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Efficient, Solvent-Free Oxidation of Organic Compounds with Potassium Dichromate in the Presence of Lewis Acids

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Abstract: The synthetic utility of potassium dichromate in the presence of Lewis acids under solid phase conditions is described. This reagent efficiently oxidizes alcohols, acyloins, oximes and semicarbazones to their corresponding carbonyl compounds, while trimethylsilyl and tetrahydropyranyl ethers, ethylene acetals and ketals undergo oxidative deprotection to produce carbonyl compounds efficiently.

Keywords: Oxidation, Organic compounds, Dichromate, Lewis acids, Solvent-free conditions.

Introduction

The total syntheses of complex molecules demand new methods in different areas of organic chemistry. Therefore, the development of reagents is always rewarding to synthetic organic chemistry. Oxidation is one of the most important classes of organic reactions from different points of view and effecting them under non-aqueous and aprotic conditions has found valuable applications in modern organic syntheses [1].

Potassium dichromate has been used extensively for the oxidation of different organic compounds under varied aqueous acidic conditions [1-6], but some of these methods suffer from disadvantages such as high reaction temperature, overoxidation of primary alcohols to carboxylic acids, long reaction times, low yields of the products and tedious workup. Its use as an oxidant under neutral conditions is also limited by its very low solubility in most organic solvents.

Heterogeneous reactions facilitated by reagents supported on various solid inorganic surfaces have gained special attention in recent years [7-9]. The advantages of these methods over conventional homogeneous reactions are typically higher selectivity, enhanced reaction rates, milder reaction conditions, cleaner products and manipulative simplicity. As a continuation of our ongoing work on development of environmentally benign methods using solid supports [10], we now report a convenient method for the oxidation of different classes of organic compounds with potassium dichromate in the presence of Lewis acids under solid phase conditions.

Results and Discussion

Potassium dichromate is a readily available and inexpensive reagent. The catalytic effects of several Lewis acids upon the activity of this oxidant were thoroughly studied. For this purpose the oxidation of benzhydrol to benzophenone was investigated in the presence of $AlCl_3$, $FeCl_3$, $BiCl_3$, $NiCl_2$, $CeCl_3$, $ZrCl_4$, $SnCl_2.2H_2O$, $CuCl_2.2H_2O$, $MnCl_2.4H_2O$ and $CoCl_2.6H_2O$. The experimental results show $AlCl_3$ to be the most effective catalyst for this purpose (Table 1).

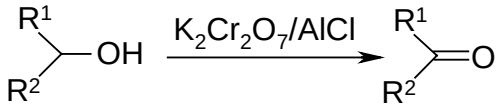
Table 1. Percent Conversion of Benzhydrol to Benzophenone with $K_2Cr_2O_7$ in the Presence of Different Lewis Acids Under Solid Phase Conditions

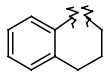
	Time (Min)			
Lewis acid	**5**	**10**	**15**	**30**
$AlCl_3$	100	-	-	-
$FeCl_3$	65	75	77	80
$BiCl_3$	80	85	90	90
$NiCl_2$	30	50	60	60
$CeCl_3$	50	65	75	80
$ZrCl_4$	70	80	85	85
$SnCl_2.2H_2O$	30	60	85	90
$CuCl_2.2H_2O$	60	75	80	90
$MnCl_2.4H_2O$	25	50	75	80
$CoCl_2.6H_2O$	60	65	70	75

Reagent ratio: Ph_2CHOH: $K_2Cr_2O_7$: $AlCl_3$= 1:1:1

Primary and secondary benzylic alcohols are oxidized to their corresponding aldehydes and ketones with potassium dichromate in the presence of $AlCl_3$ in high yield (Table 2). No overoxidation of primary alcohols to the corresponding carboxylic acids was observed under these conditions.

Table 2. Oxidation of Alcohols to Carbonyl Compounds[a]



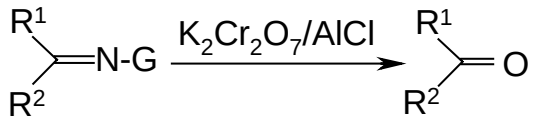
Entry	R^1	R^2	Time (Min)	Yields (%)[b]
1	C_6H_5	H	5	95
2	2-$MeOC_6H_4$	H	3	95
3	3-$MeOC_6H_4$	H	4	90
4	4-$MeOC_6H_4$	H	3	98
5	3,4-$(MeO)_2C_6H_3$	H	2	95
6	2-$NO_2C_6H_4$	H	30	72
7	3-$NO_2C_6H_4$	H	30	74
8	4-$NO_2C_6H_4$	H	25	75
9	4-ClC_6H_4	H	10	93
10	4-BrC_6H_4	H	15	87
11	5-MeFuryl	H	4	88
12	C_6H_5	CH_3	10	95
13	4-ClC_6H_4	CH_3	15	93
14	4-BrC_6H_4	CH_3	15	90
15	4-PhC_6H_4	CH_3	10	90
16	3,4-$(MeO)_2C_6H_3$	CH_3	3	98
17	C_6H_5	C_6H_5	5	93[c]
18	2-Pyridyl	C_6H_5	15	80
19	$C_6H_5CH{=}CH$	H	30	65[d]
20	C_6H_5	C_6H_5CO	10	95
21	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4CO$	3	96
22			10	90
23			30	10
24	$CH_3(CH_2)_6$	H	30	10

