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Indirect Photo-induced Phosphorylation via a Photolabile Troika Acid C-Ester: *o*-Nitrobenzyl (*E*)-(Hydroxyimino)(dihydroxyphosphinyl)acetate

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Abstract—*Indirect* photo-induced phosphorylation of hydroxylic solvents via UV photolysis of a *C*-*o*-nitrobenzyl ester (*E*-**9**: anilinium salt) of (*E*)-(hydroxyimino)(dihydroxyphosphinyl)acetic acid (*E*-**1**, 'troika acid') is demonstrated. Comparable phosphorylation (MeOH) was observed for the dicyclohexylammonium salt (*E*-**10**). Photolysis of *E*-**9** in 1:1 EtOH/*t*-BuOH gave Et-phosphate/*t*-Bu-phosphate in a ratio (~3:1) suggesting phosphorylation involves dissociative fragmentation of *E*-**1** formed via photo-induced de-esterification of *E*-**9**. Broad-band (Hg-lamp), 308 nm (XeCl excimer laser) or 355 nm (YAG laser) UV irradiation of *E*-**9** also promoted significant *E*→*Z* isomerization and concurrent photolysis leading to phosphorocyanidate. C-Me esters of *E*-**1** and *Z*-**1** were photo-isomerized by the 308 nm laser but not the 355 nm laser, showing that the *o*-nitrobenzyl group is required for photo-isomerization at 355 nm. © 2000 Elsevier Science Ltd. All rights reserved.

E and *Z* 'troika acids' (**1**) can be prepared in situ by alkaline cleavage of the C-methyl esters (*E*-**2** and *Z*-**2**).[1] At neutral pH and room temperature, **1** undergoes hydrolytic fragmentation. This process is stereospecific: the *E* isomer cleaves at the P–C_α bond, phosphorylating the solvent via a presumed monomeric metaphosphate intermediate (**3**) to produce inorganic phosphate (**4**, R=H); the *Z* isomer cleaves at the C_α–$C_\beta$bond, forming phosphorocyanidate (**5**). Similar fragmentation occurs on heating *E*-**2** in alcohols, giving monoalkyl phosphates (**4**, R=Et, *i*-Pr, *t*-Bu) (Scheme 1†).[1]

Previous work[2–4] has demonstrated photo-induced phosphorylation using substrates in which the photolabile group was directly attached to a phosphonate moiety (P-ester). Thus, Breuer and Quin reported phosphorylation of ethanol by UV photolysis of *o*-nitrobenzyl or benzyl P,P-diesters of the α-oxime of benzoylphosphonic acid.[3] In their work, the photosubstrates were mixtures of *E* and *Z* isomers. Photo-de-esterification was proposed to lead to the corresponding *E*-acid, which fragmented producing monomeric metaphosphate. The latter highly reactive intermediate then phosphorylated the solvent alcohol.

In troika acid **1**, the status of the carboxylate group modulates the reactivity of the neighboring phosphonate moiety,[1] suggesting to us that photolysis of a susceptible *C*-ester of **1** could lead to *indirect* photo-induced phosphorylation—indirect in the sense that photolysis occurs at a site that is distal from the phosphonate group to be activated. To this end, we have synthesized two amine salts of *o*-nitrobenzyl (*E*)-(hydroxyimino)(dihydroxyphosphinyl)acetate (*E*-**9** and *E*-**10)**, troika acid derivatives with a UV light-sensitive C-ester caging group, and investigated their photochemistry using broad band UV (Hg lamp), 308 nm XeCl excimer laser or 355 nm YAG laser irradiation in neutral aqueous buffer and in alcohol solvents.‡ The *o*-nitrobenzyl group is a commonly used photolabile caging group for esters, undergoing photo-induced cleavage via an internal redox process.[6,7] Irradiation of *E*-**9** and *E*-**10** (and, for comparison, *E*-**2** and *Z*-**2**) was carried out at several different wavelengths in an attempt to distinguish photocleavage of the *o*-nitrobenzyl caging group from any photo-induced isomerization of the oxime moiety.

