Oxidation of Alcohols by Clay-Supported Iron(III) Nitrate; A New Efficient Oxidizing Agent

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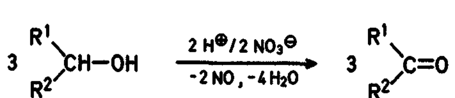
We have developed a convenient oxidation of alcohols **1** into carbonyl compounds **2** under mild reaction conditions, using a supported reagent[1,2]. Our method, based on the use of iron(III) nitrate impregnated on K 10 bentonite clay, offers an attractive, easy to perform and inexpensive alternative to the numerous existing procedures[3]. The overall reaction is best formulated as shown in the scheme with subsequent air oxidation of NO to NO_2.



The reagent is easily prepared by dissolution of iron(III) nitrate nonahydrate in acetone, resulting in a muddy, light brown suspension, to which bentonite clay is added. Rotary evaporation of the solvent affords the powdered reagent which, while slightly unstable, may, however, be kept without special care for at least two weeks.

Conversion of alcohols **1** into aldehydes or ketones **2** is effected by adding the reagent to a solution of **1** in pentane or hexane. Evaporation of the solvent and slight heating under vacuum (method A) or gentle reflux of the solution (method B) induces the reaction, which is easily detected and followed from the evolution of nitrogen oxides. The product **2** is easily isolated by filtration of the reagent suspended in a suitable solvent, followed by evaporation of the latter.

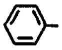
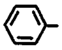
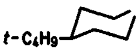
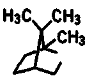
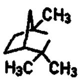
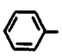
Satisfactory results have been obtained with a variety of secondary aliphatic, alicyclic, and benzyl alcohols, and with primary benzyl alcohols (Table 1). With primary aliphatic alcohols, complex mixtures of products result.

Association of the reagent with the clay support provides a favorable reaction microenvironment, with strong reactivity enhancement as demonstrated by control experiments (Table 2).

Clay-Supported Iron(III) Nitrate:
Iron(III) nitrate nonahydrate (45 g) is added to acetone (750 ml) and the mixture is stirred vigorously in the presence of air for ~5 min until complete dissolution of the crystals of hydrated iron(III) nitrate. The first-formed homogeneous rusty brown solution turns, after a short time, into a muddy, light brown suspension. Clay (bentonite K 10; 60 g) is then added in small amounts and stirring is continued for another 5 min. The resulting suspension is placed in a rotary evaporator, and the solvent is eliminated under reduced pressure on a water bath at 50 °C. After 30 min, the dry solid crust adhering to the walls of the flask is flaked off with a spatula, and solvent evaporation is resumed for another 30 min. This procedure yields about 100 g of a clay-supported iron(III) nitrate which can be kept for several days in a non-hermetic powder box (a small loss of nitrogen dioxide occurs).

Warning: It is important not to evaporate solvent at higher temperatures (>50 °C) or for longer periods of time (>1 h), which leads

Table 1. Oxidation of Alcohols **1** to Carbonyl Compounds **2** with Clay-Supported Iron(III) Nitrate

Product	R¹	R²	Reaction conditions (Method/solvent/time)	Yield [%]		m.p. [°C] or b.p. [°C]/torr	
				crude	isolated	found	reported
2a[a,b]		H	A/pentane/1.5 h	90[d]	81[e]	170–180°/760	178.1°/760[4]
			B/pentane/3 h	85[d]	76[e]	172–180°/760	
2b[a,b]		CH_3	A/pentane/1.5 h	98[d]	88[e]	195–202°/760	202°/760[4]
			B/pentane/3 h	89[d]	81[e]	195–202°/760	
2c[a,b]	n-C_6H_{13}	CH_3	B/hexane/1 h	98[d]	83[e]	170–175°/760	173°/760[4]
2d[a,b]			B/hexane/15 h	74[d,f]	65[e]	50–55°/0.1	63–67°/3[5]
2e[a,b,c]			B/hexane/2 h	92[d]	80[g]	175–179°	178.8°[4]
2f[a,b]			B/hexane/3 h	89[d]	82[e]	194–201°/760	193–194°/760[4]
2g[b,c]			B/hexane/1.5 h	100	88[e]	43–47°; 180–187°/30	48.5[6] 175.8°/20[6]; 195.7°/40[6]

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[a] Identified by coinjection on two G.L.C. columns: carbowax 20 M and DC 550 on chromosorb WAW DMCS.

