{16}H_{19}O_3P$: C, 63.75; H, 6.56. Found: C, 63.50; H, 6.50.

Ethyl 4-tert-butyl-2-(4-methylphenyl)-1,3-oxaphosphole-5-carboxylate (14i). Yield: 66 mg (39%), (**Method A**); IR ($CHCl_3$) ν 1715 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 111.9 (s); ^{1}H NMR ($CDCl_3$) δ 1.64 (t, 3H, $^{3}J_{H,H}$=7.2 Hz, –$CO_2CH_2CH_3$), 1.72 [d, 9H, $^{4}J_{H,P}$=1.9 Hz, –$C(CH_3)_3$], 2.58 (s, 3H, *p*-CH_3, aryl), 4.61 (q, 2H, $^{3}J_{H,H}$=7.2 Hz,

$-CO_2CH_2CH_3$], 7.39, 7.97 (each d, 4H, aryl-H); ^{13}C NMR ($CDCl_3$) δ 14.2 (s, $-CO_2CH_2CH_3$), 21.4 (s, *p*-CH_3, aryl), 31.3 [d, $^3J_{C,P}$=11.2 Hz, $-C(CH_3)_3$], 33.7 (d, $^2J_{C,P}$=15.2 Hz, $-C(CH_3)_3$], 61.1 (s, $-CO_2CH_2CH_3$), 124.5 (d, $^3J_{C,P}$=12.9 Hz, *o*-C, aryl), 129.4 (s, *m*-C, aryl), 131.2 (d, $^2J_{C,P}$=12.9 Hz, *ipso*-C, aryl), 139.8 (d, $^5J_{C,P}$=4.0 Hz, *p*-C, aryl), 143.9 (d, $^2J_{C,P}$=5.6 Hz, C5), 158.9 (d, $^3J_{C,P}$=1.6 Hz, $-CO_2CH_2CH_3$), 163.5 (d, $^1J_{C,P}$=53.0 Hz, C4), 192.5 (d, $^1J_{C,P}$=55.4 Hz, C2); MS (EI, 70 eV) *m/z* 304 (100.0) $[M]^+$, 259 (6.7) $[M-C_2H_5O]^+$, 243 (52.0) $[M-C_2H_5O_2]^+$, 91 (12.0) $[Me\text{-}C_6H_4]^+$; HRMS Calcd. for $C_{17}H_{21}O_3P$: 304.1228. Found: 304.1233.

Ethyl 4-(1,1-dimethylpropyl)-2-phenyl-1,3-oxaphosphole-5-carboxylate (14j). Yield: 100 mg (85%), (**Method B**); IR ($CHCl_3$): ν 1716 cm^{-1} (vs, CO); ^{31}P NMR ($CDCl_3$) δ 117.1 (s); ^1H NMR ($CDCl_3$) δ 0.81 (t, 3H $^3J_{H,H}$=7.2 Hz, $-CMe_2CH_2CH_3$), 1.42 (t, 3H, $^3J_{H,H}$=7.2 Hz, $-CO_2CH_2CH_3$), 1.46 [d, 6H, $^4J_{H,P}$=2.2 Hz, $-C(CH_3)_2$-CH_2CH_3], 1.94 [q, 2H, $^3J_{H,H}$=7.2 Hz, $-C(CH_3)_2CH_2CH_3$], 4.39 (q, 2H, $^3J_{H,H}$=7.2 Hz, $-CO_2CH_2CH_3$), 7.40–7.90, (each m, 5H, aryl-H); ^{13}C NMR ($CDCl_3$) δ 9.7 (s, $-CMe_2CH_2CH_3$), 14.5 (s, $-CO_2CH_2CH_3$), 29.7 [d, $^3J_{C,P}$=12.9 Hz, $-C(CH_3)_2CH_2CH_3$], 34.7 [d, $^3J_{C,P}$=5.6 Hz, $-C(CH_3)_2CH_2CH_3$], 37.4 [d, $^2J_{C,P}$=13.7 Hz, $-C(CH_3)_2$-CH_2CH_3], 61.2 (s, $-CO_2CH_2CH_3$), 124.9 (d, $^3J_{C,P}$=12.0 Hz, *o*-C, phenyl), 129.0 (s, *m*-C, phenyl), 129.9 (d, $^5J_{C,P}$=3.0 Hz, *p*-C, phenyl), 134.1 (d, $^2J_{C,P}$=12.9 Hz, *ipso*-C, phenyl), 144.6 (d, $^2J_{C,P}$=4.8 Hz, C5), 159.5 (s, $-CO_2CH_2CH_3$), 162.3 (d, $^1J_{C,P}$=53.0 Hz, C4), 192.5 (d, $^1J_{C,P}$=54.6 Hz, C2); MS (EI, 70 eV) *m/z* 304 (84.3) $[M]^+$, 275 (19.2) $[M-C_2H_5]^+$, 259 (2.9) $[M-C_2H_5O]^+$, 243 (4.1) $[M-C_2H_5O_2]^+$, 105 (18.8) $[Ph\text{-}CO]^+$, 77 (13,6) $[C_6H_5]^+$, 51 (2,5) $[C_4H_3]^+$; $C_{17}H_{21}O_3P$ (304.33).

Crystal structure analysis of 14b

Crystal data. $C_{16}H_{19}O_4P$, M_r=306.28, orthorhombic, space group P_{nma}, a=912.6, b=699.8, c=2445.8 pm, $\alpha=\beta=\gamma$=90.00°, V=1.5620(5) nm^3, Z=4, $d_{calc.}$=1.302 Mg/m^3.

Data collection. The data collection was performed using an automatic four circle diffractometer (Siemens P4) at r.t. Crystal dimensions: 0.60×0.30×0.25 mm. The measurements were made in the range $3.03<\theta<24.15°$, λ=0.71073 MoKα (graphite monochromator), $-9\le h\le 10$, $-8\le k\le 7$, $-27\le l\le 28$, a total of 8041 reflections, of which 1319 were independent reflections.

Structure solution and refinement. The structure was solved using direct methods (SHELXS-86)[18] and refined with the full matrix least squares procedure against F^2 (SHELXL-93).[19] The anisotropic refinement converged at R1=0.0366 and wR2=0.0982 [$I>2\sigma(I)$] and R1=0.0412, wR2=0.1011 [all data]. The difference Fourier synthesis on the basis of the final structural model showed a maximum of 225 e/nm^3 and a minimum of -147 e/nm^3. Anisotropic thermal parameters of non-hydrogen atoms, atomic coordinates, bond lengths and bond angles involving hydrogen atoms will be deposited at the Cambridge Crystallographic Centre (CCDC 12 46 78).

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