Results and Discussion

Synthesis of E-**9** *and E*-**10**. (Scheme 2) (Dimethoxyphosphinyl)acetic acid **6**,[8] from trimethyl phosphonoacetate (1 equiv. of KOH in cold MeOH; acidification with Dowex 50W×8-200 H^+ ion-exchange resin)[9] was

Keywords: photochemistry; troika acid; phosphorylation; monomeric metaphosphate.

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† For convenience, **1** and related compounds expected to ionize under given conditions are shown fully protonated in the Schemes.

‡ A preliminary account of this work was given at the XIVth International Conference on Phosphorus Chemistry, Cincinnati, OH, USA, July 12–17, 1998.[5]

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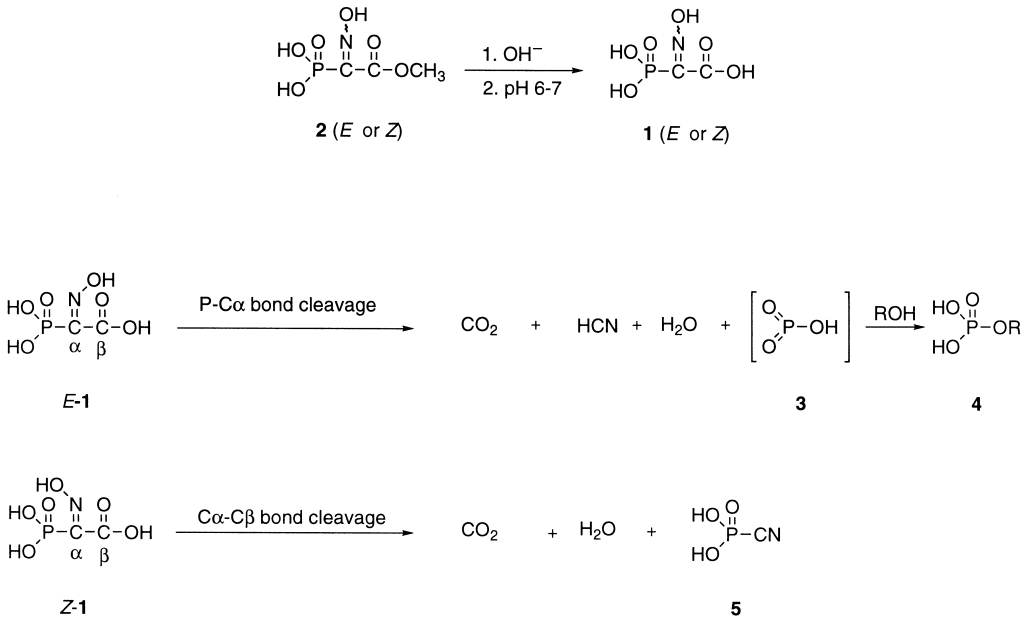
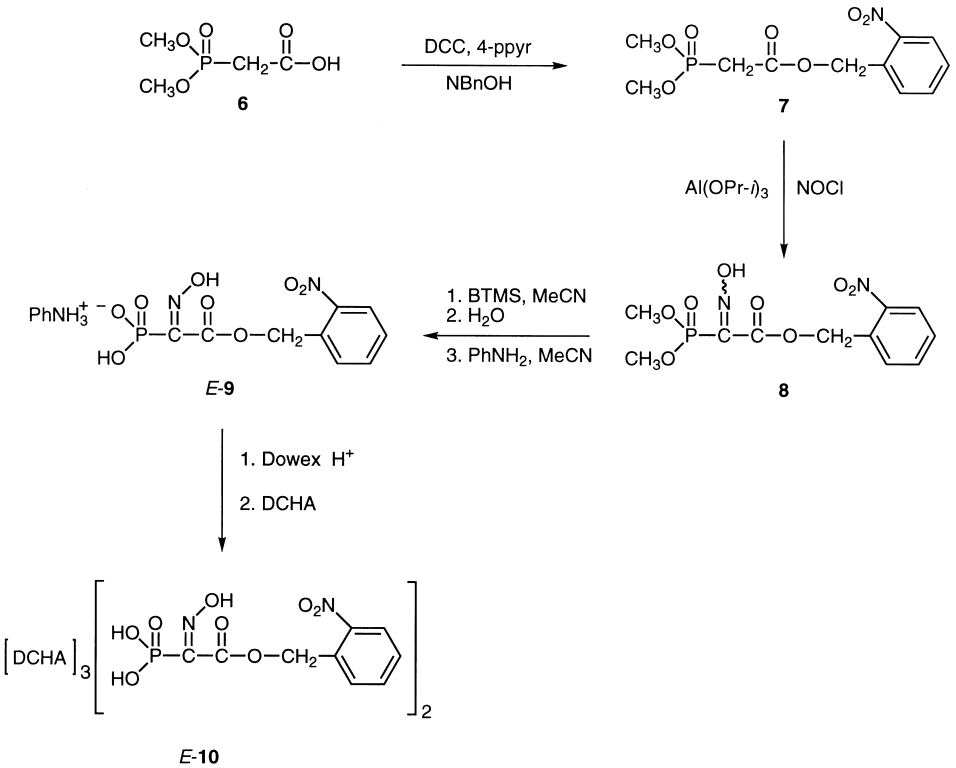


