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Hydroxylamine-*O*-sulfonic acid: As a dual role reagent

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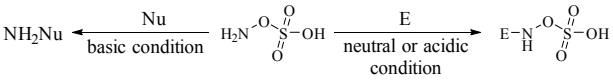
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

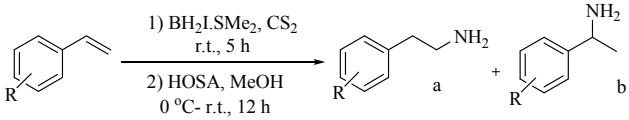
Hydroxylamine-*O*-sulfonic acid (HOSA) as a dual role reagent with formula H_3NO_4S. It is a white solid with a melting point of 210°C. It is soluble in cold water, methanol, only slightly soluble in ethanol and insoluble in ether and Chloroform. HOSA is commercially available and has been synthesized by reacting hydroxylamine sulfate with 30% fuming H_2SO_4 [1] or 60% oleum [2] at room temperature, or by heating a mixture of hydroxylamine sulfate and chlorosulfonic acid at 100°C for several hours [3]. It is hygroscopic and should be stored properly in tightly containers in refrigerator. HOSA has a wide variety of applications in organic syntheses such as amination at carbon [4], nitrogen [5] and sulfur [6], reduction [7], conversion of oximes to diazo compounds [8], conversion of methyl sulfones to sulfonamides [9], due to its ability to act both as a nucleophile and as an electrophile (Scheme 1).



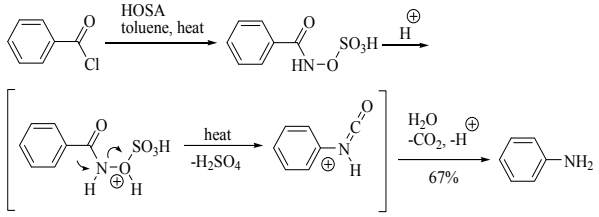
Scheme 1.

Abstracts

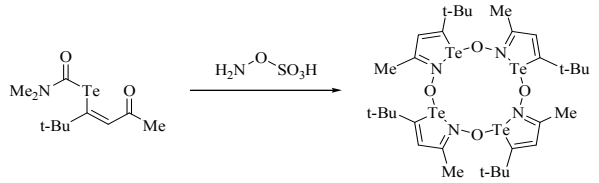
(A) Ramachandran and co-workers reported regioselective hydroboration-amination of fluoro-substituted styrenes with $BH_2I.SMe_2$ and hydroxylamine-*O*-sulfonic acid respectively. After hydroboration of 4-fluorostyrene, the reaction mixture was cooled to 0°C, quenched with methanol and aminated using hydroxylamine-*O*-sulfonic acid to obtain a 72% yield of essentially pure primary amine (ratio of a:b= 97:3). Similarly, the hydroboration-amination of 3-trifluoromethyl styrene gave a 65% yield of primarily the primary amine (ratio of a:b = 92:8) [10].



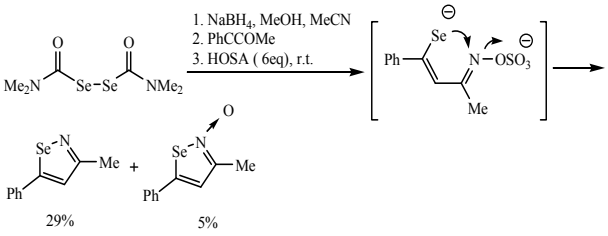
(B) An alternative procedure for replacement of classical Hofmann, Lossen, and Curtis procedures, Wallace *et al*. [11] have reported an one-pot synthetic manner without use of hazardous azides for preparation of aromatic amines.



