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One-Step Transformation of Ammonium Dialkyl Phosphoroselenoates into Dialkyl Phosphoramidates

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ABSTRACT: *Ammonium dialkyl phosphoroselenoates are directly converted into the dialkyl phosphoramidates by iodosobenzene and iodoxybenzene. The inversion of configuration at the phosphorus atom, using model diastereoisomeric ammonium* cis- *and* trans-*2-oxo-2-seleno-4-methyl-1,3,2-dioxaphosphinan system, was observed. The mechanistic scheme of this transformation is discussed.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:121–127, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10110

INTRODUCTION

Reactions of organic monothio-, dithio-, monoseleno-, and selenothioacids of phosphorus, as well as their metal or ammonium salts with 0.5 equiv of halogens or sulfuryl chloride, are commonly used as methods of choice for the synthesis of organophosphorus disulfides [1–9] and diselenides [10–13]. Similarly, high yield formation of bis(thiophosphoryl)disulfides in the oxidation of phosphorodithioic acids and their salts with nitric acid, nitrogen oxides [14–17], hydrogen peroxides [6,7], and dimethyl sulfoxide (DMSO) [18] was also observed. On the other hand, the oxidative desulfurization of phosphino-, phosphono-, and phosphorothioic acid esters in their reactions with DMSO [19,20] as well as potassium dialkyl phosphorothioate in the reaction with peroxymonosulfate (Oxone®) [21], were reported. Recently, we described [22] the quantitative formation of bis(dialkoxyphosphinyl) disulfide as a major product of the oxidation reaction of ammonium dialkyl phosphorothioate by iodoxybenzene.

Herein we report that the ammonium dialkyl phosphoroselenoates **1a–c** undergo facile reactions with iodoso (**2**) or iodoxybenzene (**3**) to produce dialkyl phosphoramidates **4a–c**. The formation of ammonium dialkyl hydrogen phosphates **5a–c** and diselenide **6** in same cases of these reactions was also observed (Scheme 1).

The reactions were performed in an acetonitrile solution at room temperature in the absence or presence of montmorillonite K10 used in 0.5 weight ratio in relation to **2** or **3**, respectively. Efficient oxidation reaction with the use of iodosobenzene activated by montmorillonite K10 as well as the natural clays, namely KSF and bentonite, was recently reported [23]. ^{31}P NMR spectroscopy was used to monitor the progress of the reactions. The reactions were rapid and precipitation of elemental selenium from the solution in the short time after mixing of the reagents was observed. Results of the experiments are given in Table 1.

The reaction of **1a** with **2** performed in the absence as well as in the presence of montmorillonite K10 gave only poor yields of amide **4a** (runs 1 and 2). During the oxidation of **1a** with **2** in the presence of montmorillonite K10, the formation of diselenide **6**

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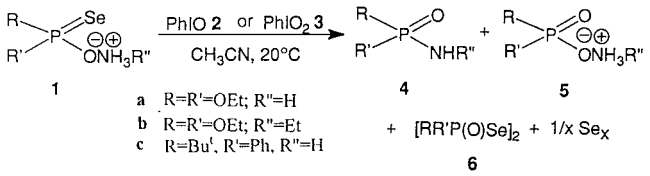
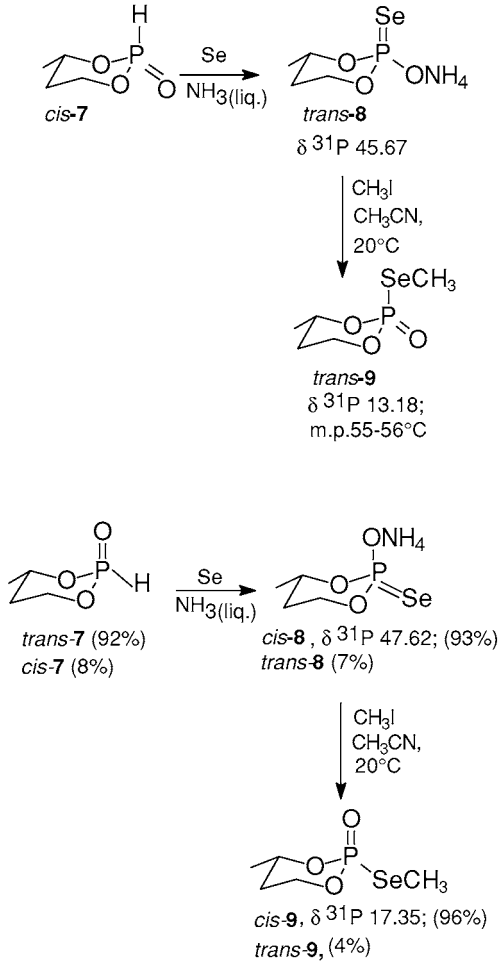