Scheme 1.

converted to its *o*-nitrobenzyl (NBn) ester **7** (81%) using DCC (N,N′-dicyclohexylcarbodiimide) coupling catalyzed by 4-pyrrolidinopyridine (4-ppyr).[10] Reaction of **7** with nitrosyl chloride in the presence of aluminum isopropoxide[11] gave the oxime **8** (22%) as a 24:1 *E:Z* mixture. P-selective[12] silyldemethylation[13] using bromotrimethylsilane (BTMS) in acetonitrile gave *o*-nitrobenzyl (*E*)-(dihydroxyphosphinyl)-(hydroxyimino)acetate, isolated (62%) and characterized as its monoanilinium salt, *E*-**9**. Recrystallization from methanol/ether gave isomerically pure *E*-**9**. The oxime isomers were assigned on the basis of correlative ^{31}P NMR δ values[14] and ^{13}C NMR $^{1}J_{CP}$ values.[15] Acidification of *E*-**9** with Dowex 50W×8-200 H^+ ion-exchange resin followed by addition of excess dicyclohexylamine (DCHA) produced the dicyclohexylammonium salt (71%) *E*-**10** (>97% *E*).



Scheme 2.

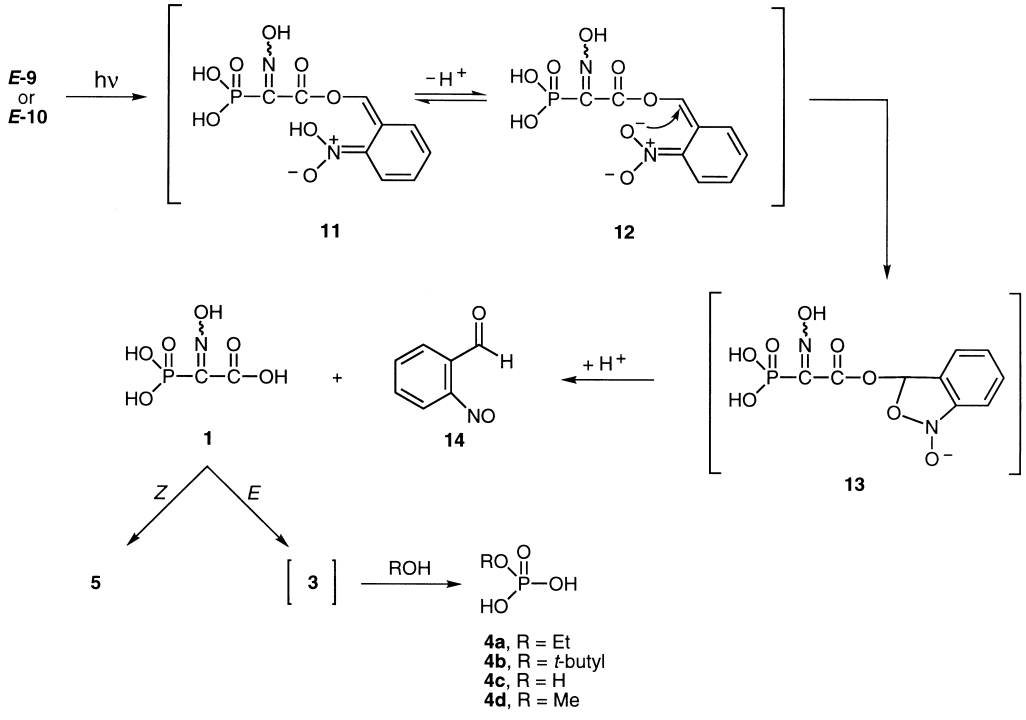
Table 1. Photolysis and isomerization of troika acid esters

