Regioselective phosphorylation of α-*N*-alkylamino ketones

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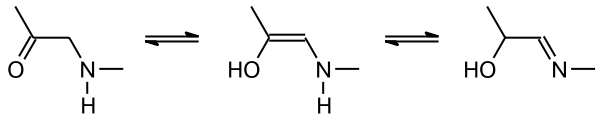
General preparative methods for regioselective functionalization of α-amino ketones with organophosphorus reagents were developed. Stable phosphorylated derivatives of all their prototropic forms (α-amino ketones, α-hydroxy imines, and β-hydroxy enamines) were obtained for the first time. The relative thermodynamic stability sequence of α-amino ketones was found to be reversed upon their phosphorylation: *O*-substituted forms were more stable than *N*-substituted ones, in contrast to the equilibrium between the prototropic isomers.

Key words: α-amino ketones, α-hydroxy imines, β-hydroxy enamines, phosphorylation, tautomerism, thermodynamic stability.

Amino ketones and their derivatives exhibit high biological activity of various kinds, which is why problems of their synthesis, structures, and reactivities have attracted much attention.[1] At the same time, organoelement reagents play an important role in organic synthesis. Selective introduction of phosphorus-, silicon-, or boron-containing fragments followed by transformations of the corresponding organoelement intermediates allows substantial extension of the synthetic potentials of polyfunctional substrates.[2] However, this approach has not been applied to amino ketones so far, selective introduction and removal of modifying (protective) groups have been impossible for the lack of appropriate methods, and the structures of the products obtained have not been clearly correlated with the reaction conditions and the nature of the reagents.

α-Amino ketones are labile molecular entities with various kinds of tautomerization and isomerization due to the vicinity of two functional (oxo and amino) groups. Amino ketones with at least one α-H atom in the alkyl radical can exist as three prototropic isomers or tautomers **1**, **2**, and **3** (Scheme 1).

Scheme 1



1 **2** **3**

Usually, equilibrium between prototropic isomers is virtually completely shifted to form **1**; however, derivatives of minor tautomers can also be obtained in reactions. Earlier, we have described Δ^4-1,3,2-oxazaphospholines and Δ^4-1,3,2-oxazasilolines[3] (derived from hydroxy enamine **2**) and first representatives of *N*-phosphorylated amino ketones **1** and *O*-phosphorylated hydroxy imines **3** (see Refs 4, 5).

Our investigation showed that under conditions that ensure a competition between nucleophilic sites of amino ketone, reactions with electrophilic organophosphorus reagents can both be regioselective and give a mixture of isomers. By varying reagents and reaction conditions, we developed selective methods for the synthesis of phosphorylated derivatives of α-amino ketones **1** and β-hydroxy enamines **3**.

For instance, α-amino ketones containing a secondary amino group easily react with tri- and pentavalent phosphorus acid monochlorides to give *N*- or *O*-phosphorylation products or their mixture, depending on the structures of the reagents and the reaction conditions (Scheme 2).

Phosphinous and phosphinic acid chlorides, in which the P atom bears the sole fugitive grouping, reacted most definitely. The resulting *N*- or *O*-phosphorylated derivatives are stable and can be isolated in the individual state. The ratio of the *N*- and *O*-phosphorylation products is mainly determined by steric factors (the sizes of the substituents at the phosphorus and nitrogen atoms). For instance, *N*-methylaminopinacolin (**4a**) reacted with dimethyl phosphinochloridate in diethyl ether at room temperature in the presence of triethylamine to give *N*-derivative **5a** as the major product (>90%). Under the same conditions, *N*-isopropylaminopinacolin (**4b**) yielded a mixture of *N*- and *O*-isomers **5b** and **6b** in the ratio 3 : 2. The reaction between *N*-*tert*-butylaminopinacolin (**4c**) and diethyl phosphinochloridate, which have still bulkier

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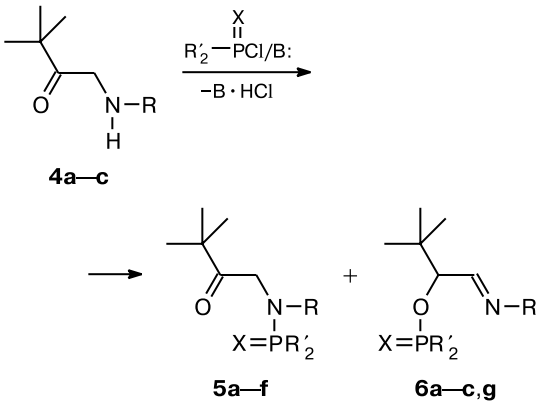
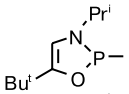
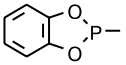
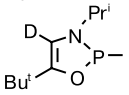
Scheme 2



