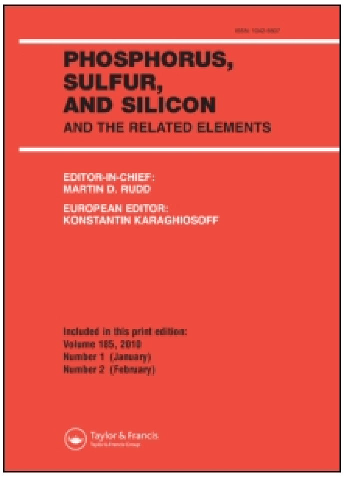

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IMMEDIATE AND HIGH YIELDING SOLVENT-FREE OXIDATION OF SILYL AND PYRANYL ETHERS TO THEIR CORRESPOUNDING CARBONYL COMPOUNDS WITH ZINC DICHROMATE TRIHYDRATE ($ZnCr_2O_7 \cdot 3H_2O$)

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IMMEDIATE AND HIGH YIELDING SOLVENT-FREE OXIDATION OF SILYL AND PYRANYL ETHERS TO THEIR CORRESPOUNDING CARBONYL COMPOUNDS WITH ZINC DICHROMATE TRIHYDRATE ($ZnCr_2O_7{\cdot}3H_2O$)

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Zinc dichromate trihydrate ($ZnCr_2O_7{\cdot}3H_2O$) is an efficient reagent for the immediate deprotection of aromatic and aliphatic silyl and pyranyl ethers into their corresponding carbonyl compounds in high yields at room temperature under solvent-free conditions.

Keywords: Carbonyl compounds; deprotection; oxidation; pyranyl ethers; silyl ethers; solvent-free; zinc dichromate trihydrate

Transformation of hydroxy functional groups into their silyl and pyranyl ethers is a common way for their protection during the total synthesis of complex organic molecules.[1–3] Direct oxidation of silyl and pyranyl ethers into their carbonyl compounds is a useful transformation during the process of a multistep synthesis of organic compounds. This transformation has been under attention and varieties of methods have been reported by investigators. The reported methods include; Tris[trinitratocerium(IV)] paraperiodate ($[(NO_3)_3Ce]_3{\cdot}H_2IO_6$),[4] $Fe(NO_3)_3{\cdot}1.5N_2O_4$, and $Cu(NO_3)_2{\cdot}N_2O_4$,[5] silver and sodium bromate in the presence of aluminum chloride,[6] 2,3-Dichloro-5,6-dicyanoquinone (DDQ),[7,8] cerric ammonium nitrate (CAN),[9] N-bromosuccinimide (NBC),[10] potassium permanganate in the presence of Lewis acids,[11] nitrosonium tetrafluoroborate ($NO^+BF_4^-$),[12] bis[trinitrato cerium (IV)] chromate $[(NO_3)_3Ce]_2CrO_4$,[13] Jones reagent (CrO_3/H_2SO_4/acetone),[14–16] zinc chlorochromate nonahydrate (ZCCNH),[17] bis(triphenylsilyl)chromate ($(Ph_3SiO)_2CrO_2$),[18] pyridinium fluorochromate

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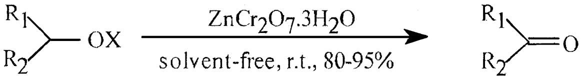
(PFC),[19] trimethylsilyl chlorochromate [$ClCrO_2(OSiMe_3)$],[20] Collins reagent ($CrO_3{\cdot}2Py$),[21] phridinum chlorochromate (PCC),[22,23] 3-carboxypyridinium chlorochromate (CPCC),[24] alumina supported chromium(VI) oxide,[25] and pyridinium dichromate(PDC).[20]

Some of the reported procedures for the oxidation of silyl and pyranyl ethers suffer at least from one of the following disadvantages: using expensive reagents,[4,13] high acidity of the media,[14–16] long reaction times,[18,19] dangerous procedure for preparation,[21–24] and difficult procedures.[18] Therefore, efficient and one-pot direct oxidation of silyl and pyranyl ethers under mild and solvent-free conditions can be considered as a useful procedure for further manipulation of the hydroxy functionality in organic synthesis. In this article, we report a new efficient method for deprotection of various types of silyl and pyranyl ethers into their corresponding carbonyl compounds under solvent-free conditions using zinc dichromate trihydrate (ZDC)[26] as an easily prepared, stable, and inexpensive reagent (Scheme 1, Tables I–III).



X= TMS, TBDMS, THP
R_1= Ph, alkyl
R_2= Ph, alkyl, H

SCHEME 1

Primary and secondary benzylic trimethylsilyl ethers were oxidized easily to the corresponding aldehydes and ketons in good to excellent yields (Table I, entries 1–12). Cinnamyl trimethylsilyl ether was oxidized to cinnamylaldehyde in 88% yield by this method (Table I, entry 9). Saturated primary and secondary trimethylsilyl ethers were converted into the corresponding carbonyl compound in good yields (Table I, entries 13–16).