Exp	Cmpd	UV Source[a]	T (h)	Solvent (pH)	%*E* (^{31}P δ ppm)	%*Z* (^{31}P δ ppm)	% 4[b] (^{31}P δ ppm)	% 5 (^{31}P δ ppm)
1	*E*-**9**	None	0	MeOH	96.4 (0.22)	3.6 (0.49)	0	0
2	*E*-**9**	None	8	MeOH	88.8 (0.22)	11.2 (0.49)	0	0
3	*E*-**9**	BBUV	8	MeOH	26.1 (2.00)	9.9 (2.95)	15.7 (2.52)	34.3 (−19.9)
4	*E*-**9**	308 nm	8	MeOH	3.7 (2.14)	<1	28.1 (2.49)	68.2 (−20.2)
5	*E*-**9**	355 nm	8	MeOH	17.1 (2.10)	4.7 (2.93)	27.9 (2.46)	50.3 (−20.0)
6	*E*-**10**	None	0	MeOH	92.8 (−0.65)	7.2 (−0.53)	0	0
7	*E*-**10**	None	8	MeOH	55.9 (−0.65)	44.1 (−0.53)	0	0
8	*E*-**10**	355 nm	8	MeOH	10.7 (−0.64)	14.3 (−0.49)	33.0 (3.43)	41.9 (−18.6)
9	*E*-**2**	None	0	H_2O (3.36)	100.0 (−1.13)	0	0	0
10	*E*-**2**	None	8	H_2O (3.81)	100.0 (−1.14)	0	0	0
11	*Z*-**2**	None	0	H_2O (7.15)	0	100.0 (2.38)	0	0
12	*Z*-**2**	None	8	H_2O (7.33)	37.2 (−0.80)	62.8 (2.38)	0	0
13	*E*-**2**	308 nm	8	H_2O (3.43)	84.0 (−1.14)	16.0 (−3.83)	0	0
14	*Z*-**2**	308 nm	8	H_2O (7.19)	53.0 (−0.83)	47.0 (2.34)	0	0
15	*E*-**2**	355 nm	8	H_2O (3.79)	100.0 (−1.14)	0	0	0

[a] BBUV: broad-band UV (Hg lamp).
[b] Exps. 1–8, **4d** (methyl phosphate); 9–15, **4c** (phosphate). Relative amounts of phosphorus-containing products were measured using ^{31}P NMR peak area integration.

Photochemical Studies. Aqueous neutral solutions of *E*-**9** kept in the dark for 24–48 h showed a small tendency to isomerize to *Z*-**9** (9–15%). A trace of inorganic phosphate (2–3%) (**4c**) was observed, likely derived from *E*-**1**, formed from hydrolysis of *E*-**9**. Broad band UV irradiation over the same period gave a net increase in **4c** (14–16%, total) plus 4–6% **5**, the product expected from hydrolytic C_α–C_β cleavage of *Z*-**1**,[1] together with 13–16% of *Z*-**9** (products identified by ^{31}P NMR). Formation of a brown precipitate, assumed to be *o*-nitrosobenzaldehyde (**14**),[16] prompted a change of solvent to MeOH, which provided homogenous reaction mixtures. For all subsequent experiments the reaction time was decreased to 8 h.