4: R = Me (**a**), Pr^i (**b**), Bu^t (**c**)

	R	X=PR′$_2$		R	X=PR′$_2$
5a, **6a**	Me	$Me_2P(O)$			
5b, **6b**	Pr^i	$Me_2P(O)$			
5c, **6c**	Pr^i	Ph_2P	**5e**	Pr^i	
5d	Pr^i				
6g	Bu^t	$Et_2P(O)$	**5f**	Pr^i	

substituents at the phosphorus and nitrogen atoms, exclusively gave *O*-phosphorylated derivative **6g**.

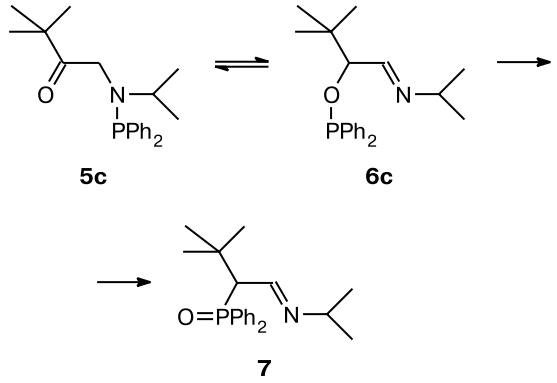
The temperature also substantially affects the reaction outcome. A decrease in the temperature suppressed *O*-phosphorylation and an *N*-derivative could be obtained in high yield. For instance, the reaction of amino ketone **4b** with chloro(diphenyl)phosphine at 10 °C predominantly gave *N*-derivative **5b** (>90%). In the case of dimethyl phosphinochloridate, the same selectivity was reached at –5 °C.

An increase in the reaction temperature did not give rise to an *O*-derivative as the major product; instead, an equilibrium between *N*- and *O*-isomers was established. For instance, mixing of amino ketone **4b** with dimethyl phosphinochloridate in chloroform at room temperature gave a mixture of *N*- and *O*-derivatives **5a** and **6a** in the ratio 10 : 1. Refluxing for 20 h changed this ratio to 1 : 5, which then remained constant. Under the same conditions, chloro(diphenyl)phosphine yielded an equilibrium 1 : 4 mixture upon 30-h refluxing.

Interconversions between the *N*- and *O*-phosphorylated forms of α-amino ketones were also observed during chemical reactions. For instance, heating of a mixture of diphenylphosphinous acid derivatives (**5c** ⇌ **6c**) caused the Arbuzov rearrangement leading to phosphine oxide **7** (Scheme 3).

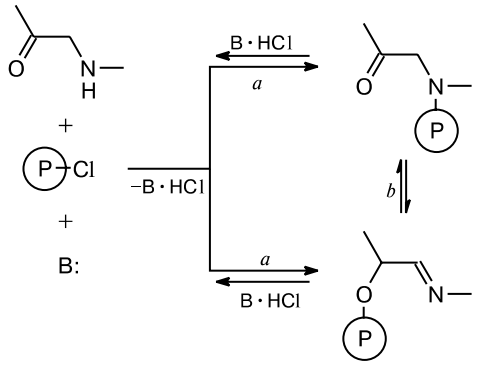
The ratio of isomers **5c** and **6c** remained constant up to completion of the reaction according to Scheme 3; this confirms that they are in equilibrium since transformations at the final step are irreversible.

Scheme 3



The most probable pathways to equilibrium can be generally represented by Scheme 4 (pathway *a* and pathway *b*).