[a] All of the products are known compounds and were identified by comparison with authentic samples. [b] Isolated yields. [c] In the absence of $AlCl_3$, benzhydrol was converted to benzophenone in only 10% yield after 30 min with $K_2Cr_2O_7$. [d] 10% of benzaldehyde was obtained from the reaction mixture.

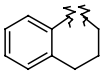
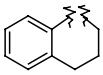
α-Hydroxy ketones are converted to α-diketones in excellent yields without any carbon-carbon bond cleavage (entries 20, 21). Saturated alcohols such as cyclohexanol and 1-heptanol are resistant towards oxidation with this reagent and the corresponding carbonyl compounds are obtained in poor yields (entries 23, 24). The oxidation of larger amounts (5-10 mmol) of some alcohols was also investigated. The results were comparable to those of the small scale experiments, therefore, it seems that the methodology is also applicable for medium to large scale operations. In order to stress the selectivity of this method, an equimolar mixture of 4-methoxybenzyl alcohol and 1-heptanol was treated with an equimolar of potassium dichromate and aluminium chloride. The experimental results show that only 4-methoxybenzyl alcohol was oxidized selectively. It is noteworthy that many of the other chromium (VI) based oxidants either do not display such selectivity [11-19] or they require much longer reaction times [20, 21]. Therefore, this selectivity represents a useful practical achievement in such oxidation reactions.

Potassium dichromate in the presence of aluminium chloride is also able to convert benzylic oximes and semicarbazones to their corresponding aldehydes and ketones in high yields (Table 3).

Table 3. Conversion of Oximes and Semicarbazones to Carbonyl Compounds[a]



Entry	R^1	R^2	G	Time(Min)	Yield(%)[b]
1	C_6H_5	H	OH	10	92
2	2-$MeOC_6H_4$	H	OH	5	90
3	4-$MeOC_6H_4$	H	OH	5	95
4	3,4-$(MeO)_2C_6H_3$	H	OH	5	95
5	3-$NO_2C_6H_4$	H	OH	30	75
6	4-$NO_2C_6H_4$	H	OH	30	85
7	5-MeFuryl	H	OH	10	85
8	C_6H_5	CH_3	OH	15	90
9	4-BrC_6H_4	CH_3	OH	15	95
10	4-ClC_6H_4	CH_3	OH	15	91
11	4-BrC_6H_4	CH_2Br	OH	5	85
12	4-PhC_6H_4	CH_3	OH	15	86
13	C_6H_5	C_6H_5	OH	15	85

14			OH	10	77
15			OH	30	10
16	C_6H_5	H	$NHCONH_2$	10	90
17	4-$CH_3OC_6H_4$	H	$NHCONH_2$	5	95
18	4-$NO_2C_6H_4$	H	$NHCONH_2$	30	77
19	4-ClC_6H_4	H	$NHCONH_2$	10	87
20	3,4-$(MeO)_2C_6H_3$	H	$NHCONH_2$	5	95
21	5-MeFuryl	H	$NHCONH_2$	5	80
22	C_6H_5	CH_3	$NHCONH_2$	10	88
23	4-BrC_6H_4	CH_3	$NHCONH_2$	10	85
24	4-ClC_6H_4	CH_3	$NHCONH_2$	15	85
25	4-BrC_6H_4	CH_2Br	$NHCONH_2$	10	92
26	4-PhC_6H_4	CH_3	$NHCONH_2$	20	93
27	C_6H_5	C_6H_5	$NHCONH_2$	10	90
28			$NHCONH_2$	30	88
29			$NHCONH_2$	30	5

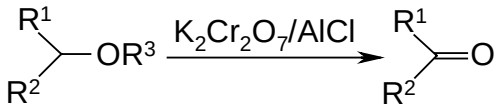
[a] All of the products are known compounds and were identified by comparison with authentic samples. [b] Isolated yields.

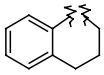
Further oxidation of aldehydes to their carboxylic acids was not observed. Under the same reaction conditions, saturated oximes and semicarbazones are converted to their corresponding carbonyl parent compounds in poor yields (Table 3, entries 15, 29).

In contrast to the method described in this paper, deoximation using pyridinium chlorochromate (PCC) suffers from long reaction times (12-94 h), low yields and low selectivity [22]. PCC-H_2O_2 system is not sutiable for aldoximes and overoxidation products are usually produced and show low selectivity as well [23]. Therefore, this method is superior to PCC and PCC-H_2O_2 system in terms of reaction times, yields and selectivity.