A 0.1% solution of *E*-**9** in MeOH slightly isomerized in the dark, but no fragmentation was evident (Table 1, Exps. 1, 2). On irradiation with broad-band UV (Exp. 3), significant (50%) photo-induced fragmentation was observed, yielding both methyl phosphate (**4d**), the expected phosphorylation product from the *E* isomer, and phosphorocyanidate (**5**), the expected *Z* isomer fragmentation product (**4d**:**5**, 1:2). A small amount of *E*-**9** was transesterified by the solvent to form methyl (hydroxyimino)(dihydroxyphosphinyl)acetate (14%). Transesterification was not observed with laser irradiation. Laser irradiation at 308 nm or 355 nm (Exps. 4, 5) increased the yield of P-containing fragmentation products to 96% and 78% respectively, although the *Z* isomer product again predominated in both cases (Scheme 3).



Scheme 3.

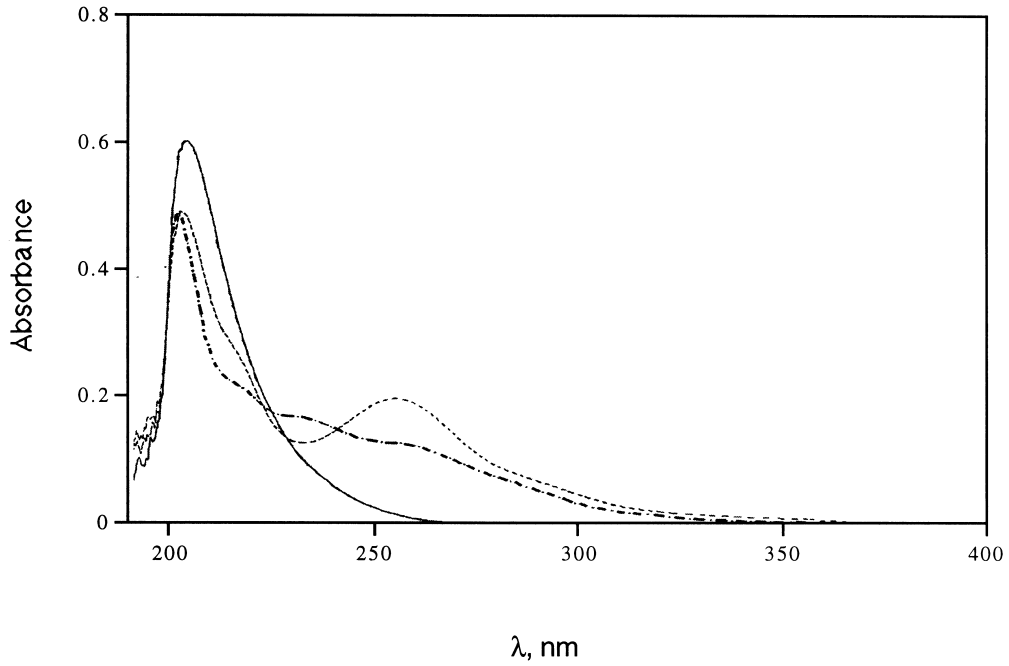


Figure 1. UV spectra of troika acid C-esters in methanol. (—) *E*-**2** (0.115 mM, λ_{max} 205 nm, ϵ_{max} 5.2 $\times 10^3$). (— ● —) *E*-**9** (0.025 mM, λ_{max} 204 nm, ϵ_{max} 2.0×10^4). (— —) *E*-**10** (0.034 mM, λ_{max} 205 nm, ϵ_{max} 1.5×10^4).