SCHEME 1

as a major product was observed. Under similar reaction conditions, the oxidation of **1a** with iodoxybenzene (**3**) produced amidate **4a** in a satisfactory yield (runs 3 and 4). The obtained results suggest that the use of montmorillonite K10 in the reaction of salts **1a,b** with either **2** or **3** had a negative influence on the yield of the formed amidate **4a** (runs 2 and 3).

On the other hand, the reaction between **3** and ammonium *t*-butylphenyl/phosphinoselenoate (**1c**) occurred in boiling acetonitrile solution, in the presence of montmorillonite K10. Under these conditions, the formation of a major product ammonium salt **5c** and only a small amount of *t*-butylphenylphosphinic amide (**4c**) was observed.

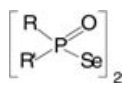
To examine the stereochemical course of the transformation of ammonium phosphoroselenoates → phosphoramidates, the ammonium salts *trans*- and *cis*-2-hydroxy-2-seleno-4-methyl-1,3,2-dioxaphosphinans (**8**) were selected. They were synthesized by the reaction of the elemental selenium with *cis*- and *trans*-2-hydrogen-2-oxo-4-methyl-1,3,2-dioxaphosphinans (**7**) respectively. The synthesis was performed in a liquid ammonia solution, according to our method described earlier [24]. Then, *trans*- and *cis*-**8** were transformed by reaction with methyl iodide into *trans*- and *cis*-2-methylseleno-2-oxo-4-methyl-1,3,2-dioxaphosphinans (**9**), respectively. The cis and trans configuration of esters **9** was established earlier [25]. The reaction sequence (Scheme 2) shows that the addition of elemental selenium to the cyclic *cis*- and



SCHEME 2

trans-phosphites **7** in the liquid ammonia solution is a completely stereospecific process. The possible epimerization of the labile *trans*-**7** into thermodynamically stable *cis*-**7** was not observed under these reaction conditions (Scheme 2). The obtained results correspond well with known stereochemistry of the

TABLE 1 Reactions of Salts **1a–c** with **2** or **3** in Acetonitrile Solution at 20°C

Run	Substrate	Oxidant	Activator	Products Yield (%)		
						
1	R=R′=OEt; R″=H **1a**	**2**	–	R″=H **4a** (36)[a]	**5a** (12)[a]	–
2	**1a**	**2**	+	**4a** (28)[a]	**5a** (9)[a]	**6** (63)[a]
3	**1a**	**3**	+	**4a** (74)[a]	–	–
4	**1a**	**3**	–	**4a** (85)[a] (71)[b]	–	–
5	R=R′=OEt; R″=Et **1b**	**3**	–	**4b** (42)[a] (26)[b]	**5b** (26)[a]	–
6	R=Bu^t, R′=Ph, R″=H **1c**	**3**	+	**4c** (12)[a]	**5c** (72)[a] (66)[b]	–

[a]Yields calculated from ^{31}P NMR spectra.
[b]Yields after isolation.

