

Potassium Ferrate



[13718-66-6] FeK_2O_4 (MW 198.05)

InChI = 1S/Fe.2K.4O/q;2*-1;;;2*-1

InChIKey = ICBFRPYDFGVTEQ-UHFFFAOYSA-N

(selective oxidant for alcohols and amines¹)

Solubility: sol water; insol typical organic solvents.

Form Supplied in: violet solid; typical impurities present include potassium chloride and iron(III) oxide.

Analysis of Reagent Purity: analysis of K_2FeO_4 by chromite ion has been reported.² The ferrate concentration may be determined by measurement of the absorption band at 510 nm.³

Drying: Preparative Methods: NaOCl (20 g) is added to a solution of NaOH (30 g in 75 mL H_2O) while keeping the solution temperature under 20 °C. Solid NaOH (70 g) is added with stirring, while maintaining the solution temperature at 25–30 °C, the solution cooled to 20 °C and filtered. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (25 g) is added slowly, and the solution saturated with NaOH while being kept at 30 °C. After filtration, the filtrate of sodium ferrate is placed in a 20 °C bath and treated with saturated aqueous KOH (100 mL), stirred for 5 min, and filtered. The precipitate is washed several times with 10 mL portions of 3 M KOH into 50 mL of chilled saturated KOH solution, and a further 50 mL of chilled saturated KOH solution added to the washings. After stirring for 5 min, the solution is filtered, and the precipitate washed with benzene (10 mL) and several times with ethanol (20 mL). The precipitate is stirred with ethanol (1 L) for 20 min and the ethanol removed by filtration; this process is repeated three times. The precipitate is finally washed with Et_2O under a drying tube, and drying continued in a vacuum desiccator.⁴

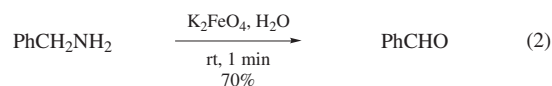
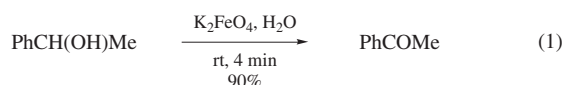
Handling, Storage, and Precautions: dry K_2FeO_4 is stable and should be stored in a desiccator. K_2FeO_4 is very unstable in acidic solutions, but decomposes only slowly in basic solutions.

Original Commentary

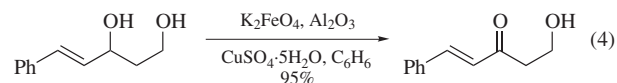
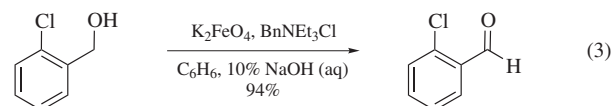
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Oxidations. Potassium ferrate has been reported to be a mild reagent for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively (eq 1).^{1–6} In addition, primary and secondary amines are also oxidized to aldehydes and ketones (eq 2). Allylic and benzylic alcohols react much more readily than saturated ones, and primary alcohols react more readily than secondary ones. Reactions are normally carried out in basic aqueous (or water/*t*-butanol) solution. Yields are normally high with allylic and benzylic alcohols and amines, but much more variable for saturated alcohols. Several functional groups are stable to this reagent, including carbon–carbon double bonds, nitro groups, tertiary alcohols and amines, aldehydes, and ketones. Sulfur compounds (sulfides, sulfoxides) do not tolerate this reagent.