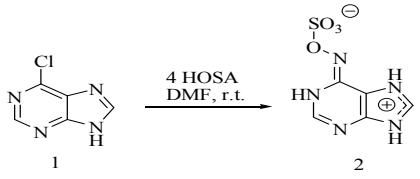
(C) Kubel *et al.* reported the formation of the first twelve-membered ring periodic repetition of the -O-Te-N- sequence from the reaction between a *β*-(*N*,*N*-dimethylcarbamoyl-chalcogeno)-alkenyl ketone with hydroxylamine-*O*-sulfonic acid [12].



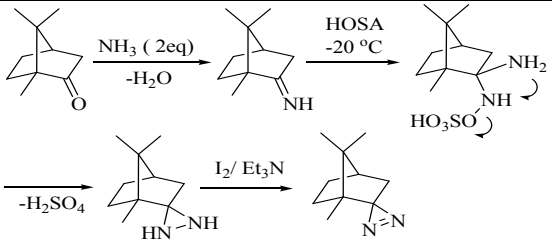
(D) Diselenide treated with $NaBH_4$ and acetylenic ketone gives the corresponding carbamate, which, in the presence of HOSA, provides isoselenazole and its corresponding *N*-oxide [13] as a by-product.The actual pathway leading to the formation of *N*-oxide remains unclear.



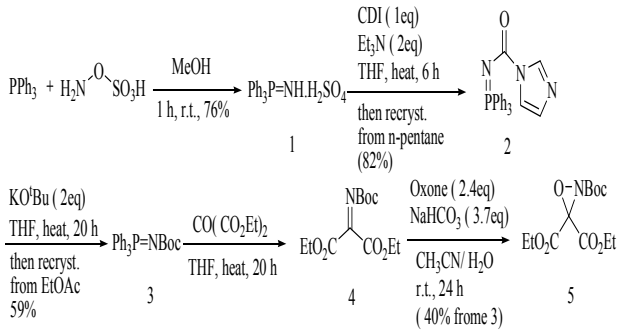
(E) The reaction of 6-chloropurine **1** with fourfold excess of hydroxylamine-*O*-sulfonic acid provided (Z)-1*H*-purin-6-ylideneaminooxysulfonic acid **2** which could be regarded as a secondary metabolite of ultimate mutagen 6-hydroxylaminopurine (6-HAP) [14].



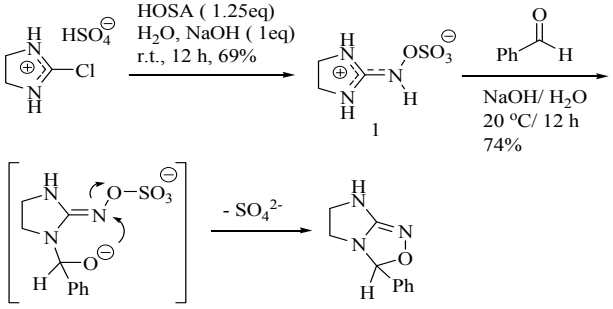
(F) HOSA has been used as a reagent for conversion of carbonyl functional group to diaziridine. The reaction is functional even for sterically hindered ketones [15].



(G) Armstrong *et al.* have developed a novel route to oxaziridine which is amenable to large-scale synthesis [16]. Amination of triphenylphosphine with hydroxylamine-*O*-sulfonic acid and subsequent *N*-protection via the acyl imidazolide 2 afforded iminophosphorane 3. Following aza-Wittig reaction with diethyl ketomalonate and oxidation of imine 4 with aqueous Oxone in CH_3CN/H_2O have been occurred.



(H) HOSA has been used as nucleophile and reacted with activated heterocyclic halides by Saczewski and co-workers [17]. 2-chloro-4,5-dihydroimidazole reacts with a slight excess of HOSA in aqueous solution at room temperature, giving rise to the formation of 2-hydroxylamino-4,5-dihydro imidazolium-*O*-sulfonate. Treatment of 1 with a good range of aromatic aldehydes in aqueous NaOH solution gave the 3-substituted 6,7-dihydro-5*H*-imidazo[2,1-*c*][1,2,4]oxadiazoles



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