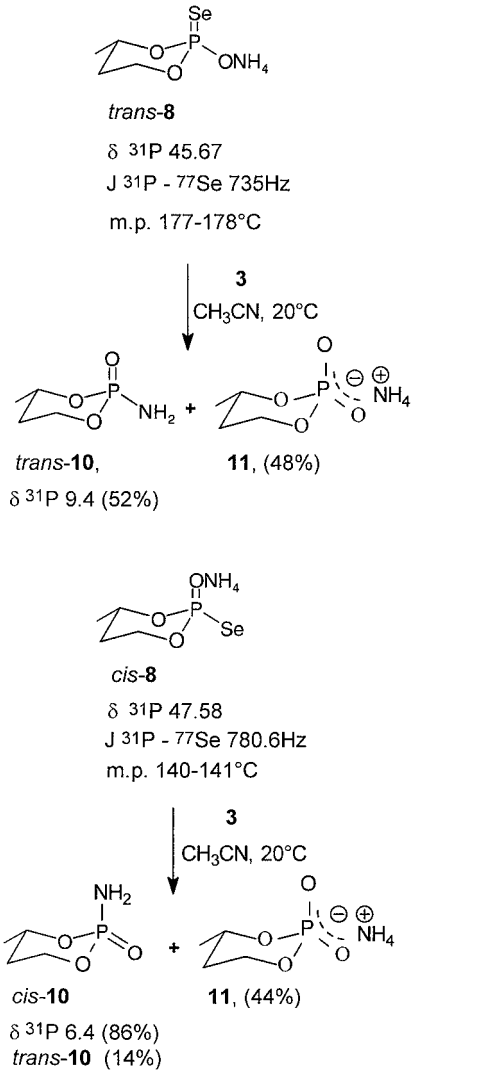
addition of elemental sulfur and selenium to the *cis*- and *trans*-**7** performed in the presence of amines at room temperature [25].

The individual isomers, *trans*-**8** and *cis*-**8** were treated with iodoxybenzene **3** in acetonitrile solution at room temperature, and reaction course was monitored by ^{31}P NMR spectroscopy. Within few minutes of the addition of **3** to the stirred suspension of *trans*-**8** in acetonitrile, yellow color of the reaction mixture appeared, and after about 1 h the slow precipitation of fine red-brown solid material was observed. After 12 h, the formation of 52% of *trans*-2-amino-2-oxo-4-methyl-1,3,2-dioxaphosphinan (**10**, δ ^{31}P 9.4) and 48% of ammonium 2-hydroxy-2-oxo-4-methyl-1,3,2-dioxaphosphinan (**11**, δ ^{31}P −4.68) was identified in the reaction mixture.

Under similar reaction conditions, *cis*-**8** reacts more readily than isomer *trans*-**8** with **3** and the formation of amidate **10**, 55.6% yield, (*cis*-**10** δ 6.4 (86%) and *trans*-**10**, δ 9.4 (14%)), together with ammonium salt **11** (44%) was registered by ^{31}P NMR. The obtained results show that the oxidation of *trans*- and *cis*-**8** by **3** leads to the formation of the amidates *trans*- and *cis*-**10**, respectively (Scheme 3).

The configurational assignment for cis- and trans-amidates **10** has been already established [26]. The data shown in Scheme 3 evidenced the inversion of configuration at phosphorus atom, as the stereochemical result of **8** → **10** transformation. Both starting isomers *cis*- and *trans*-**8** have the same absolute configuration as the product of their transformations **10**, which results from the priority order of the substituents on the phosphorus. However, the spatial arrangements of the substituents around the phosphorus in the products **10**, in comparison to their precursors **8**, are changed. The obtained results offer a direct reaction the transformation of the ammonium dialkyl phosphoroselenoates into dialkyl phosphoramidates. In this process the amido groups in products **4a–c** and **10** origins formally from the ammonium cation of the salts moieties **1a–c** and **8**.

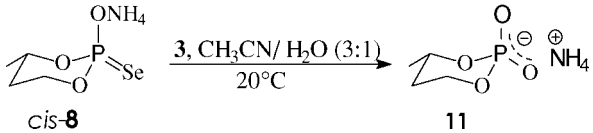
The observed formation of the ammonium phosphates **5a–c** and **11** in these reactions can be due to the direct oxidative deselenization of **1** and **8** by **2** and/or **3**, similar to the well-known oxidative desulphurization of organic thioacids of phosphorus as well as their salts [19–21]. Alternatively, the observed formation of ammonium phosphates **5a–c** and **11** result most probably from the participation of water in this reactions. We have observed that the reaction of iodoxybenzene **3** with *cis*-**8** performed in a solution of acetonitrile/water (3:1) result in the formation of the ammonium 2-hydroxy-2-oxo-4-methyl-1,3,2-dioxaphosphinan (**11**) as the sole reaction product (Scheme 4).