Scheme 4



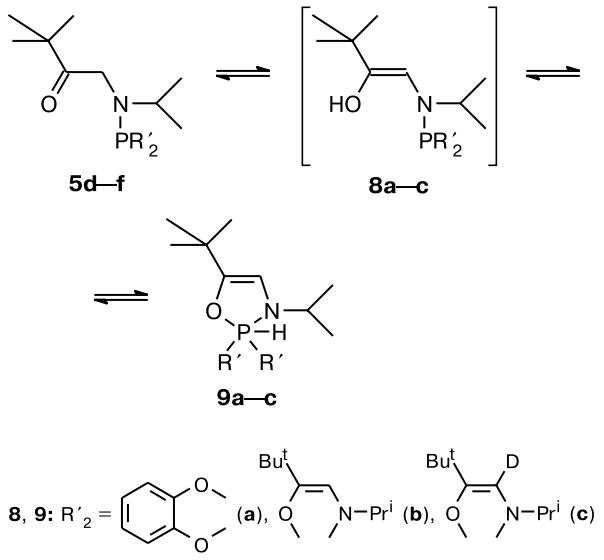
Based on known data on possible acid-catalyzed cleavage of P—N and P—O bonds,[6] one can assume that heating of the initially formed *N*- and *O*-isomers in chloroform containing triethylamine hydrochloride partially converts them into the starting amino ketone and phosphorus chloride, which react with each other to give a mixture with a changed ratio of the *N*- and *O*-isomers (pathway *a*). As the result, the equilibrium ratio of isomers should be determined by the ratio of their rates of formation and transformation into the starting reagents.

Pathway *b* implies direct reversible isomerization of P—N and P—O derivatives *via* intramolecular 1,4-migration of the substituent at phosphorus. Such isomerization was detected by us earlier;[7] however, we found that in the absence of a solvent (chloroform), P—N derivatives both specially purified and containing catalytic amounts of acid impurities completely and irreversibly isomerize into P—O derivatives; *i.e.*, only N→O phosphorotropic migration takes place. Therefore, pathway *a* seems to be more prob-

able for the interconversions of the N—O isomers in solutions.

Reactions of α-amino ketones with cyclic phosphorus acid chlorides (*e.g.*, 1,2-phenylene phosphorochloridite and 2-chloro-Δ^4-1,3,2-oxazaphospholine derivatives) gave rise to no P—O derivatives, affording only the corresponding P—N derivatives **5d—f** in equilibrium with isomeric P—H phosphoranes **9a—c** (Scheme 5). According to NMR data, the equilibrium content of phosphorane **9a** was about 20%, while those of phosphoranes **9b**,**c** were 10%.

Scheme 5



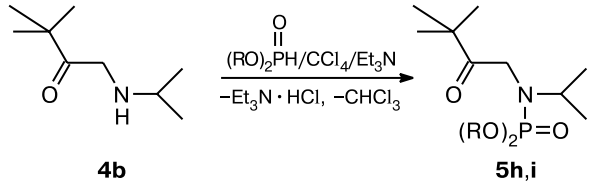
Ring—chain tautomerism in the series of cyclic phosphite derivatives has been studied thoroughly and occurs when the exocyclic substituent at the P atom contains a hydroxy or amino group in the β- or γ-position. Hence, one can assume that tautomerization **5** ⇌ **9** involves the formation of enol intermediate **8**, which, however, was not detected by spectroscopic methods. Obviously, the equilibrium concentration of the enol form is very low because of the low rate of its formation and the high rate of its transformation into compound **5** or **9**.

As noted above, the reactions of amino ketones with phosphorus acid chlorides are not always regioselective. For this reason, we studied alternative methods of phosphorylation, *viz.*, the Todd—Atherton phosphorylation[8] widely used in the chemistry of amines.

α-Amino ketone **4b** was easily phosphorylated with dialkyl phosphites and carbon tetrachloride in the presence of triethylamine according to the Todd—Atherton method (Scheme 6).

The reaction at 0 °C was completed in 1 h to give *N*-phosphorylated derivatives only. The yields of products **5h**,**i** substantially depend on the reaction conditions.

Scheme 6

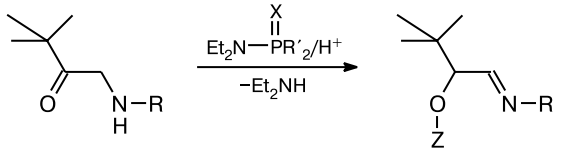


5: R = Me (**h**), Et (**i**)

With CCl_4 as the solvent, the yield did not exceed 60% because of strong resinification of the reaction mixture. In diethyl ether with a slight excess of CCl_4 (with respect to the stoichiometric amount), the yield increased to 90%. Apparently, this method is most appropriate for the synthesis of *N*-phosphorylated amino ketones.

Phosphorylation of α-amino ketones **4b**,**c** with amides of phosphorus acids[9] gave *O*-phosphorylated derivatives of α-hydroxy imines **6b**,**j**,**k** (Scheme 7).

