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POTASSIUM FERRATE, A NEW SELECTIVE OXIDIZING AGENT

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Potassium ferrate, which can be easily and economically prepared but has never been used in organic syntheses, was found to be a new efficient selective oxidizing agent. It works at room temperature on a variety of benzyl alcohols to yield benzaldehydes without further oxidation.

Potassium ferrate (K_2FeO_4), a sexivalent iron compound, can be easily prepared by oxidizing ferric nitrate with sodium hypochlorite and the subsequent treatment with potassium hydroxide.[1] There are some inorganic reactions which involve potassium ferrate as an oxidizing agent, i.e., oxidations of trivalent chromium into sexivalent one,[2] and nitric oxide (NO) into nitrogen dioxide (NO_2).[3] However no specific organic reaction has been found for this reagent whatsoever.[4] The principal advantage of this reagent is that it works readily at room temperature, yielding aldehydes instead of carboxylic acids. The oxidation reaction can be expressed by the following equation:

$$3\ RCH_2OH + 2\ K_2FeO_4 = 3\ RCHO + Fe_2O_3 + 4\ KOH + H_2O$$

Examples of the reactions using this reagent are summarized in the table. Nerol and geraniol were not oxidized in this reaction. A possible reason for this is, unlike other compounds, the transition state of nerol and geraniol in the oxidation process was not stabilized by conjugation enough. A typical example is given below to illustrate the oxidation procedure.

Potassium ferrate (3 g; 15.1 mmol), suspended in 10 ml of 10% aqueous potassium hydroxide, was added dropwise to a solution of p-methylbenzyl alcohol (100 mg; 0.819 mmol) in 5 ml of t-butyl alcohol, and was stirred at room temperature. The purple color of the ferrate ion fades with the progress of the oxidation.

After 50 min., small pieces of ice were put into the flask, and 5 ml of 10% sulfuric acid was added to acidify the solution (pH$\lesssim$6). The reaction mixture was extracted with benzene, and the extracts were evaporated in vacuo to leave an almost pure oily product 93.3 mg (95%), which showed identical the IR spectrum identical with that of the authentic p-tolualdehyde.

Table[a]

Materials	Reaction Time	Products	Yield(%)[d]
Benzyl alcohol	60 min.	Benzaldehyde[c]	40
Benzylamine	30 min.	Benzaldehyde[c]	44
p-Methylbenzyl alcohol	50 min.	p-Tolualdehyde[b]	95
Piperonyl alcohol	30 min.	Piperonal[b]	71
p-Anisyl alcohol	5 min.	p-Anisaldehyde[b]	81
Vanillyl alcohol	27 min.	Vanillin[b]	90
Veratryl alcohol	7 min.	Veratraldehyde[b]	85
Cinnamyl alcohol	60 min.	Cinnamaldehyde[b,f]	96
Nerol	20 hr.	no reaction	
Geraniol	22 hr.[e]	no reaction	

[a]Unless otherwise indicated, the oxidation was performed at room temperature.

[b]Products were identified by comparison of their spectra (IR and NMR) with those of the authentic materials.

[c]Products were isolated and identified as the 2,4-dinitrophenylhydrazones (IR, TLC and NMR).

[d]Yield refers to pure isolated compounds or pure 2,4-dinitrophenylhydrazones.

[e]No reaction occurred at 90 °C for 5 min.

[f]A trial to oxidize further to cinnamic acid resulted in mere recovery of the starting aldehyde.

References

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