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A New Technique for the Generation of Alkyl Metathiophosphates

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A NEW TECHNIQUE FOR THE GENERATION OF ALKYL METATHIOPHOSPHATES

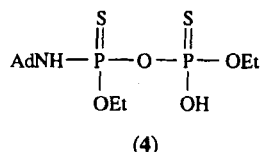
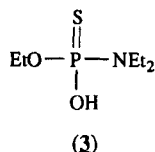
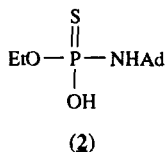
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We have recently described a technique for the generation of alkyl metaphosphates, ROPO_2 , by thermolysis of phosphoramidic acids of structure $\text{ROP}(\text{O})(\text{OH})\text{NHR}$ (**1**) [1]. We have now successfully shown that alkyl metathiophosphates, $\text{ROP}(\text{S})(\text{O})$, which have received but little previous consideration [2], can be generated by the same approach. Compounds **2** (Ad = 1-adamantyl) and **3** were synthesized for this study. Both were easily fragmented on heating in an inert solvent. When an alcohol trapping agent was present each gave $\text{EtO}-\text{P}(\text{S})(\text{OR})(\text{OH})$ consistent with $\text{EtOP}(\text{S})(\text{O})$ as an intermediate. In the absence of a trap, **2** was cleanly converted to the pyrophosphate derivative **4** in a process established to follow first-order kinetics, thus proving that decomposition of **2** proceeded by elimination of $\text{EtOP}(\text{S})(\text{O})$. Compound **3** decomposed by mixed first and second order kinetics, and gave a more complex mixture of products. $\text{EtOP}(\text{S})(\text{O})$ generated from **2** phosphorylated the OH groups on the surface of silica gel, a process previously demonstrated for ROPO_2 . With a monoester of phosphoric acid, the mixed monothiopyrophosphate $\text{EtOP}(\text{S})(\text{OH})-\text{O}-\text{P}(\text{O})(\text{OH})(\text{OR})$ was formed in a new synthetic approach to these valuable compounds.



[1] Quin, L.D. and Jankowski, S. *J. Org. Chem.*, **59**, 4402 (1994)

[2] Quin, L.D., Sadanani, N.D. and Wu, X.-P. *J. Am. Chem. Soc.*, **111**, 6852 (1989); Quin, L.D., Wu, X.-P., Sadanani, N.D., Lukes, I., Ionkin, A.S. and Day, R.O. *J. Org. Chem.*, **59**, 120 (1994); Bodalski, R., Jankowski, S., Glowka, M.L., Filipiak, T. and Quin, L.D. *J. Org. Chem.*, **59**, 5173 (1994)