[b] Identified by I.R. and N.M.R. spectra.

[c] Identified by melting point and mixture melting point of the 2,4-dinitrophenylhydrazone derivative.

[d] Verified by G.L.C. to have at least 95% purity; major impurities when present consist of starting alcohol and traces of nitrate impurities which are destroyed upon distillation.

[e] Short path distillation.

[f] From column chromatography (silica gel/toluene).

[g] Sublimation.

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Table 2. Control Experiments with Benzyl Alcohol[a]

Oxidizing agent	Amount	Conversion to benzaldehyde [%]
clay-supported $Fe(NO_3)_3$	10 g	100
$Fe(NO_3)_3 \cdot 9H_2O$	5 g	20 (+5% unidentified product)
$Fe(NO_3)_3 \cdot 9H_2O$/water	5 g/25 ml	0
K 10 clay	6 g	0

[a] Reaction of benzyl alcohol (20 mmol) in pentane (50 ml) at reflux for 4 h.

to an unstable reagent, which will decompose exothermally in 1–2 h with evolution of nitrogen dioxide.

Oxidation of Alcohols 1 with Clay-Supported Iron(III) Nitrate:
Method A: The reagent (10 g) is added in small portions to a solution of the alcohol **1** (20 mmol) in pentane or hexane (50–100 ml), under vigorous stirring. The onset of the reaction, which if necessary can be brought about by moderate heating, corresponds to the appearance of brown nitrogen dioxide vapors. As soon as these are observed, the reaction vessel is connected to a rotary evaporator, reduced pressure (~100 torr) is applied, until nitrogen dioxide is no longer evolved. The powder residue is suspended in ether (50 ml), the suspension is filtered on sintered glass, and extracted with ether (2 × 50 ml). The solvent is removed by rotary evaporation under moderately reduced pressure (~100 torr) and the non-volatile residue is dissolved in pentane (50 ml). The pentane solution is then washed three or four times with water (50 ml), until disappearance of any color extractable into the aqueous phase. The organic phase is then dried with magnesium sulfate, filtered, and the solvent is finally evaporated under reduced pressure (~100 torr) at room temperature (20 °C).

Method B: The reagent (10 g) is added in small portions to a solution of alcohol **1** (20 mmol) in pentane or hexane (50–100 ml) under vigorous stirring. The mixture is then heated in an oil bath, and gentle reflux is maintained until the end of evolution of nitrogen dioxide. The reaction mixture is filtered on sintered glass, and the solid residue is washed with ether (3 × 50 ml). The organic extracts are gathered, and work up is continued as in method A.

While this procedure worked out very nicely and totally safely in our hands, it is to be stressed that nitrates are potentially dangerous compounds, and appropriate caution should be applied in all steps.

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[1] A. McKillop, D. W. Young, *Synthesis* **1979**, 401, 481.

[2] G. H. Posner, *Angew. Chem.* **90**, 527 (1978); *Angew. Chem. Int. Ed. Engl.* *17*, 487 (1978).

[3] M. Hudliky, *J. Chem. Ed.* **54**, 100 (1977).

[4] *Handbook of Chemistry and Physics*, 59th Edn., R. C. West, Ed., CRC press, Boca Raton, 1978.

[5] *Beilstein*, 4th edn., VII, 1st. Suppl., Springer Verlag, Berlin, 1931, p. 29.

[6] *The Merck Index*, 8th Edn., P. G. Stetcher, Ed., Merck and Co., Rahway, 1968, p. 134.