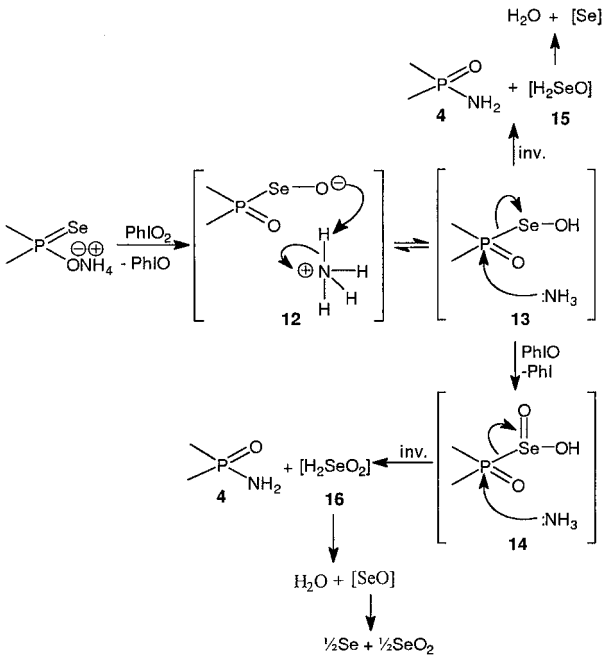
SCHEME 3

Most probably, in the first step of the reaction of salts **1** with **3**, the oxygen atom transfer from **3** to the selenium atom in **1** takes place and the intermediate product **12** is formed (Scheme 5).

The proton transfer from the ammonium cation to oxygen gave selenenic acid **13**. Subsequent formation of seleninic acid **14** is also possible. The nucleophilic attack of ammonia on the phosphorus atom in both **13** and **14** leads to the formation of the corresponding amidates with inversion



SCHEME 4



SCHEME 5

of configuration at phosphorus atom. Formation of both selenic **15** and seleninic **16** acids as unstable reaction products as well as their being the final the sources of the water molecules cannot be excluded. The easy proton abstraction by strongly basic oxygen atom bounded to the selenium is known from the literature [27].

Further studies on the synthetic and mechanistic aspects of the oxidation reaction of ammonium salts of organophosphorus monoselenic acids by iodoxybenzene are in progress.

EXPERIMENTAL

The solvents were dried by standard methods before use. ^{1}H NMR spectra were determined at 200.13 MHz with a Bruker AC 200 spectrometer, using TMS as an internal standard. ^{31}P NMR spectra were taken on a Bruker AC 200 spectrometer at 81 MHz. Positive chemicals shifts are downfield from 85% H_3PO_4 used as an external reference. LSIMS spectra were recorded on a Finnigan MAT 95 spectrometer, in glycerol or 4-nitrobenzyl alcohol, using cesium as the primary ion beam. CIMS spectra were recorded on the same apparatus, using isobutane as a reagent gas. Ammonium *t*-butylphenyl phosphinoselenoate **1c** was synthesized by the reaction of *t*-butylphenylphosphine oxide with elemental selenium in the liquid ammonia solution. Synthesis of **1a** was described recently [24]. Ethylammonium diethyl phosphoroselenoate **1b** was synthesized as pale yellow oil by the addition of elemental selenium to diethyl phosphite in the presence of ethylamine in toluene solution at room temperature, ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.1 $J_{31P\text{-}77Se}$ 775 Hz, MS–FAB *m/z*, 217 [M − NH_4].

