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Research Note

KBr Catalyzed Oxidation of Alcohols and Trimethylsilyl and Tetrahydropyranyl Ethers with $Fe(NO_3)_3.9H_2O$

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Alcohols and trimethylsilyl and tetrahydropyranyl ethers are efficiently oxidized to their corresponding carbonyl compounds, using Fe(NO3)3.9H2O, in the presence of KBr, under mild and completely heterogeneous reaction conditions, with good to high yields.

INTRODUCTION

Aldehydes and ketones are considered as important precursors for the preparation of many organic compounds, including valuable fine chemicals, such as fragrances, vitamins and drugs [1]. Amongst the methods used for the preparation of aldehydes and ketones, oxidation of alcohols and trimethylsilyl and tetrahydropyranyl ethers has attracted the attention of many organic chemists. Several methods are reported for oxidation of the above-mentioned substrates to their corresponding carbonyl compounds [2]. However, some of these methods suffer from disadvantages, such as long reaction time, low yield of product and tedious work-up procedures. Therefore, the introduction of new methods for such functional group transformations is still in demand.

RESULTS AND DISCUSSION

In recent years, $Fe(NO_3)_3.9H_2O$, as a cheap, non-toxic and commercially available reagent, has been used for oxidation processes, either as supported on silica gel and K10-clay [3], or mixed with HZSM-5 zeolite [4], tungstophosphoric acid [5] and molibdatophosphoric acid [6]. In continuation of the ongoing research program on the application of KBr in organic reactions [7], it has been found that the oxidation of alcohols to their corresponding carbonyl compounds using $Fe(NO_3)_3.9H_2O$ is efficiently promoted in the presence of a catalytic amount of KBr in refluxing CH_3CN (Figure 1).

Yields and reaction times are given in Table 1. Benzylic alcohols, including halogen and alkyl substituents and ethereal linkages (Table 1, entries 1-7, 11-13) are efficiently converted to their corresponding aldehydes and ketones under the selected reaction conditions. The oxidation of benzylic alcohols containing nitro groups, using this reagent system, is so slow that, after a long reaction time, the yield of the obtained carbonyl compounds is not more than 30% (Table 1, entries 8-10). This method is also effective for the oxidation of aliphatic alcohols (Table 1, entries 14-16). Over-oxidation of the products was not observed in this method.

The authors' investigation clarified that $Fe(NO_3)_3.9H_2O/KBr$ can also be used for direct oxidation of trimethylsilyl and tetrahydropyranyl ethers to their corresponding carbonyl compounds. All reactions were performed under mild and completely heterogeneous reaction conditions (Table 1, Figure 2).

Because of the production of a mixture of prod-

$$R^1R^2CHOH \xrightarrow[CH_3CN,\ reflux]{Fe(NO_3)_3.9H_2O/KBr} R^1R^2CO$$

Figure 1. Oxidation of alcohols with $Fe(NO_3)_3.9H_2O$ catalyzed by KBr.

