SYNLETT
Spotlight 99

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Phosphorus Pentasulfide (P_4S_{10})

Compiled by Vivek Polshettiwar

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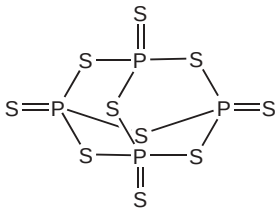
Dedicated to my guide, Prof. M. P. Kaushik, on his 50th birthday.

Introduction

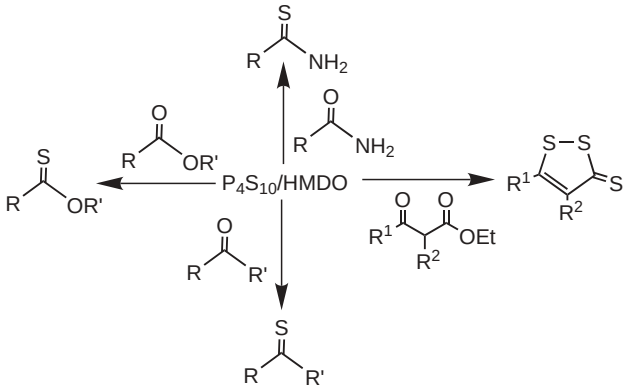
Organosulfur compounds are valued not only for their rich and varied chemistry, but also for many important biological properties. Phosphorous pentasulfide (P_4S_{10}) is very useful and versatile reagent for the synthesis of various organosulfur compounds. P_4S_{10} is widely available as a light yellow crystalline solid. It is highly flammable and decomposes in the presence of moisture.



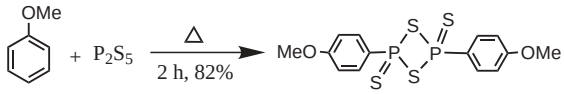
P_4S_{10} has been extensively used as a thionating agent for the conversion of carbonyls into thiocarbonyls in the preparation of organosulfur compounds. It also activates the free hydroxyl group of an acid or an alcohol to create a good leaving group. It can also be used as a deoxygenating and dehydrating agent.

Abstracts

(A) *As a thionating agent:* Various carbonyl groups can be converted into the corresponding thiocarbonyl groups by treatment with P_4S_{10}.[1] Recently, the combination of P_4S_{10} and HMDO has proved to be a very useful thionating reagent over P_4S_{10} alone.[2]



(B) *In the synthesis of Lawesson's reagent:* The most popular thionating reagent can be synthesized by reaction of P_4S_{10} with anisole.[3]



Lawesson's Reagent

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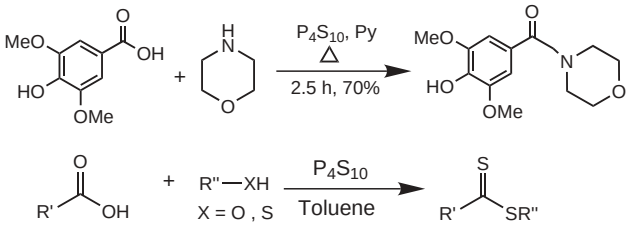
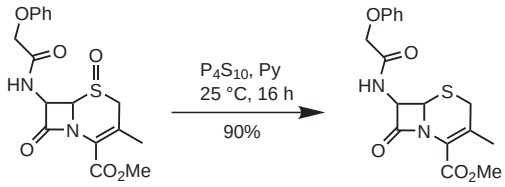
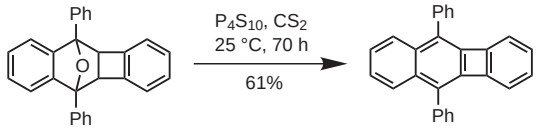
(C) *As an activating agent:* P_4S_{10} activates the free hydroxyl group of carboxylic acids or alcohols to create a good leaving group. When this activation is done in the presence of another nucleophile, a substitution reaction occurs.[4] It is also used for the synthesis of dithiocarboxylic esters.[5]



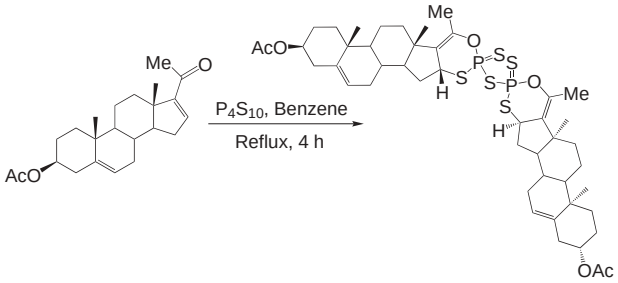
(D) *As a deoxygenating agent:* P_4S_{10} is one of the mildest selective reagents for the conversion of sulfoxides to sulfides.[6] The reduction takes place selectively without affecting functional groups such as esters, amides or ketones. Interestingly, sulfones are also unreactive under these conditions.[7]



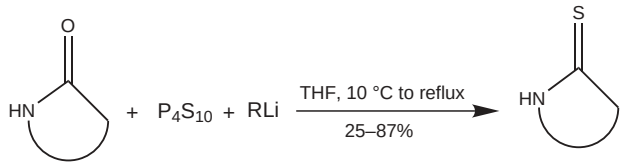
(E) *As a dehydrating agent:* Use of P_4S_{10} as a dehydrating agent has been reported. The aromatization of a furan Diels–Alder adduct using P_4S_{10} in CS_2 has been found to be superior than with other reagents like HCl/HOAc or polyphosphoric acid.[8]



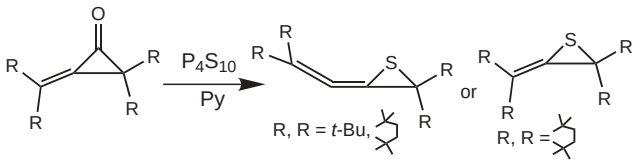
(F) *As an adduct:* The reaction of steroidal molecule 16-dehydropregnenolone acetate (16-DPA) with P_4S_{10} in refluxing benzene afforded a novel adduct 16-DPA–P_2S_5. This adduct undergoes [4+2] cycloaddition with alkyne dienophiles to afford biologically active steroidal (17,16-c)pyrans.[9]



(G) *In the synthesis of thiolactams:* Phosphorus pentasulfide reacts under mild conditions with organolithiums to give solutions in tetrahydrofuran. This in situ reagent converts lactams to thiolactams and shows significant selectivity in the type of reactive lactams.[10]



(H) *In the synthesis of episulfides:* Sterically hindered methylenecyclopropanones can be thionated with P_4S_{10} in pyridine to afford novel 1,2,3-butatriene episulfides and a thiiranoradialene derivative.[11]



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