*t-Butylphenyl Phosphinoselenoate (***1c***)*

Reaction flask containing mixture of 0.45 g (0.24 mmol) *t*-butylphenylphosphine oxide [28] and 0.2 g (0.24 mmol) selenium in a solution of 25 ml of liquid ammonia was cooled and stirred at −35°C for 8 h. The cooling bath was removed and gaseous ammonia was distilled off. The crude solid was dissolved in dry CH_2Cl_2 (30 ml) and the solution was filtered through Cellite. The solvent was evaporated in vacuo and the remaining crude salt was crystallized twice from dry acetonitrile. Salt **1c** 1.37 g (86%) was obtained as a pale yellow prism, mp 74–75°C, ^{31}P{^{1}H} NMR (D_2O): δ 79.8, $J_{31P\text{-}77Se}$ 601 Hz, MS–FAB *m/z* 261 [M − NH_4] (calculated for ^{80}Se). Anal. calcd. for $C_{10}H_{18}NOPSe$: C, 43.13; H, 6.52; N, 5.03; P, 11.13; Found: C, 43.40; H, 6.26; N, 5.25; P, 11.39.

*Ammonium trans-2-Hydroxy-2-seleno-4-methyl-1,3,2-dioxaphosphinan (***8***)*

In a stirred suspension of finely powdered selenium (0.27 g; 0.34 mmol) in 30 ml of dry liquid ammonia, 0.47 g (0.34 mmol) of *cis*-2-hydrogen-2-oxo-4-methyl-1,3,2-dioxaphosphinan (**7**) [29] in 2 ml of dry ethyl ether was added at −35°C. The reaction mixture was stirred on the bath at temperatures between −33 and −35°C for 8 h. Then the cooling bath was removed and stirring was continued until all amount of ammonia was distilled off. The remaining crude solid product was recrystallized from *i*-propanol/ethyl ether, yield *trans*-**8** 0.69 g (88.5%), mp 177–178°C, ^{31}P{^{1}H} NMR (D_2O): δ 45.67, $J_{31P\text{-}77Se}$ 735 Hz; MS–FAB *m/z* 215 [M − NH_4] (calculated for ^{80}Se); ^{1}H: δ 1.24 (dd, 3H, $J_{H\text{-}CH_3}$ 6.31 Hz, $J_{P\text{-}H}$ 1.82 Hz); δ 1.72–1.86 (m, 2H); δ 4.03–4.13 (m, 1H); δ 4.29–4.35 (m, 1H); δ 4.52–4.60 (m, 1H); IR (KBr): 545.75 (m), 599.32 (m), 756.99 (s), 791.36 (m), 845.25 (w), 885.17 (w), 921.81 (m), 962.74 (w), 980.57 (w), 1028.71 (m), 1070.30 (s), 1079.94 (s), 1120.44 (s), 1156.45 (s), 1224.01 (w), 1250.51 (w), 1375.00 (m), 1385.17 (m), 1462.76 (m), 1655.37 (vw), 2971.79 (m), 3179.60 (m), 3412.27 (w) cm^{-1}. Anal. calcd. for $C_4H_{12}NO_3PSe$: C, 20.70; H, 5.21; N, 6.03; P, 13.34. Found: C, 20.86; H, 5.21; N, 6.08; P, 14.24.

*Reaction of trans-***8** *with Methyl Iodide*

To a stirred suspension of *trans*-**8** (δ ^{31}P 45.7; 0.23 g; 1 mmol) in 15 ml of dry acetonitrile, 0.35 g

(2.5 mmol) of methyl iodide was added. After 18 h the solvent was evaporated in vacuo and the remaining oily product was dissolved in 20 ml of chloroform and filtered. Evaporation of filtrate and evacuation of the remaining material at 20°C under pressure 1 mm Hg for 4 h afforded *trans*-2-methylseleno-2-oxo-4-methyl-1,3,2-dioxaphosphinan (**9**) 0.21 g (94%), mp 55–56°C, $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.18, $J_{31P\text{-}77Se}$ 469 Hz; (Ref. [25] mp 58–59°C, δ ^{31}P 11.7, $J_{31P\text{-}77Se}$ 444.7 Hz); CIMS *m/z* 231 [M + 1] (calculated for ^{80}Se).