To ascertain what effect the aromatic anilinium cation in *E*-**2** might have on the observed photochemistry, the dicyclohexylammonium (DCHA) salt *E*-**10** was investigated. In the dark (Exps. 6, 7), a 0.1% solution of *E*-**10** in methanol initially consisting of 93:7 *E:Z*, isomerized to ~5:4 *E:Z*. Irradiation at 355 nm (Exp. 8) gave 75% of **4d** plus **5**, similar to the total yield of these products from the anilinium salt (Exp. 5), with slightly more phosphorylation product **4d**. Thus, the absence (DCHA) or presence (anilinium) of a UV-absorbing cation has at most a small effect on the photochemical reaction pathways. The more rapid dark isomerization of *E*-**10** compared with *E*-**9** may be attributable to the greater basicity of DCHA compared to aniline, catalyzing *E*→*Z* conversion in solution.[14]

The UV spectra of *E*-**2**, *E*-**9** and *E*-**10** are presented in Fig. 1. The oxime groups in *E*-**2**, *E*-**9** and *E*-**10** absorb UV light strongly near 205 nm, but unlike the two *o*-nitrobenzyl esters, the methyl ester *E*-**2** exhibits virtually no absorption in the near UV region. To separate the contributions of the oxime and *o*-nitrobenzyl chromophores to *E*-**9** and *E*-**10** photochemistry, we separately exposed aqueous solutions of *E*-**2** (0.2%) to 308 and 355 nm laser light: no UV-dependent fragmentation could be observed (Exps. 9–15). Irradiation of *Z*-**2** at 308 nm (Exp. 14) also failed to give fragmentation products. *E* and *Z* isomers of **2** were detected by ^{31}P NMR and confirmed by HPLC.

After 308 nm UV laser irradiation, isomerization of *E*-**2** and *Z*-**2** was evident (Table 1, Exps. 13, 14). Significantly, *E*-**2,** which is stable to isomerization in the dark at pH 3–4,[¶] was not detectably isomerized by 355 nm UV irradiation (Exp. 15). In contrast, irradiation of *E*-**10** at 355 nm produced a substantial amount of **5**, indicating that photo-isomerization of *E*-**10** depends in part on the *C-ester* photochemistry, possibly via an energy transfer or charge transfer effect.

Broad band UV irradiation of *E*-**9** (0.1%) in 1:1 EtOH/*t*-BuOH produced a mixture of ethyl phosphate (**4a**) (^{31}P NMR δ −0.06) and *t*-butyl phosphate (**4b**) (^{31}P NMR δ −3.97) (**4a**:**4b**, 3.1:1, total 17%), plus phosphorocyanidate (**5**, 35%) (^{31}P NMR δ −21.8). The balance was unreacted **9**. Under the same conditions, the 308 nm laser produced a 2.4:1 ratio of **4a** (^{31}P NMR δ −0.21):**4b** (^{31}P NMR δ −4.13) (**4a**+**4b**, 28%), with 51% **5** (remainder, unreacted starting material). Competitive phosphorylation of *t*-BuOH and primary alcohols at comparable rates (i.e. minimal steric effect) is a marker for dissociative fragmentation.[17,18]

Scheme 3 presents a proposed pathway for photochemical activation of the *o*-nitrobenzyl caging group, leading via a succession of dark reaction intermediates **11**–**13**[16] to formation of the parent troika acid **1**. Dissociative fragmentation of *E*-**1** would give monomeric metaphosphate **3** (at least in the alcohols), which is then quenched by a solvent nucleophile. An alternative pathway could involve fragmentation concerted with cleavage of an activated ester product such as **13**.

In conclusion, we have demonstrated that photo-removal of the C-*o*-nitrobenzyl ester group in *E*-**9** and *E*-**10** under mild conditions serves as a trigger for a novel indirect photo-induced phosphorylation process involving P–C_α bond cleavage, accompanied by oxime isomerization leading to characteristic C_α–C_β bond cleavage in the *Z*-isomer formed. Previous work with alkyl esters of troika acids had shown that acidic (P-methyl ester of **1**)[9] or alkaline (C-methyl

[¶] Unlike *Z*-**2** at neutral pH (Exp. 12). The latter isomer produces a higher pH because it is isolated as a bis(DCHA) salt.[1]

ester, **2**)[1] conditions were required for activation.[§] Design of a photo-activated troika acid system permitting control of the isomerization process would be of interest. The observed dependence of photo-isomerization on the C-ester caging group as well as oxime functionalization[14] suggests a future approach to this problem.