A modification employing a two-phase system (benzene/10% aqueous NaOH) and *Benzyltriethylammonium Chloride* as a phase-transfer catalyst has been reported to be highly successful for allylic and benzylic substrates (eq 3).⁷ A second modification using a mixture of K_2FeO_4 (8 mmol), aluminum oxide (0.8 g), and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.8 g) for 2 mmol of substrate affords a simple workup and highly selective oxidations (eq 4).⁶

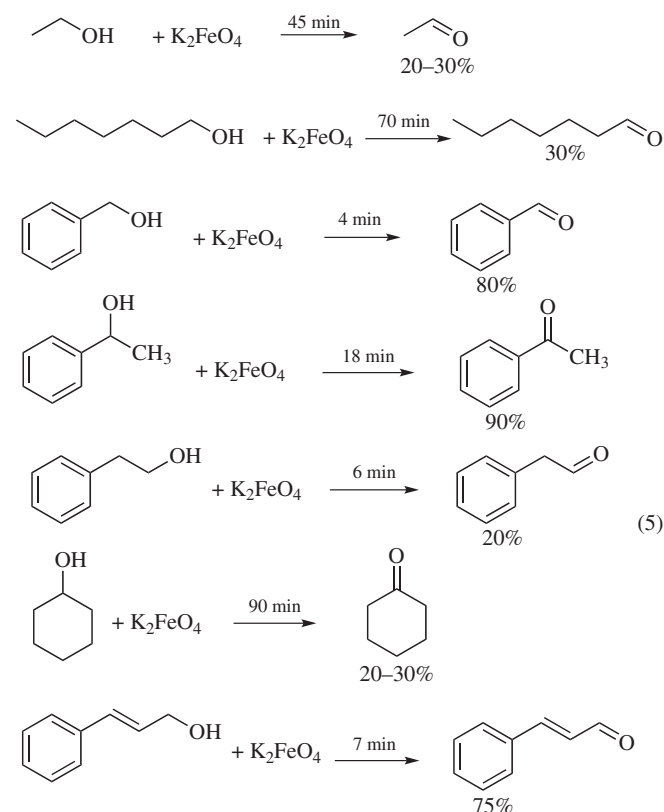


First Update

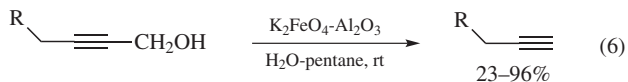
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Oxidation of Alcohols. Potassium ferrate is a selective oxidizing agent at room temperature in water and mixed solvents. Primary alcohols and secondary alcohols are rapidly converted to the corresponding aldehydes or ketones. The reactions are usually complete within a few hours. A single product is obtained in all cases. Isolated yields are usually high.^{1a,7,8}

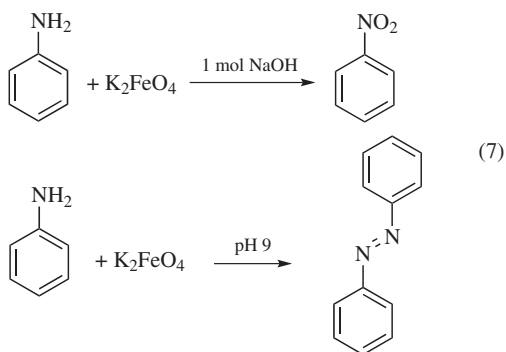


Treatment of monoprotected diol with wet $K_2FeO_4-Al_2O_3$ in pentane at room temperature gave the terminal alkyne. This remarkable C–C bond cleaving process was also observed with substrates that incorporate an alkyl spacer group between the protected oxygen functionality and the reactive centers. The ability of potassium ferrate to promote such carbon–carbon bond cleaving reactions is without precedent.⁹



R = THPO, $CH_3(CH_2)_5O$, $CH_3(CH_2)_5OCH_2$, $CH_3(CH_2)_5OC_2H_5$

Oxidation of Arylamines. The selective oxidation of anilines represents an important transformation. The ferrate oxidations of anilines were carried out either in 1M NaOH or at pH 9. Under these conditions, the oxidations proceed essentially quantitatively to the products shown. Usage of an aqueous solution of potassium ferrate provides for a homogeneous oxidation medium. Substituted anilines were found to produce both azobenzenes or nitrobenzenes, depending upon reaction conditions.¹⁰



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