*Ammonium cis-2-Hydroxy-2-seleno-4-methyl-1,3,2-dioxaphosphinan (**8**)*

In the reaction of 1.46 g (10.7 mmol) of *trans*-2-hydrogen-2-oxo-4-methyl-1,3,2-dioxaphosphinan(**7**) [29], contaminated by 8% *cis*-(**7**) isomer, with 0.83 g (10.7 mmol) of selenium, in 35 ml liquid ammonia solution, performed as described above, a mixture of two products δ ^{31}P 47.62 (93%) and δ ^{31}P 43.32 (7%) was obtained. From this, 1.92 g (77% yield), mp 140–141°C (*i*-PrOH/Et_2O) of pure *cis*-**8** ($^{31}P\{^1H\}$ NMR (D_2O): δ 47.58, $J_{31P\text{-}77Se}$ 780.6 Hz, MS–FAB, *m/z* 215 [M − NH_4]) was isolated by crystallization. ^1H: δ 1.19 (dd, 3H, $J_{H\text{-}CH_3}$ 6.39Hz, $J_{P\text{-}H}$ 1.13 Hz); δ 1.69–1.76 (m, 1H); δ 1.83 (m, 1H); δ 4.02 (m, 1H); δ 4.25 (m, 1H); δ 4.5 (m, 1H); IR (KBr): 552.78 (w), 593.97 (vw), 765.60 (m), 844.21 (w), 880.80 (m), 923.74 (s), 962.14 (s), 978.53 (m), 1025.83 (m), 1066.44 (vs), 1133.34 (m), 1156.65 (m), 1251.58 (vw), 1386.57 (m), 2972.63 (m), 3153.65 (m), 3414.42 (w) cm^{-1}. Anal. calcd. for $C_4H_{12}NO_3PSe$: C, 20.70; H, 5.21; N, 6.03; P, 13.34. Found: C, 20.64; H, 5.21; N, 6.06; P, 14.24.

*Reaction of cis-**8** with Methyl Iodide*

In the reaction of 0.102 g (0.43 mmol) of **8** (93% cis, 7% trans) with 0.2 g (1.4 mmol) of methyl iodide, in 15 ml of acetonitrile, 0.09 g (96%) of *cis*-(**9**) was obtained as an oily liquid, $n^{20}{}_D = 1.5173$, $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.35, $J_{31P\text{-}77Se}$ 501 Hz, CIMS *m/z* 231 [M + 1] (calculated for ^{80}Se) (Ref. [25] δ ^{31}P 14.0, $J_{31P\text{-}77Se}$ 476.3 Hz).

*Reaction of **1a** with Iodosobenzene **2***

In a stirred solution of 0.23 g (1 mmol) of **1a** in 5 ml of acetonitrile, 0.22 g (1 mmol) of **2** was added at 20°C and stirred continuously for 1 h. ^{31}P NMR analysis of the reaction mixture showed the presence of ammonium diethyl hydrogen phosphate (**5a**; δ −0.42; 12%) and diethyl phosphoroamidate (**4a**; δ 9.8; 36%). In ^{31}P NMR spectrum of the reaction mixture, a broad signal of unidentified product was observed at δ 12.9 (51%). During the prolongation of the reaction time the broad line at 12.9 disappeared slowly and a mixture of organophosphorus compounds with δ −0.1, 3.6, 10.2, 11.5, 12.6 near amidate **4a** (42%) and salt **5a** (14%) was formed.

*Oxidation of **1a** by **2** in the Presence of Montmorillonite K10*

In a stirred suspension of 0.3 g (1.38 mmol) of **2** and 0.15 g of montmorillonite K10 in 10 ml acetonitrile, 0.32 g (1.38 mmol) of **1a** dissolved in 5 ml of acetonitrile was added at room temperature. After 2 h the following organophosphorus products were observed: amidate **4a** with δ 9.92 (28%), salt **5a** with δ −0.49 (9%), tetraethyl pyrophosphate δ 13.0 (5%), and a compound characterized by broad line at δ 19.63 (63%), $J_{31P\text{-}77Se}$ 548 Hz. The broad line at δ 19.6 is most probably a characteristic of bis(diethylphosphinyl)diselenide (**6a**) (Ref. [30] δ ^{31}P 13.0, $J_{31P\text{-}77Se}$ 580 Hz; Ref. [31] δ ^{31}P 11.1, $J_{31P\text{-}77Se}$ 498 Hz).

