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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Chemo- and Stereoselectivity of Nucleophilic Substitution in Mixed Phosphorus-Carboxylic Anhydrides

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To cite this Article Woźniak, Lucyna A. , Chworoś, Arkadiusz and Stec, Wojciech J.(1999) 'Chemo- and Stereoselectivity of Nucleophilic Substitution in Mixed Phosphorus-Carboxylic Anhydrides', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 147: 1, 435

To link to this Article: DOI: 10.1080/10426509908053697

URL: <http://dx.doi.org/10.1080/10426509908053697>

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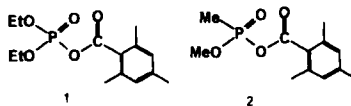
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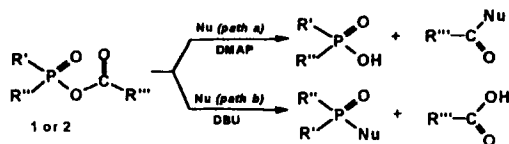
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Mixed phosphorus-carboxylic anhydrides have demonstrated both acylating and phosphorylating properties. [1] Here we report the reactivity of *O,O*-diethyl (*O*-2,4,6-trimethylbenzoyl) phosphates (1), and *O*-methyl (*O*-2,4,6-trimethylbenzoyl) dimethylphosphonates (2) with nucleophiles in the presence of different strong organic bases (DBU, DMAP).



It was found that 1 acts as acylating agent towards nucleophiles (alcohol, water, PhNH_2) both in case of DBU (path a), and DMAP activation (path a), while 2 can be either acylating reagent if DMAP is used as a base (path a), or selective phosphorylating agent, if reaction with nucleophile (ROH , H_2O , PhSH) is catalyzed by DBU (path b).



Fluoride anion was found chemoselective P-attacking nucleophile in reactions with 1 and 2.

References

- [1] A.R. Todd, *Proc. Nat. Sci.*, **45**, 1389 (1959); V.M. Clark, *et al. Angew. Chem. Internat. Edit.* **3**, 678 (1964); A. J. Lambie, *Tetrahedron Letters*, 3709 (1966).
- [2] L.A. Woźniak, A. Chworoś, W.J. Stec, submitted.