In order to further assess the capabilities of this reagent, we decided to also perform oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers, ethylene acetals and ketals. The treatment of a variety of TMS and THP ethers, ethylene acetals and ketals with potassium dichromate in the presence aluminium chloride under solid phase conditions afforded the corresponding carbonyl compounds in high yields (Tables 4 and 5).

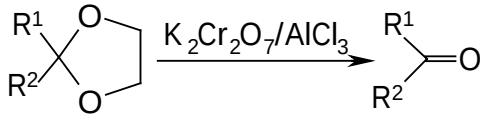
Table 4. Conversion of TMS and THP Ethers to Carbonyl Compounds[a]

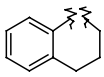


Entry	R^1	R^2	R^3	Time(Min)	Yield (%)[b]
1	C_6H_5	H	TMS	15	90
2	2-$MeOC_6H_4$	H	TMS	15	95
3	4-$MeOC_6H_4$	H	TMS	10	95
4	2-$NO_2C_6H_4$	H	TMS	30	80
5	4-$NO_2C_6H_4$	H	TMS	30	81
6	$C_6H_5CH{=}CH$	H	TMS	30	65[c]
7	C_6H_5	CH_3	TMS	20	82
8	4-ClC_6H_4	CH_3	TMS	25	85
9	4-BrC_6H_4	CH_3	TMS	25	90
10	4-PhC_6H_4	CH_3	TMS	25	77
11	3,4-$(MeO)_2C_6H_3$	CH_3	TMS	10	96
12	C_6H_5	C_6H_5	TMS	25	95
13	4-ClC_6H_4	C_6H_5	TMS	20	90
14			TMS	15	85
15			TMS	30	5
16	C_6H_5	H	THP	5	95
17	2-$CH_3OC_6H_4$	H	THP	5	95
19	4-$CH_3OC_6H_4$	H	THP	3	96
20	3-$NO_2C_6H_4$	H	THP	30	75
21	4-$NO_2C_6H_4$	H	THP	30	80
22	4-ClC_6H_4	H	THP	10	90
23	3,4-$(MeO)_2C_6H_3$	H	THP	3	96
24	C_6H_5	CH_3	THP	10	87
25	4-ClC_6H_4	CH_3	THP	10	80
26	4-PhC_6H_4	CH_3	THP	15	90
27	C_6H_5	C_6H_5	THP	5	87
28	4-ClC_6H_4	C_6H_5	THP	15	90
29			THP	30	5

[a] All of the products are known compounds and identified by comparison with authentic samples. [b] Isolated yields. [c] 15% of benzaldehyde was obtained from the reaction mixture.

Table 5. Conversion of Ethylene Acetals and Ketals to Carbonyl Compounds[a]



Entry	R^1	R^2	Time(Min)	Yields(%)[b]
1	C_6H_5	H	5	92[c]
2	3-$MeOC_6H_4$	H	5	90
3	4-$MeOC_6H_4$	H	3	95
4	3,4-$(MeO)_2C_6H_3$	H	2	98
5	3-$NO_2C_6H_4$	H	30	75
6	4-ClC_6H_4	H	10	90
7	C_6H_5	CH_3	10	95
8	4-ClC_6H_4	CH_3	15	90
9	4-BrC_6H_4	CH_3	15	86
10	4-PhC_6H_4	CH_3	20	90
11	3,4-$(MeO)_2C_6H_3$	CH_3	3	96
12	4-BrC_6H_4	CH_2Br	10	92
13	C_6H_5	C_6H_5	20	88
14			15	85
15			30	15

[a] All of the products are known compounds and identified by comparison with authentic samples. [b] Isolated yields. [c] 2-phenyl-1,3-dioxolane remained intact after 30 min in the presence of $K_2Cr_2O_7$ without $AlCl_3$

Conclusions

We present new methodology for the oxidation of organic compounds under solid phase conditions. In addition, the commercial availability and low cost of the reagent, high yields of the products, mild reaction conditions, easy workup and short reaction times are noteworthy advantages of this method and make this reagent practical bench-top oxidant.

Acknowledgements

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Experimental

General

All of the starting materials used in this work are commercially available or were prepared according to published procedures [24-27]. All of the products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. Reported yields refer to isolated pure products.

General Procedure for the Oxidation of Organic Compounds

A mixture of substrate (1 mmol), potassium dichromate (1-2 mmol) and aluminium chloride (1 mmol) in a mortar was ground with a pestle for the time specified in Tables 2-5. The progress of the reaction was monitored by TLC or GLC. The mixture was extracted with CH_2Cl_2. The solvent was evaporated and the resulting crude material was purified on a silica-gel plate or silica-gel column with appropriate eluent to afford the pure product (Tables 2-5). In oxidation of alcohols, 1 mmol $K_2Cr_2O_7$ and in other cases, 2 mmol $K_2Cr_2O_7$ was used

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Sample Availability: All products reported in this paper are available from the authors.

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