*Reaction of **1a** with Iodoxybenzene **3***

To a stirred solution of 1.17 g (5 mmol) of **1a** in a dry acetonitrile (10 ml) at 20°C under nitrogen, 1.18 g (5 mmol) of **3** was added. Stirring was continued for 1 h and to the red-brown solution were added 2 g of Cellite and neutral Al_2O_3 (1:1). The reaction mixture was stirred for the next 25 min and solid materials were filtered off and washed with CH_3CN (3 × 5 ml). The solvent was distilled off in vacuo at room temperature and yellow colored viscous liquid was obtained. In this, the presence of diethyl phosphoramidate **4a** (δ 9.9; 85%) together with two other unidentified products (δ 12.2; 10% and δ 6.1; 5%) was found by ^{31}P NMR. From this mixture, 0.56 g (71%) of **4a** with mp 53–55°C (Ref. [32] mp 55.5°C, Ref. [33] δ ^{31}P 10.9) was separated by flash column chromatography, eluent: petroleum ether (bp 40–60°C): diethyl ether (4:1), MS–FAB *m/z* 152 [M − 1], *m/z* 154 [M + 1].

*Reaction of **1b** with Iodoxybenzene **3***

To a stirred solution of 2.8 g (10.8 mmol) of **1b** in 20 ml of acetonitrile, 2.3 g (10.8 mmol) of **3** at 20°C was added and stirring was continued for 1 h. ^{31}P NMR analysis of the reaction mixture performed after this showed the presence of diethyl *N*-ethylphosphoramidate (**4b**; δ 9.47; 42%), ethylammonium diethylhydrogen phosphate (**5b**; δ 0.15; 26%), and two unidentified products (δ 11.66; 9% and δ 4.29; 22%). The solvent was distilled off and

red-brown viscous liquid was obtained. The MS–FAB and CIMS analysis of this crude material showed the presence of lines: *m/z* 153, characteristic for anion $(EtO)_2PO_2^-$ and *m/z* 182 [M + 1], characteristic for **4b**. To this 20 ml of $CHCl_3$ and 2 g of Cellite was added. The solution was stirred for 20 min and the solid material was filtered off and washed with chloroform (2 × 10 ml). The solution was distilled off and from the residual oil amidate **4b** (0.43 g; 26%) was separated by distillation. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.87, bp 63–66°C/0.2–0.3 mm Hg, (bath temp. 100–105°C), $n^{20}{}_D = 1.4286$ (Ref. [34] $\delta^{31}P$ 9.9, $n^{20}{}_D = 1.4300$).

Reaction of Salt **1c** *with* **3** *in the Presence of Montmorillonite K10*

A mixture of 0.27 g (1 mmol) of **1c** and 0.23 g (1 mmol) of **3** was stirred and heated under reflux in 15 ml of dry acetonitrile for 1.5 h. ^{31}P NMR spectrum of the reaction solution showed the presence of only one line at δ 78.0 characteristic for the substrate **1c**. To this reaction solution 0.1 g of dry montmorillonite K10 was added, and the reaction mixture was heated under reflux for 1.5 h. After this the formation of salt **5c** (δ 44.30; 72%) together with 12% yield of amidate **4c** (δ 39.33; Ref. [35] δ ^{31}P 41.4) and another unidentified organophosphorus compounds (δ 50.48; 9% and δ 49.9; 7%) was observed by ^{31}P NMR. The solvent was distilled off and into the remaining red-brown, syrupy liquid of 20 ml dry ethanol, 2.0 g charcoal, and 2.0 g Cellite were added. The mixture was stirred for 30 min at 20°C and filtered through Cellite. The solvent was distilled off and the remaining oily, slowly solidifing liquid was keep standing for 1 h under pressure 1 mm Hg at temperature 25°C. Recrystallization of crude material from *i*-propanol/ethyl ether gave 0.13 g (66%), mp 153–154°C, MS–FAB *m/z* 197 [$Bu^tPhP(O)O^-$] of ammonium *t*-butylphenyl phosphinoate (**5c**). The isolated salt **5c** was identical with the one obtained in an independent way in the reaction of *t*-butylphenyl phosphinic acid [28] with gaseous ammonia in chloroform solution, $^{31}P\{^1H\}$ NMR (D_2O): δ 43.05, mp 153–154° C, Anal. calcd. for $C_{10}H_{18}NO_2P$: C, 55.81; H, 8.42; N, 6.50; P, 14.39; Found: C, 55.63; H, 8.16; N, 8.38; P, 14.26.

