

Potassium Nitrosodisulfonate (Fremy's salt)

Compiled by Toktam Faal Rastegar

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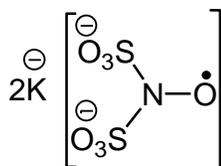
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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

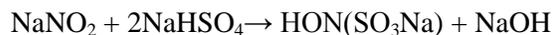
One of the major trends in modern organic synthesis is the development of very selective reagents. In the area of oxidation of organic compounds, the number of such selective oxidizing agents is still fairly small. Potassium nitrosodisulfonate or Fremy's salt is one of the few [1]. It is discovered in 1845 by Edmond Fremy, is a typical long-lived radical that can oxidizes phenols and Aromatic amines [2]. The first oxidation of an organic compound by Fremy's salt was achieved by Raschig who converted aniline into nitrosobenzene [3].



Scheme 1. Fremy's salt

Preparation

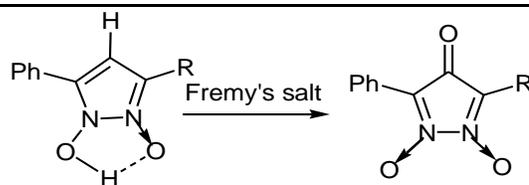
Fremy's salt is commercially available but can also be readily prepared. Practically it involves an oxidation of hydroxylaminedisulfonate, $\text{HON}(\text{SO}_3\text{K})_2$, in an alkaline solutions. $\text{HON}(\text{SO}_3\text{K})_2$ is easily prepared by the reaction between sodium bisulfite and sodium nitrite.



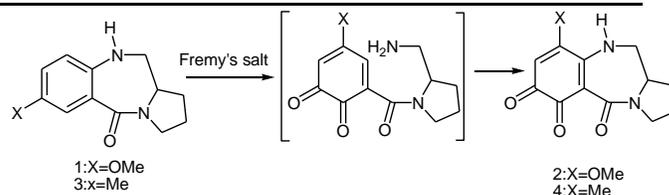
According to ref. [1], potassium permanganate used as an oxidizing agent. The precipitated manganese dioxide is removed by gravity filtration. The filtrate is allowed to come to room temperature, and stirred steadily while saturated potassium chloride solution is added dropwise over a period of about 45 min. The orange solid is collected on a Büchner funnel washed with ammoniacal saturated potassium chloride solution, twice with ammoniacal methanol and finally with acetone. The orange crystals are stored in a desiccator over calcium oxide, in the presence of ammonium carbonate in a separate dish to provide an ammoniacal atmosphere. Under these conditions even this relatively crude material is stable for several months.

Abstracts

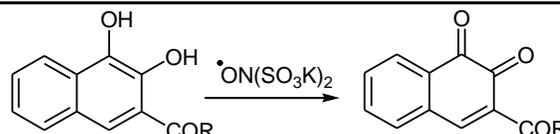
(A) Fremy's salt was chosen as a very mild free-radical oxidizing agent for mild oxidation of 1-hydroxypyrazole2-oxide to give the corresponding 3,4-diazacyclopentadienone3,4-dioxides [4].



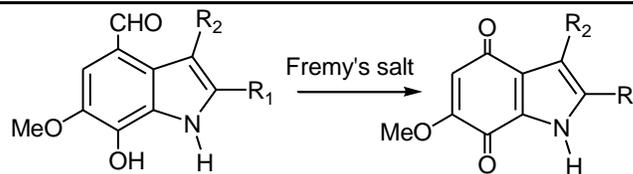
(B) The reaction of anilines with 4.4 equivalents of Fremy's salt affords ortho-quinones in good yields via a one-pot five-step sequence [5].



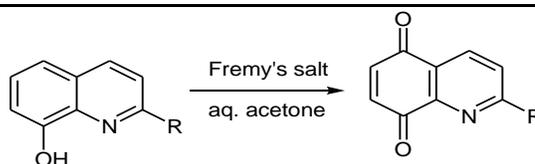
(C) Takuwa and Kai have used Fremy's salt for oxidation of 3-Acyl-1,2-naphthalendiols to 3-Acyl-1,2-naphthoquinone [6].



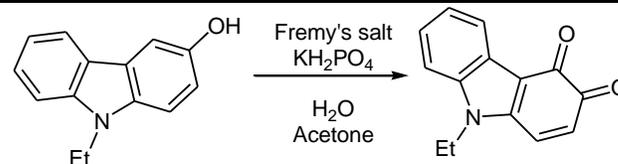
(D) Fremy's salt promoted oxidative degradation of 4-formyl-7-hydroxyindoles to the desired orange-red 4,7-indoloquinonones [7].



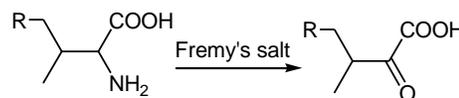
(E) Harper and Co-workers synthesized 8-hydroxyquinolines by oxidation using potassium nitrosodisulfonate [8].



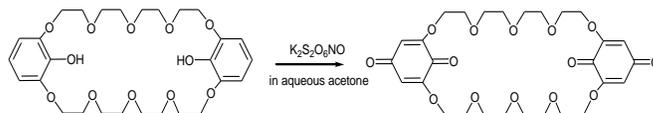
(F) Oxidation of 2- and 3-hydroxycarbazoles with Fremy's salt gave the corresponding ortho-carbazolequinones [9].



(G) Saa and co-workers have reported the Fremy's salt oxidation of some α -amino and α -hydroxy acids to the corresponding α -keto acids [10].



(H) Czech and co-workers produced corand quinines and corand bisquinone upon oxidation by Fremy's salt [11].



References

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