We also studied oxidative deprotection of *tert*-butyldimethylsilyl ethers of similar alcohols with ZDC under solvent-free conditions. We found that this reagent was also very effective for this purpose and converted *tert*-butyldimethylsilyl ethers effectively to their carbonyl compounds in 80–94% yields under solvent-free conditions and at room temperature (Scheme 1, Table II). Primary and secondary benzylic *tert*-butyldimethylsilyl ethers were oxidized easily to the corresponding aldehydes and ketones in good to excellent yields (Table II, entries 1–12). Cinnamyl *tert*-butyldimethylsilyl ether was transformed into

TABLE I Deprotection of Trimethylsilyl Ethers with ZDC under Solvent-Free Conditions and at Room Temperature

Entry	R_1	R_2	Oxidant/substrate	Yield[a,b] (%)
1	Ph	H	1/1	90[c]
2	4-ClC_6H_4	H	1.2/1	92
3	4-MeC_6H_4	H	1/1	92
4	4-BrC_6H_4	H	1.2/1	93
5	4-$NO_2C_6H_4$	H	1.4/1	90
6	2-$NO_2C_6H_4$	H	2/1	89
7	4-$MeOC_6H_4$	H	1/1	95
8	2-$NH_2C_6H_4$	H	1.5/1	88
9	Cinnamyl	H	1.2/1	88
10	Ph	Ph	1/1	95
11	Ph	Me	1/1	94
12	Ph	Et	1/1	92
13	$PhCh_2Ch_2$	H	1/1	88
14	$PhCh_2$	H	1/1	90
15	C_7H_{15}	H	3/1	85
16	C_6H_{13}	CH_3	3/1	85

[a] Isolated yields.
[b] GC purity >96%.
[c] Benzaldehyde was isolated as its 2,4-dinitrophenyl hydrazine derivative.

TABLE II Deprotection of *tert*-Butyldimethylsilyl Ethers with ZDC under Solvent-Free Conditions and at Room Temperature

Entry	R_1	R_2	Oxidant/substrate	Yield[a,b] (%)
1	Ph	H	2/1	90[c]
2	4-ClC_6H_4	H	2/1	91
3	4-MeC_6H_4	H	2/1	92
4	4-BrC_6H_4	H	2.5/1	92
5	4-$NO_2C_6H_4$	H	3/1	90
6	2-$NO_2C_6H_4$	H	4/1	88
7	4-$MeOC_6H_4$	H	2/1	94
8	2-$NH_2C_6H_4$	H	2.5/1	88
9	Cinnamyl	H	2/1	90
10	Ph	Ph	4/1	94
11	Ph	Me	4/1	93
12	Ph	Et	4/1	92
13	$PhCH_2CH_2$	H	4/1	85
14	$PhCH_2$	H	5/1	85
15	C_7H_{15}	H	5/1	80
16	C_6H_{13}	CH_3	5/1	80

[a] Isolated yields.
[b] GC purity >96%.
[c] Benzaldehyde was isolated as its 2,4-dinitrophenyl hydrazine derivative.

cinnamylaldehyde in 90% yield (Table II, entry 9). Saturated primary and secondary *tert*-butyldimethylsilyl ethers were also converted to the corresponding carbonyl compounds in high yields under similar reaction conditions (Table II, entries 13–16).

Oxidative deprotection of tetrahydropyranyl ethers of various alcohols with zinc dichromate trihydrate under solvent-free condition and at room temperature were also investigated (Scheme 1, Table III). By this procedure, various types of aromatic tetrahydropyranyl ethers with electron-releasing and electron-withdrawing groups (Table III, entries 1–13) were immediately converted to their corresponding carbonyl compounds (85–94%). Primary and secondary aliphatic THP-ethers also were oxidized to the corresponding aldehydes and ketones in 80–85% yields (Table III, entries 13–16).

In this study, we have introduced a new and useful applications of $ZnCr_2O_7{\cdot}3H_2O$ in organic synthesis. By using this reagent under solvent-free and mild reaction conditions, we have presented immediate and high yielding conversions of TMS, TBDMS and THP ethers into their aldehydes and ketones. Isolation of the products is easy, clean and not a time consuming process. Quantitative preparation of the reagent from cheap and available compounds; $ZnCO_3$ and aqueous solution CrO_3 is also worthy of mention for the presented method.

TABLE III Deprotection of Tetrahydropyranyl Ethers with ZDC under Solvent-Free Conditions and at Room Temperature

Entry	R_1	R_2	Oxidant/substrate	Yield[a,b] (%)
1	Ph	H	2/1	90[c]
2	4-ClC_6H_4	H	2/1	91
3	4-MeC_6H_4	H	2/1	90
4	4-BrC_6H_4	H	2.5/1	89
5	4-$NO_2C_6H_4$	H	3/1	89
6	2-$NO_2C_6H_4$	H	4/1	85
7	4-$MeOC_6H_4$	H	2/1	92
8	2-$NH_2C_6H_4$	H	2.5/1	86
9	Cinnamyl	H	2/1	90
10	Ph	Ph	4/1	94
11	Ph	Me	4/1	92
12	Ph	Et	4/1	92
13	$PhCH_2CH_2$	H	4/1	85
14	$PhCH_2$	H	5/1	84
15	C_7H_{15}	H	5/1	80
16	C_6H_{13}	CH_3	5/1	80

[a] Isolated yields.
[b] GC purity >96%.
[c] Benzaldehyde was isolated as its 2,4-dinitrophenyl hydrazine derivative.

EXPERIMENTAL

An immediate reaction occurred by mixing silyl or pyranyl ethers (1 mmol) with $ZnCr_2O_7{\cdot}3H_2O$ (1–5 mmol) at room temperature. To the resulting solid mixture, ether (20 mL) was added and after vigorous shaking the mixture was filtered through a silica gel pad (3 Cm thick). The resulting filter cake was poured into ether (20 mL) and was shaken vigorously and filtered. Evaporation of the combined filtrates resulted in the desired known carbonyl compounds in high yields (Tables I–III).

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