*Reaction of trans-***8** *with* **3**

In a stirred solution of 0.34 g (1.46 mmol) of *trans*-**8** in 5 ml dry acetonitrile, 0.34 g (1.46 mmol) of dry iodoxybenzene (**3**) was added at 20°C. Stirring was continued at this temperature, and after 90 min the formation of red-brown precipitate in the reaction mixture was observed. Stirring was continued for the next 12 h. The solvent was distilled off, and the remaining black-gray colored syrupy material was dissolved in 15 ml of ethanol and filtered through Cellite. After removal of the solvent, $^{31}P\{^1H\}$ NMR (EtOD) spectrum of the crude product showed the presence of two lines at δ 9.40 (52%), which was identified as a characteristic for amidate *trans*-**10** (Ref. [26] δ ^{31}P 9.1 (EtOD)), and δ −4.68 (48%) characteristic for ammonium-2-hydroxy-2-oxo-4-methyl-1,3,2-dioxaphosphinan salt **11**. MS–FAB *m/z* 152 [**10** + 1], *m/z* 151 [anion **11**].

*Reaction of cis-***8** *with* **3**

To a stirred solution of 0.23 g (1 mmol) of *cis*-**8** in 5 ml of acetonitrile, 0.23 g (1 mmol) of **3** was added at room temperature. After 40 min the formation of red-brown precipitate was observed. Stirring was continued for the next 12 h. The solvent was evaporated and the brown syrupy oily liquid was obtained. In this product, 56% of amidate **10**, (86% of *cis*-**10** δ 6.40 and 14% of *trans*-**10** δ 9.47) (Ref. [26] δ ^{31}P for *cis*-**10** 6.0) together with 44% of the salt **11** were identified by analysis of $^{31}P\{^1H\}$ NMR spectra; MS–FAB *m/z* 152 [**10** + 1], *m/z* 151 [anion **11**].

*Reaction of cis-***8** *with* **3** *in the Solution of Acetonitrile–Water (3:1)*

A stirred solution of 0.23 g (1 mmol) of salt *cis*-**8** in 10 ml acetonitrile–water (3:1) was treated at room temperature with 0.23 g (1 mmol) of **3**. Immediate precipitation of red-brown solid material from the reaction solution was observed. Stirring was continued for the next 4 h. ^{31}P NMR analysis of the reaction mixture showed only one product with δ −4.14. No change in this δ ^{31}P value, after treating the sample of the reaction solution with gaseous ammonia, was observed. The reaction solution was filtered through Cellite and the solvents were distilled off. The remaining material was kept standing at a temperature range of 15–20°C under pressure of 0.1–0.5 mm Hg for 6 h and 0.12 g (75%) of a syrupy oil that slowly solidified at 5°C ($^{31}P\{^1H\}$ NMR δ: −4.04, MS–FAB *m/z* 151 [M − NH_4]) was obtained. The same product, synthesized on the independent route in the reaction of gaseous ammonia with 2-hydroxy-2-oxo-4-methyl-1,3,2-dioxaphosphinan [36] in ethanol solution, was syrupy oily liquid, $^{31}P\{^1H\}$ NMR δ: −3.67.

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