Experimental

Reagents were AR grade from Aldrich, Inc. NMR (Bruker AM 360) spectra were referenced to TMS (^{1}H, ^{13}C) or ext. 85% H_3PO_4 (^{31}P). NMR spectral data were processed using: Nuts 2D (ver. 4.27, Acorn NMR, Inc.) and Mac FID 1D (ver. 5.2, Techmag, Inc.) software. Melting points were recorded on a Thomas Hoover apparatus and are uncorrected. Broad band UV photochemistry was investigated using a Rayonet photochemical reactor equipped with eight GE G8T5 germicidal lamps. Laser experiments were performed using a Questek 2000 308 nm XeCl excimer laser (60 mJ constant, 10 Hz) and a Spectrophysics GRII 355 nm YAG laser (20 mJ constant, 10 Hz). Elemental analyses were done by Galbraith Laboratories, Inc.

***o*-Nitrobenzyl (dimethoxyphosphinyl)acetate 7.** A mixture of **6** (20 mmol, 3.36 g), *o*-nitrobenzyl alcohol (18 mmol, 2.76 g), and 4-pyrrolidinopyridine (1 mmol, 0.14 g) in dry CH_2Cl_2 was added dropwise to a solution of DCC (20 mmol, 4.13 g) in 30 mL CH_2Cl_2 at <30°C. After 24 h at rt, the mixture was filtered, and the filtrate washed with 30 mL water, 30 mL 5% HOAc, 2×30 mL water and dried with anh. sodium sulfate. Evaporation under vacuum left **7**: 4.91 g (81%). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.07 (d, $^2J_{CP}$=18.5 Hz, 2H, PCH_2), 3.79 (d, 6H, OCH_3), 5.59 (s, 2H, OCH_2), 7.65–8.12 (m, 4H, C_6H_4). ^{31}P NMR ($CDCl_3$): δ (ppm) 22.5.

***o*-Nitrobenzyl (dimethoxyphosphinyl)(hydroxyimino)acetate 8.** The ester **7** (2.00 g, 6.6 mmol) in 40 mL CH_2Cl_2 and aluminum isopropoxide (1.34 g, 6.4 mmol) in 40 mL CH_2Cl_2 were mixed, and NOCl (0.86 g, 13 mmol) in 5 mL CH_2Cl_2 was added dropwise, at 10–15°C. After 45 min, 100 mL of CH_2Cl_2 was added and the solution washed with 3×100 mL cold water. After drying with anh. sodium sulfate, the solvent was evaporated and the product purified by silica gel chromatography (6:1 chloroform:acetone): 0.48 g (22%), mp 105–106°C. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.87 (d, 6H, OCH_3), 5.80 (s, 2H, OCH_2), 7.48–8.21 (m, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ (ppm) 54.3 (d, $^2J_{CP}$=6.1 Hz, OCH_3), 64.7 (s, CH_2), 125.2, 129.0, 129.1, 130.9, 134.2, 142.1 (C_6H_4), 145.8 (d, $^1J_{CP}$=220.9 Hz, P–C=N), 160.3 (d, $^2J_{CP}$=24.4 Hz, C=O). ^{31}P NMR ($CDCl_3$) δ (ppm) 7.1 (*E*) 96.1%, 6.7 (*Z*) 3.9%. Calcd for $C_{11}H_{13}O_8N_2P$: C, 39.77; H, 3.94; N, 8.43. Found C, 39.81; H, 3.91; N, 8.36.

