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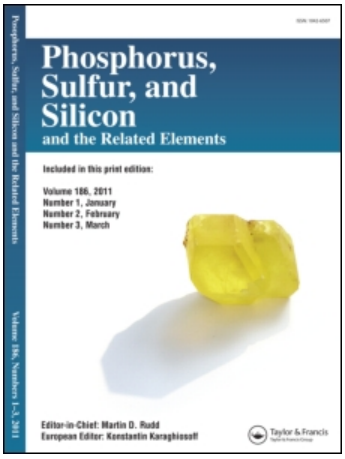

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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Indirect Photo-Induced Phosphorylation Via a C-Ester Caged Troika Acid

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To cite this Article Carrick, James M. , Kashemirov, Boris A. and McKenna, Charles E.(1999) 'Indirect Photo-Induced Phosphorylation Via a C-Ester Caged Troika Acid', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 65
To link to this Article: DOI: 10.1080/10426509908053513
URL: http://dx.doi.org/10.1080/10426509908053513

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Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 65-65
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Indirect Photo-Induced Phosphorylation Via a C-Ester Caged Troika Acid

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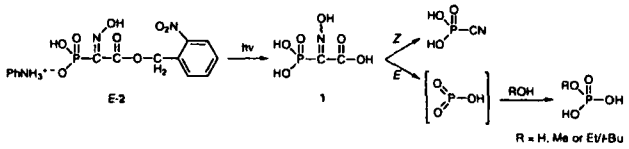
Use of a photoremovable "caging" group allows the generation of reactive molecules under mild conditions. Photo-induced phosphorylations typically have involved attachment of the photosensitive group at phosphorus.[1] We now have investigated *indirect* photolytic activation of an *un*modified phosphonic acid group using broad band UV (Hg lamp), 308 nm XeCl excimer laser or 355 nm YAG laser irradiation of the *o*-nitrobenzyl C-ester of "troika acid" [(*E*)-**1**[2]], (*E*)-**2**. In alcohols or neutral buffer, irradiation of (*E*)-**2** gave phosphorylation of the solvent plus phosphorocyanidate, the expected *Z*-isomer product.[2] All three UV sources gave ~1:2 *E*:*Z* product distribution in MeOH. In the (*E*)-**1** methyl C-ester, the oxime functionality absorbed strongly near 205 nm (ε_{max} 5200), weakly at 308 nm and negligibly above 355 nm, and no photo-isomerization was seen using the 355 nm source. Thus, oxime isomerization in (*E*)-**2**, at least using 355 nm irradiation, requires the *o*-nitrobenzyl group, and possibly involves an energy- or charge-transfer effect. Phosphorylation of EtOH/*t*-BuOH mixtures by photolysis of (*E*)-**2** showed little alkyl selectivity, consistent with photo-induced formation of an intermediate, plausibly (*E*)-**1**, which undergoes spontaneous dissociative fragmentation via a monomeric metaphosphate-like species.



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