Scheme 7

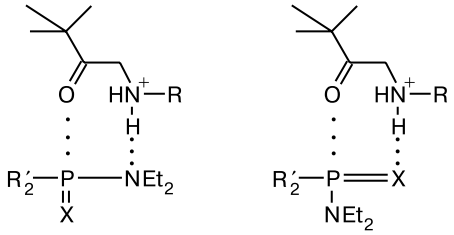


6	R	Z
b	Pr^i	$Me_2P(O)$
j	Pr^i	Et_2P
k	Bu^t	$Me_2P(O)$

The reaction occurred at 140—160 °C in the presence of hydrochlorides of amines or of the starting amino ketones as acid catalysts. The reaction was not impeded by the bulky substituents at the N atom of amino ketone, yet being highly sensitive to the size of the substituent at the P atom. For instance, *N*,*N*-diethyldimethylphosphinamide smoothly reacted with amino ketone **4b**, while its closest homolog *N*,*N*-diethyldiethylphosphinamide did not react with *N*-methyl- or *N*-isopropylaminopinacolins even at 180 °C; at higher temperatures, the amino ketone decomposed.

Transamidation is a highly regioselective reaction: in all cases, phosphorylation occurs at the oxygen atom, since P—N isomers (even in trace amounts) have not been detected by spectroscopic methods. Without an acid catalyst, the reaction is not initiated below the decomposition temperature of amino ketone, which suggests phosphorylation of its protonated form. In this case, the amino group becomes passive toward an electrophilic reagent but it catalyzes an interaction of an organophosphorus reagent with the carbonyl group through the formation of

a cyclic transition complex of the type **10** or **11**, in which phosphorus is much more electrophilic because of equilibrium protonation.



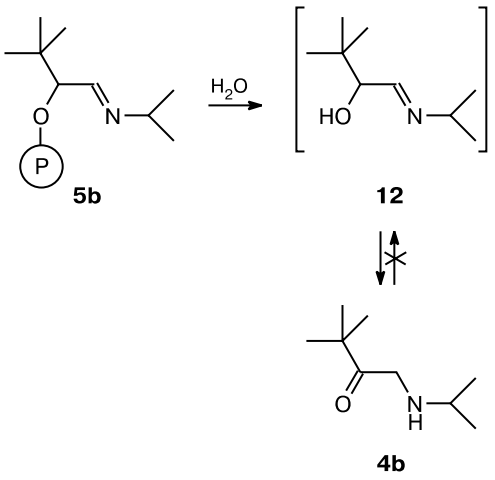
10 **11**

An alternative scheme may involve the formation of intermediate phosphorus acid chlorides.

The data obtained allow us to conclude that the formation of N—P derivatives is kinetically controlled, while more stable O—P derivatives form under thermodynamic control.

In contrast, amino ketone **1** is thermodynamically most stable among prototropic isomers **1**—**3**. For instance, heating of amino ketone **4b** at 200 °C in a sealed tube both alone and together with ammonium sulfate resulted only in its slow decomposition into several products; the ^{1}H NMR spectra showed no noticeable signals for the α-hydroxy imine **12**. Nor was hydroxy imine **12** obtained by mild hydrolytic removal of the phosphorous moiety from compound **5b**, which exclusively yielded amino ketone **4b** (Scheme 8).

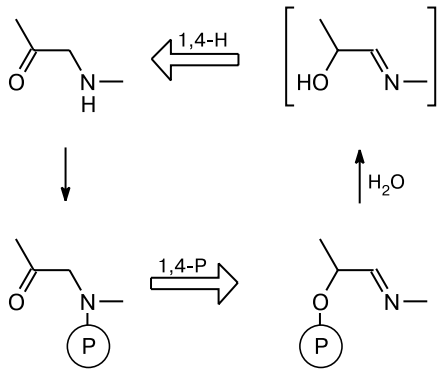
Scheme 8



5b **12** **4b**

Thus, phosphorylation changes the relative thermodynamic stability sequence of the isomeric and tautomeric forms of amino ketones **1**—**3** and affords derivatives of compounds that are unstable or do not exist in the free state. The behavior of α-amino ketones and their organophosphorus derivatives is sketched out in Scheme 9.

Scheme 9



Experimental

IR spectra were recorded on a UR-20 spectrophotometer. ^{1}H and ^{31}P NMR spectra were recorded on a Varian Gemini-200 spectrometer (200.13 and 81.02 MHz, respectively). Chemical shifts are given relative to Me_4Si (^{1}H) as the internal standard and relative to 85% H_3PO_4 (^{31}P) as the external standard.

All reactions were carried out in an atmosphere of dry argon and in anhydrous solvents.