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Table 1. Oxidation of alcohols and trimethylsilyl and tetrahydropyranyl ethers.[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1	2-BrC$_6$H$_4$CH$_2$OH	2-BrC$_6$H$_4$CHO	1	92
2	2-ClC$_6$H$_4$CH$_2$OH	2-ClC$_6$H$_4$CHO	1	90
3	4-ClC$_6$H$_4$CH$_2$OH	4-ClC$_6$H$_4$CHO	0.67	95
4	2-MeC$_6$H$_4$CH$_2$OH	2-MeC$_6$H$_4$CHO	0.67	87
5	4-Me$_2$CHC$_6$H$_4$CH$_2$OH	4-Me$_2$CHC$_6$H$_4$CHO	1	90
6	4-Me$_3$CC$_6$H$_4$CH$_2$OH	4-Me$_3$CC$_6$H$_4$CHO	1	88
7	4-MeOC$_6$H$_4$CH$_2$OH	4-MeOC$_6$H$_4$CHO	2	85
8	2-NO$_2$C$_6$H$_4$CH$_2$OH	2-NO$_2$C$_6$H$_4$CHO	5	25
9	3-NO$_2$C$_6$H$_4$CH$_2$OH	3-NO$_2$C$_6$H$_4$CHO	3.3	30
10	4-NO$_2$C$_6$H$_4$CH$_2$OH	4-NO$_2$C$_6$H$_4$CHO	4	30
11	PhCH(OH)Me	PhCOMe	1	90
12	Ph$_2$CHOH	Ph$_2$CO	2	92
13	PhCH(OH)COPh	PhCOCOPh	4	90
14	PhCH$_2$CH$_2$CH$_2$Oh	PhCH$_2$CH$_2$CHO	1	90[c]
15	PhCH$_2$CH(OH)CH$_3$	PhCH$_2$COCH$_3$	1.7	90
16			1	85[c]
17	PhCH=CHCH$_2$OH	PhCH=CHCHO	0.67	—[d]
18	2-BrC$_6$H$_4$CH$_2$OTMS	2-BrC$_6$H$_4$CHO	0.67	85
19	2-ClC$_6$H$_4$CH$_2$OTMS	2-ClC$_6$H$_4$CHO	0.5	90
20	4-ClC$_6$H$_4$CH$_2$OTMS	4-CLC$_6$H$_4$CHO	0.67	90
21	2-MeC$_6$H$_4$CH$_2$OTMS	2-MeC$_6$H$_4$CHO	0.25	92
22	4-Me$_2$CHC$_6$H$_4$CH$_2$OTMS	4-Me$_2$CHC$_6$H$_4$CHO	0.42	87
23	4-Me$_3$CC$_6$H$_4$CH$_2$OTMS	4-Me$_3$CC$_6$H$_4$CHO	0.33	90
24	4-MeOC$_6$H$_4$CH$_2$OTMS	4-MeOC$_6$H$_4$CHO	0.75	85
25			0.42	85
26	Ph$_2$CHOTMS	Ph$_2$CO	2	87
27	3-NO$_2$C$_6$H$_4$CH$_2$OTMS	3-NO$_2$C$_6$H$_4$CHO	3.3	30
28	4-NO$_2$C$_6$H$_4$CH$_2$OTMS	4-NO$_2$C$_6$H$_4$CHO	2	30
29	PhCH$_2$CH$_2$OTMS	PhCH$_2$CHO	1.67	90
30	PhCH$_2$CH(OTMS)CH$_3$	PhCH$_2$COCH$_3$	2.2	90
31			0.5	85
32			1	80
33	PhCH=CHCH$_2$OTMS	PhCH=CHCHO	1	—[d]
34	2-BrC$_6$H$_4$CH$_2$OTHP	2-BrC$_6$H$_4$CHO	0.58	90
35	2-ClC$_6$H$_4$CH$_2$OTHP	2-ClC$_6$H$_4$CHO	0.58	87
36	4-ClC$_6$H$_4$CH$_2$OTHP	4-ClC$_6$H$_4$CHO	0.5	92

Table 1. countinued.

Entry	Substrate	Product	Time (h)	Yield (%) [b]
37	2-$MeC_6H_4CH_2OTHP$	2-MeC_6H_4CHO	0.17	90
38	4-$Me_2CHC_6H_4CH_2OTHP$	4-$Me_2CHC_6H_4CHO$	0.33	90
39	4-$Me_3CC_6H_4CH_2OTHP$	4-$Me_3CC_6H_4CHO$	0.25	86
40	4-$MeOC_6H_4CH_2OTHP$	4-$MeOC_6H_4CHO$	0.25	85
41			0.33	87
42	$PhCH(OTHP)CH_3$	PhCOMe	0.5	90
43	$Ph_2CHOTHP$	Ph_2CO	1.67	85
44	3-$NO_2C_6H_4CH_2OTHP$	3-$NO_2C_6H_4CHO$	2	25
45	4-$NO_2C_6H_4CH_2OTHP$	4-$NO_2C_6H_4CHO$	3	30
46	$PhCH_2CH_2OTHP$	$PhCH_2CHO$	1	90
47	$PhCH_2CH_2CH_2OTHP$	Ph_2CH_2CHO	2	85
48	$PhCH_2CH(OTHP)CH_3$	$PhCh_2COCH_3$	1.5	90
49			0.5	90
50			0.5	85
51	$PhCH{=}CHCH_2OTHP$	$PhCH{=}CHCHO$	1	— [d]
52	4-$ClC_6H_4CH_2OH$	4-ClC_6H_4CHO	1	10[e]

