

Note

Oxidative transformation of alcohols and oximes to carbonyl compounds by quinolinium fluorochromate (QFC)

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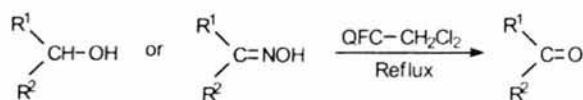
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Oxidation of selected alcohols and oximes to the corresponding carbonyl compounds has been achieved with quinolinium fluorochromate (QFC) in dichloromethane solvent under reflux conditions. The oxidation reactions have been found to be smooth and gave the products in good yield.

Oxidation in organic chemistry is apparently of great value as a fundamental process and the oxidation of an alcohol to a carbonyl compound constitutes a very useful functional group transformation in synthetic organic chemistry. A number of oxidising agents based on Cr(VI)¹ has been developed for this purpose and the most important among them are the halochromates prepared from pyridine²⁻⁴, quinoline⁵⁻⁸, 2,2'-bipyridine⁹, imidazole¹⁰ and 1-methyl imidazole¹¹. However, some of the reported reagents suffer from instability, hygroscopicity, low selectivity and the need for a large excess of the reagent. Thus, still there exists scope for a stable and a selective reagent for this functional group transformation.

We first reported the preparation, characterisation and the synthetic utility of quinolinium fluorochromate¹² (QFC) as a stable oxidising agent. In this note we present the selective oxidation of certain aliphatic and aromatic alcohols and oxidative deoxygenation of aromatic aldoximes and ketoximes to the corresponding carbonyl compounds brought about by QFC using dichloromethane as a solvent under reflux conditions.



Benzylic and aromatic alcohols are oxidised more readily with a higher yield than their aliphatic counterparts. Among the aliphatic alcohols the primary alcohols are readily oxidised with a higher yield than the secondary alcohols and further oxidation of aldehydes to carboxylic acids are not observed. QFC oxidises cinnamyl alcohol to cinnamaldehyde in good yield and hence it can be a very useful oxidant for the oxidation of allyl alcohols and alcohols having acid sensitive groups. QFC brings about the oxidative deoxygenation of benzylic and aromatic aldoximes and ketoximes to the respective carbonyl compounds in high yield. The results of the oxidation reactions are summarised in **Table I**. Thus quinolinium fluorochromate (QFC) is a mild, stable, selective and inexpensive reagent prepared easily from commercially available materials. Hence, it can be used as a useful reagent for the oxidation of organic compounds.

Experimental Section

The alcohols were of extrapure quality (E.Merck, Aldrich and Fluka) and were used without further purification. Oximes were prepared by the standard procedures and QFC was prepared by our previous method¹². The products of oxidation were identified by comparison with authentic samples (IR, GC analysis and melting points). Melting points were recorded using Raga hot stage apparatus and are uncorrected. IR spectra were recorded on a Hitachi infrared spectrophotometer (model: 270-50) and GC analyses were carried out on a Hewlett- Packard 5890A gas chromatograph.

General procedure for the oxidation of alcohols and oximes. To a stirred suspension of QFC (10-20 mmoles) in dichloromethane (10-20 mL) in a 50 mL round bottom flask fitted with a reflux condenser, a solution of alcohol/oxime (10 mmoles) in dichloromethane (5-10 mL) was added and the reaction mixture was refluxed for the period indicated in **Table I**. The course of the reaction was monitored by GC analysis/TLC (silica gel, petroleum ether : ethyl acetate, 9:1). As soon as the reaction was complete, the reaction mixture was diluted with dry diethyl ether (30-40 mL), filtered through a short plug of silica gel and washed with diethyl ether (4×10 mL). The combined filtrates on evaporation gave the crude

Table I — Oxidation of alcohols and oximes with QFC

Substrate	Substrate/ Oxidant mole ratio	Reaction period (hr)	Product ^a	Yield ^b (%)	b.p.(lit b.p.) °C
2-Butanol	1:1.5	5.0	2-Butanone	57	80(79)
1-Pentanol	1:1.5	6.0	1-Pentanal	79	103(102)
2-Octanol	1:1.5	6.5	2-Octanone	74	174(173)
1-Heptanol	1:1.5	8.0	1-Heptanal	76	152.5(153)
1-Decanol	1:2	6.0	1-Decanal	68	210(209)
1-Nonanol	1:2	6.5	1-Nonanal	53	94(93)
Furfural	1:1.5	6.5	Furfural	81	163.5(162)
4-Nitrobenzyl alcohol	1:2	4.5	4-Nitrobenzaldehyde	83	102(101-04)
2-Nitrobenzyl alcohol	1:2	5.0	2-Nitrobenzaldehyde	79	42(41-43)
4-Methoxybenzyl alcohol	1:2	4.5	4-Methoxybenzaldehyde	87	249(248)
4-Methylbenzyl alcohol	1:2	4.0	4-Methylbenzaldehyde	89	206(204)
Cinnamyl alcohol	1:2	3.0	Cinnamaldehyde	76	253(252)
Benzoin	1:2	5.0	Benzil	85	94(93-95) mp(lit. mp)
Cyclopentanol	1:2	6.0	Cyclopentanone	82	132.5(131)
Cycloheptanol	1:2	7.5	Cycloheptanone	78	181(179)
Menthol	1:2	4.0	Menthone	70	209(207-10)
4-Nitrobenzaldehyde oxime	1:2	4.0	4-Nitrobenzaldehyde	87	102(101—04) mp(lit. mp)
4-Methoxybenzaldehyde oxime	1:2	3.0	4-Methoxybenzaldehyde	90	249(248)
Acetophenone oxime	1:2	4.0	Acetophenone	92	204(202)
Benzoin oxime	1:2	5.0	Benzil	85	94(93-95) mp(lit. mp)
Cinnamaldoxime	1:2	3.5	Cinnamaldehyde	86	253(252)
Cyclohexanone oxime	1:2	4.5	Cyclohexanone	84	155(154)

^awere confirmed by comparison with authentic samples (IR & GC analysis)^byield of isolated pure carbonyl compound

product which was purified by distillation under reduced pressure or recrystallised from suitable solvent in the case of solid products.

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