Reactions of alkylamino ketones with phosphorus acid monochlorides (general procedure *A*). A solution of an appropriate phosphorus acid chloride (0.1 mol) in diethyl ether (100 mL) was added dropwise to a stirred solution of amino ketone (0.11 mol) and triethylamine (0.12 mol) in diethyl ether (200 mL). After the reaction was completed, triethylamine hydrochloride was filtered off, the filtrate was concentrated *in vacuo*, and the residue was kept *in vacuo* (oil pump) to remove residual solvents and reagents. Then pentane (500 mL) was added and the precipitate that formed was filtered off. The pentane was removed and the residue was distilled or recrystallized.

Reactions of alkylamino ketones with phosphorus acid monoamides (general procedure *B*). A Claisen flask was charged with amino ketone (0.1 mol), an appropriate phosphorus amide (0.1 mol), and amino ketone or triethylamine hydrochloride (0.005 mol). The reaction mixture was heated at 140—160 °C to complete liberation of amine and then distilled. The products were purified by redistillation or crystallization.

1-[Dimethylphosphinoyl(methyl)amino]-3,3-dimethylbutan-2-one (5a) was obtained according to procedure *A*. The yield was 74%, m.p. 92—93 °C (diethyl ether, 0 °C). IR (KBr pellets), ν/cm^{-1}: 940 (P—N), 1185 (P=O), 1300 (P—Me), 1720 (C=O). ^{1}H NMR (C_6D_6), δ: 1.16 (s, 9 H, Bu^t); 1.43 (d, 6 H, Me_2P, $^2J_{P,H}$ = 13.2 Hz); 2.87 (d, 3 H, MeN, $^3J_{P,H}$ = 8.4 Hz); 4.13 (d, 2 H, NCH_2CO, $^3J_{P,H}$ = 11.06 Hz). ^{31}P NMR (C_6D_6), δ: 41.1. Found (%): N, 6.86; P, 15.13. $C_9H_{20}NO_2P$. Calculated (%): N, 6.83; P, 15.09.

1-[Dimethylphosphinoyl(isopropyl)amino]-3,3-dimethylbutan-2-one (5b) was obtained according to procedure *A*. The yield was 71%, m.p. 79—80 °C (pentane—diethyl ether (1 : 1), 0 °C). IR (KBr pellets), ν/cm^{-1}: 940 (P—N), 1185 (P=O), 1300 (P—Me), 1720 (C=O). ^{1}H NMR (C_6D_6), δ: 1.01 (d, 6 H, $\underline{Me}_2CHN$, $^3J_{H,H}$ = 6.60 Hz); 1.17 (s, 9 H, Bu^t); 1.44 (d, 6 H, Me_2P, $^2J_{P,H}$ = 13.42 Hz); 3.41 (dsept, 1 H, $Me_2\underline{CH}$, $^3J_{P,H}$ = 10.42 Hz, $^3J_{H,H}$ = 6.60 Hz); 4.08 (d, 2 H, NCH_2CO,

$^3J_{P,H}$ = 11.14 Hz). ^{31}P NMR (C_6D_6), δ: 35.9. Found (%): N, 6.06; P, 13.23. $C_{11}H_{24}NO_2P$. Calculated (%): N, 6.00; P, 13.28.

1-[Diphenylphosphanyl(isopropyl)amino]-3,3-dimethylbutan-2-one (5c) was obtained according to procedure ***A***. The yield was 64%, m.p. 55—56 °C (pentane, −10 °C). IR (KBr pellets), ν/cm^{-1}: 990 (P—N), 1440 (P—Ph), 1720 (C=O). ^{1}H NMR (C_6D_6), δ: 1.17 (s, 9 H, Bu^t); 1.56 (d, 6 H, Me$_2$CHN, $^3J_{H,H}$ = 6.50 Hz); 2.76 (dsept, 1 H, Me$_2$CH, $^3J_{P,H}$ = 6.50 Hz, $^3J_{H,H}$ = 6.50 Hz); 3.17 (d, 2 H, NCH$_2$CO, $^3J_{P,H}$ = 6.50 Hz); 7.44, 7.84 (both m, 10 H, Ph$_2$P). ^{31}P NMR (C_6D_6), δ: 47.8. Found (%): N, 4.04; P, 9.15. $C_{21}H_{28}NOP$. Calculated (%): N, 4.10; P, 9.07.