a: Products were characterized by IR and ^{1}HNMR spectral data;

b: Isolated yields;

c: Reaction was performed in the presence of 3 mmol of $Fe(NO_3)_3.9H_2O$;

d: Mixture of products;

e: Reaction was performed in the absence of KBr.

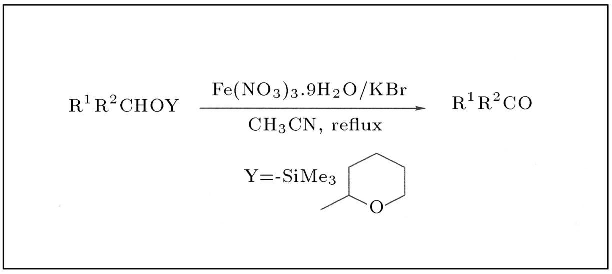

Figure 2. Oxidation of trimethylsilyl and tetrahydropyranyl ethers with $Fe(NO_3)_3.9H_2O$ catalyzed by KBr.

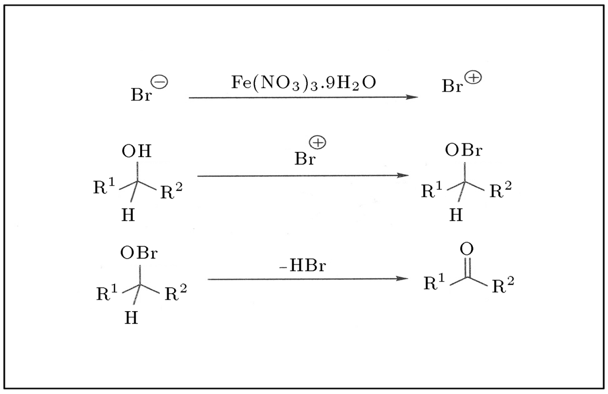

Figure 3. The proposed mechanism for the oxidation reactions with $Fe(NO_3)_3.9H_2O$/KBr.

ucts, the method is not recommended for the oxidation of allylic substrates (Table 1, entries 17, 33 and 51). It is important to note that the progress of the reaction strongly depends on the presence of KBr in the reaction mixture, so that in the absence of this reagent, after 1 h, a large amount of the starting material remains intact (Table 1, entry 52). Although the mechanism of the reaction is unclear, based on the literature [7, 8], the authors' observations and obtained results, the pathway that is shown in Figure 3 can be selected as the most plausible.

CONCLUSION

In conclusion, an efficient method for the oxidation of alcohols and trimethylsilyl and tetrahydropyranyl ethers, using $Fe(NO_3)_3.9H_2O$ in the presence of KBr, has been demonstrated. Due to short reaction time, availability and low cost of reagents, heterogeneous reaction conditions, easy work-up and good to high yield of product, it is believed that the described method would be a useful addition to available organic methodologies.

EXPERIMENTAL

General

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. All products are known compounds and were characterized by spectral analysis, in comparison with authentic samples (IR and NMR). All yields refer to the isolated products. The purity determination of the substrate and reaction monitoring were accompanied by TLC on silica-gel polygram SILG/UV 254 plates.

General Procedure

$Fe(NO_3)_3.9H_2O$ (0.808 g, 2mmol) and KBr (0.042 g, 0.35 mmol) were added to a solution of the substrate (1 mmol) in CH_3CN (5 mL) and refluxed for the appropriate time (Table 1). TLC or GC was used to follow the reaction. When the reaction was completed, the solvent was evaporated under reduced pressure and the residue was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with water and dried over $MgSO_4$. Evaporation of the solvent, followed by column chromatography on silica gel, gave the corresponding carbonyl compounds in good to high yields (Table 1).

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