Anilinium salt of *o*-nitrobenzyl (*E*)-(hydroxyimino)(dihydroxyphosphinyl)acetate *E*-9. Ester **8** (0.28 g, 0.83 mmol) in 10 mL acetonitrile was stirred with bromotrimethylsilane (0.38 g, 2.49 mmol) for 4 h. A few drops of water were added followed by freshly distilled aniline (0.155 g, 1.66 mmol) and ether. Recrystallization from MeOH/ether gave 0.21 g (62%), mp 131.5–132.5°C. ^{1}H NMR (D_2O): δ (ppm) 5.29 (s, 2H, OCH_2), 6.77–7.78 (m, 9H, C_6H_4, C_6H_5). ^{13}C NMR (1:1 D_2O:d_6-acetone): δ (ppm) 65.2 (s, CH_2), 125.4, 129.9, 131.0, 132.4, 135.7, 147.7 (C_6H_4), 123.3, 126.0, 128.9, 133.3 (C_6H_5), 152.3 (d, $^1J_{CP}$=191.7 Hz, P–C=N), 164.5 (d, $^2J_{CP}$=20.8 Hz, C=O). ^{31}P NMR (D_2O): δ (ppm) −1.3. Calcd for $C_{15}H_{16}N_3O_8P\cdot 0.5\ H_2O$: C, 44.34; H, 4.22; N, 10.34. Found C, 44.37; H, 4.24; N,10.29.

DCHA salt of *o*-nitrobenzyl (*E*)-(hydroxyimino)(dihydroxyphosphinyl)acetate, *E*-10. *E*-**9** (0.050 g, 0.12 mmol) in MeOH was treated with Dowex H^+ 50W× 8-200 ion exchange resin, and freshly distilled DCHA (3 equiv.) was added. Recrystallization from MeOH/ether, with ether wash gave 0.052 g (71%), mp 102.5–103.5 °C. ^{1}H NMR (D_2O): δ (ppm, pH 5.8) 7.27–8.07 (m, 4H, C_6H_4), 5.54 (s, 2H, CH_2), 3.02 (s, 3H, CH), 0.87–1.98 (m, 30H, C_5H_{10}). ^{13}C NMR (1:1 D_2O:d_6-acetone): δ (ppm) 24.5, 25.0, 29.3, 53.3 (cyclohexyl), 63.6 (s, CH_2), 125.0, 129.3, 129.4, 132.1, 135.0, 147.0 (C_6H_4), 152.3 (d, $^1J_{CP}$=184.3 Hz, P–C=N), 165.4 (d, $^2J_{CP}$=18.3 Hz, C=O). ^{31}P NMR (D_2O, pH 5.8): δ (ppm) 1.6 (*Z*-isomer, 2.5%), −1.1 (*E*-isomer, 97.5%). Calcd for $C_9H_9N_2O_8P\cdot 1.5$ DCHA$\cdot H_2O$: C, 54.58; H, 7.72; N, 8.25. Found C, 54.44; H, 7.94; N,8.02.

Photochemistry. Solutions of *E*-**9** or *E*-**10** (0.1% (w/v) in 100 mM Tris buffer (pH 7.0) or alcohol) and *E*-**2** and *Z*-**2** (0.2% (w/v) in D_2O) were irradiated in a quartz test tube (4 mm i.d. ×12 cm) for 24–48 h (Tris buffer) or 8 h (alcohols). Photo-products were identified (^{31}P NMR) by spiking with known compounds.

HPLC. HPLC analyses were performed using a Rainin SD-200 HPLC run isocratically. Samples (20 μL, 0.2% (w/v) in D_2O) were injected onto a Microsorb C 18 column (Varian), eluted at a flow rate of 0.5 mL/min with 0.1N phosphate, pH 7.5, containing 3 mM $(Bu)_4N(H_2PO_4)$ as ion pairing agent. Peaks were observed with a Rainin UV-DII UV-visible detector (205 nm). HPLC elution times for *E*-**2** and *Z*-**2** were 3.2 min and 3.6 min respectively.

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§ Recently, it was demonstrated that hydrolysis of the *p*-nitrophenyl C-ester of **1** near neutral pH is strongly promoted by Ni^{2+}.[19]

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