1-[Phenylene-1,2-dioxyphosphanyl(isopropyl)amino]-3,3-dimethylbutan-2-one (5d) was obtained according to procedure ***A***. The yield was 87%. In benzene, compound **5d** exists in equilibrium with compound **9a** (the content of **5d** was 80%). IR (thin film), ν/cm^{-1}: 1720 (C=O). ^{1}H NMR (C_6D_6), δ: 0.76 (s, 9 H, Bu^t); 0.86 (d, 6 H, Me$_2$CHN, $^3J_{H,H}$ = 7.00 Hz); 3.47 (dsept, 1 H, Me$_2$CH, $^3J_{P,H}$ = 7.40 Hz, $^3J_{H,H}$ = 7.00 Hz); 3.56 (d, 2 H, NCH$_2$CO, $^3J_{P,H}$ = 10.60 Hz); 6.6—7.0 (m, 4 H, Ar). ^{31}P NMR (C_6D_6), δ: 150.3. Found (%): N, 4.79; P, 10.40. $C_{15}H_{22}NO_3P$. Calculated (%): N, 4.74; P, 10.49.

4-*tert*-Butyl-2-hydrido-1-isopropyl-Δ^4-1,3,2-oxazaphospholine-2-spiro-2′,4′,5′-benzo-1′,3′,2′-dioxaphospholane (9a). ^{1}H NMR (C_6D_6), δ: 5.49 (d, 1 H, C=CH, $^3J_{P,H}$ = 30 Hz); 8.81 (d, 1 H, PH, $^1J_{P,H}$ = 879 Hz). ^{31}P NMR (C_6D_6), δ: −35.8 (dd, $^1J_{P,H}$ = 879 Hz, $^3J_{P,H}$ = 30 Hz).

1-[5-*tert*-Butyl-3-isopropyl-Δ^4-1,3,2-oxazaphospholin-2-yl(isopropyl)amino]-3,3-dimethylbutan-2-one (5e) was obtained according to procedure ***A***. The yield was 63%, b.p. 135 °C (0.05 Torr). In benzene, compound **5e** exists in equilibrium with compound **9b** (the content of **5e** was 90%). IR (thin film), ν/cm^{-1}: 1720 (C=O). ^{1}H NMR (C_6D_6), δ: 1.01 (dd, 6 H, Me$_2$CH lin., $^3J_{H,H}$ = 6.80 Hz, Δδ 0.014); 1.13 (s, 9 H, Bu^t ring); 1.16 (s, 9 H, Bu^t lin.); 1.23 (dd, 6 H, Me$_2$CH ring, $^3J_{H,H}$ = 6.60 Hz, Δδ 0.014); 3.47 (dsept, 1 H, Me$_2$CH lin., $^3J_{P,H}$ = 6.80 Hz, $^3J_{H,H}$ = 6.80 Hz); 3.65 (m, 1 H, Me$_2$CH ring); 3.84 (dd, 2 H, CH$_2$, $^2J_{H,H}$ = 20.00 Hz, $^3J_{P,H}$ = 10.80 Hz, Δδ 0.154); 5.53 (d, 1 H, =CH, $^3J_{P,H}$ = 8.20 Hz). ^{31}P NMR (C_6D_6), δ: 133.3. Found (%): N, 8.25; P, 9.15. $C_{18}H_{34}N_2O_2P$. Calculated (%): N, 8.16; P, 9.02.

4,4′-Di-*tert*-butyl-2-hydrido-1,1′-diisopropyl-2,2′-spirobi(Δ^4-1,3,2-oxazaphospholine) (9b). ^{1}H NMR (C_6D_6), δ: 5.41 (d, 1 H, C=CH, $^3J_{P,H}$ = 30 Hz); 9.22 (d, 1 H, P—H, $^1J_{P,H}$ = 850 Hz). ^{31}P NMR (C_6D_6), δ: −50.1 (dd, $^1J_{P,H}$ = 850 Hz, $^3J_{P,H}$ = 30 Hz).

1-[5-*tert*-Butyl-4-deuterio-3-isopropyl-Δ^4-1,3,2-oxazaphospholin-2-yl(isopropyl)amino]-3,3-dimethylbutan-2-one (5f) was obtained according to procedure ***A***. Its physicochemical characteristics are identical with those of compound **5e**, except for the absence of a doublet at δ 5.53 in the ^{1}H NMR spectrum. Compound **5f** exists in equilibrium with compound **9c** (the content of **5f** was 90%.

4,4′-Di-*tert*-butyl-5-deuterio-2-hydrido-1,1′-diisopropyl-2,2′-spirobi(Δ^4-1,3,2-oxazaphospholine) (9c). Its spectroscopic characteristics are identical with those of compound **9b**, except for the absence of a doublet at δ 5.41 in the ^{1}H NMR spectrum.

1-[Dimethoxyphosphoryl(isopropyl)amino]-3,3-dimethylbutan-2-one (5h). A solution of dimethyl phosphite (0.1 mol) was added dropwise at 5—10 °C to a stirred solution of amino ketone **4b** (0.11 mol) and triethylamine (0.12 mol) in carbon tetrachloride (200 mL). Stirring was continued without cooling for an additional 2 h. The reaction mixture was treated as described in general procedure ***A*** and the product was purified by distillation. The yield was 63%, b.p. 102—104 °C (0.09 Torr). IR (thin film), ν/cm^{-1}: 1030 (POC), 1260 (P=O), 1725 (C=O). ^{1}H NMR (C_6D_6), δ: 1.05 (d, 6 H, Me$_2$CHN, $^3J_{H,H}$ = 6.70 Hz); 1.20 (s, 9 H, Bu^t); 3.56 (dsept, 1 H, Me$_2$CH, $^3J_{P,H}$ = 10.00 Hz, $^3J_{H,H}$ = 6.70 Hz); 3.76 (d, 6 H, (MeO)$_2$P, $^3J_{P,H}$ = 8.00 Hz); 3.98 (d, 2 H, NCH$_2$CO, $^3J_{P,H}$ = 12.10 Hz). ^{31}P NMR (C_6D_6), δ: 11.9. Found (%): N, 5.67; P, 11.68. $C_{11}H_{24}NO_4P$. Calculated (%): N, 5.28; P, 11.68.

1-[Diethoxyphosphoryl(isopropyl)amino]-3,3-dimethylbutan-2-one (5i) was obtained analogously from amino ketone **4b** (0.11 mol), triethylamine (0.12 mol), and diethyl phosphite (0.1 mol) in diethyl ether. The yield was 91%, b.p. 109—110 °C (0.09 Torr). IR (thin film), ν/cm^{-1}: 1030 (POC), 1260 (P=O), 1725 (C=O). ^{1}H NMR (C_6D_6), δ: 1.06 (d, 6 H, Me$_2$CHN, $^3J_{H,H}$ = 6.70 Hz); 1.20 (s, 9 H, Bu^t); 1.32 (t, 6 H, CH$_3$CH$_2$O, $^3J_{H,H}$ = 6.70 Hz); 3.64 (dsept, 1 H, Me$_2$CH, $^3J_{P,H}$ = 10.00 Hz, $^3J_{H,H}$ = 6.70 Hz); 3.98 (d, 2 H, NCH$_2$CO, $^3J_{P,H}$ = 12.10 Hz); 4.14 (dq, 4 H, CH$_3$CH$_2$O, $^3J_{P,H}$ = 11.00 Hz, $^3J_{H,H}$ = 6.70 Hz). ^{31}P NMR (C_6D_6), δ: 9.3. Found (%): N, 4.71; P, 10.62. $C_{13}H_{28}NO_4P$. Calculated (%): N, 4.78; P, 10.56.

N*-Isopropyl(2-dimethylphosphoryloxy-3,3-dimethylbutylidene)imine (6b)** was obtained according to procedure ***B. The yield was 71%, b.p. 77—79 °C (0.05 Torr). IR (thin film), ν/cm^{-1}: 1020 (P—O), 1230 (P=O), 1300 (P—Me), 1670 (C=N). ^{1}H NMR (C_6D_6, δ: 0.96 (s, 9 H, Bu^t); 1.11 (dd, 6 H, Me$_2$CHN, $^3J_{H,H}$ = 6.67 Hz, Δδ 0.011); 1.19 (dd, 6 H, Me$_2$P, $^2J_{P,H}$ = 10.12 Hz, Δδ 0.017); 3.16 (sept, 1 H, Me$_2$CHN, $^3J_{H,H}$ = 6.67 Hz); 4.58 (dd, 1 H, OCHCH=N, $^3J_{H,H}$ = 5.62 Hz, $^3J_{P,H}$ = 7.30 Hz); 7.52 (d, 1 H, OCHCH=N, $^3J_{H,H}$ = 5.62 Hz). ^{31}P NMR (C_6D_6), δ: 49.1. Found (%): N, 6.20; P, 13.20. $C_{11}H_{24}NO_2P$. Calculated (%): N, 6.01; P, 13.28.

N*-*tert*-Butyl(2-diethylphosphoryloxy-3,3-dimethylbutylidene)imine (6g)** was obtained according to procedure ***A. The yield was 70%, b.p. 98—99 °C (0.05 Torr). IR (thin film), ν/cm^{-1}: 1670 (C=N). ^{1}H NMR (C_6D_6), δ: 0.96 (s, 9 H, Bu^{t}C); 1.08 (m, 6 H, CH$_3$CH$_2$P); 1.17 (s, 9 H, Bu^{t}N); 1.65 (m, 4 H, CH$_3$CH$_2$P); 4.34 (dd, 1 H, OCHCH=N, $^3J_{H,H}$ = 6.5 Hz, $^3J_{PH}$ = 7.8 Hz); 7.62 (d, 1 H, OCHCH=N, $^3J_{H,H}$ = 6.5 Hz). ^{31}P NMR (C_6D_6), δ: 56.6. Found (%): N, 5.19, P, 11.14. $C_{14}H_{30}NO_2P$. Calculated (%): N, 5.09, P, 11.25.

N*-Isopropyl(2-diethylphosphinyloxy-3,3-dimethylbutylidene)imine (6j)** was obtained according to procedure ***B. The yield was 49%, b.p. 50—52 °C (0.05 Torr). IR (thin film), ν/cm^{-1}: 1010 (P—O), 1670 (C=N). ^{1}H NMR (C_6D_6), δ: 0.97 (s, 9 H, Bu^t); 1.04 (m, 6 H, CH$_3$CH$_2$P); 1.14 (dd, 6 H, Me$_2$CHN, $^3J_{H,H}$ = 6.6 Hz, Δδ = 0.05); 1.49 (dq, 4 H, CH$_3$CH$_2$P, $^3J_{H,H}$ = 6.5 Hz, $^2J_{P,H}$ = 13.0 Hz, Δδ 0.014); 3.18 (sept, 1 H, Me$_2$CHN, $^3J_{H,H}$ = 6.6 Hz); 3.93 (dd, 1 H, OCHCH=N, $^3J_{H,H}$ = 6.3 Hz); 7.53 (d, 1 H, OCHCH=N, $^3J_{H,H}$ = 6.3 Hz). ^{31}P NMR (C_6D_6), δ: 139.8. Found (%): N, 5.82; P, 12.59. $C_{13}H_{28}NOP$. Calculated (%): N, 5.71; P, 12.63.

N*-*tert*-Butyl(2-dimethylphosphoryloxy-3,3-dimethylbutylidene)imine (6k)** was obtained according to procedure ***B. The yield was 74%, m.p. 67—68 °C (diethyl ether, −5 °C). IR (thin film), ν/cm^{-1}: 1230 (P=O), 1300 (P—Me), 1670 (C=N). ^{1}H NMR (C_6D_6), δ: 0.99 (s, 9 H, Bu^{t}C); 1.20 (s, 9 H, Bu^{t}N); 1.49 (dd, 6 H, Me$_2$P, $^2J_{P,H}$ = 10.21 Hz, Δδ 0.014); 4.41 (dd, 1 H, OCHCH=N, $^3J_{H,H}$ = 5.64 Hz, $^3J_{P,H}$ = 7.8 Hz); 7.59 (d, 1 H,

OCH<u>CH</u>=N, $^3J_{H,H}$ = 5.64 Hz). ^{31}P NMR (C_6D_6), δ: 47.3. Found (%): N, 5.64; P, 12.35. $C_{12}H_{26}NO_2P$. Calculated (%): N, 5.66; P, 12.52.

N*-Isopropyl(2-diphenylphosphoryl-3,3-dimethylbutylidene)imine (7)** was obtained according to procedure ***A in chloroform by refluxing for 120 h. The yield was 55%. IR (thin film), ν/cm^{-1}: 1105 (P=O), 1670 (C=N). ^{1}H NMR (C_6D_6), δ: 0.93 (s, 9 H, Bu^t); 1.48 (dd, 6 H, <u>Me</u>$_2$CHN, $^3J_{H,H}$ = 6.6 Hz, Δδ = 0.01); 3.08 (sept, 1 H, Me$_2$<u>CH</u>N, $^3J_{H,H}$ = 6.6 Hz); 4.46 (dd, 1 H, O<u>CH</u>CH=N, $^3J_{H,H}$ = 6.2 Hz, $^3J_{P,H}$ = 9.6 Hz); 7.69 (d, 1 H, OCH<u>CH</u>=N, $^3J_{H,H}$ = 6.2 Hz); 7.34, 7.84 (m, 10 H, Ph$_2$P). ^{31}P NMR (C_6D_6), δ: 29.1. Found (%): N, 4.02; P, 9.25. $C_{21}H_{28}NOP$. Calculated (%): N, 4.10; P, 9.07.

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