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SeO2 in water: a mild and efficient promoter for deprotection of acetyl, methoxymethyl and tetrahydropyranyl ethers and sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon

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Abstract: SeO_2 in water provided an efficient and one-pot deprotection of acetyl, tetrahydropyranyl and methoxymethyl ethers in alcohols and phenols and sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon to dicarbonyl functional groups at 80 ^{0}C in 30-60 min. Using substrate: SeO_2 in 1:3 ratio, the reaction gave excellent yield (85-95%) for the acetyl and tetrahydropyranyl deprotections and a moderate yield (35-40%) for the methoxymethyl deprotection without affecting other functional groups.

Introduction

Protection and deprotection of the functional groups is the most frequent used strategies in the multi-steps organic syntheses. In particular, the protection and the deprotection of hydroxyl and phenolic groups is extremely important because of its presence of a number of compounds of natural products, biological and synthetic compounds such as carbohydrates, macrolides, peptides, steroids, nucleotides and polyethers.[1] The protection of hydroxyl groups with 3,4-dihydro-2H-pyran (DHP) is the most common method because of the stability of the product, 2-tetrahydropyranyl ethers (THPEs) in the strong basic conditions such as Grignard reagents, organolithium, metal hydrides, catalytic hydrogenation, alkylating and acylating conditions.[2] Similarly, methoxymethyl chloride (MOMCl) and acetyl chloride/acetic anhydride (CH_3COCl/Ac_2O) reagents are used for the hydroxyl and phenolic groups protection.[3]Deprotection of these groups (acetyl, THP and MOM ethers) therefore required efficient methods to avoid the product decomposition and/or loss of other functional groups in the molecules. Several catalytic methods have been explored for the selective deacetylation of alcohols and phenols under acidic and basic conditions. For example, the deprotection of acetate includes NaOMe,[4a] micelles,[4b] Zn-MeOH,[4c] cyclodextrin,[4d] enzymes,[4e] mettallo-enzyme,[4f] metal complexes,[4g] and antibodies,[4h] montmorillonite k-10,[4i] I_2,[4j] $NaBO_3$,[4k] and $HCOONH_4$-SiO_2[4l] and of detetrahydropyranylation includes protic acids,[5a-d] Lewis acids like BF_3-etherate,[5e] LiBr,[5f] $LiBF_4$,[5g] LiOTf,[5h] $LiClO_4$,[5i] $Sc(OTf)_3$,[5j] $In(OTf)_3$,[5k] I_2,[5l] $InCl_3$,[5m] $ZrCl_4$,[5n] $CuCl_2$,[5o] NH_4Cl,[5p] graphite,[5q] clay materials,[5r] silica-supported sulfuric acid,[5s] electrogenerated acids,[5t] bis(trimethylsilyl)sulphate,[5u] Distannoxane,[5v] triphenyl phosphine dibromide,[5w] DDQ,[5x] and heteropoly acids.[5y] Similarly, for demethoxymethylation includes HCl,[6a] BBr_3,[6b] pyridinium *p*-toluene sulphonate under strong acidic condition,[6c] $ZnBr_2$ and $TiCl_4$ in aprotic solvents,[6d] Me_2BBr [6e] and $(i\text{-}PrS)_2BBr$.[6f] Most of these methods have one or other drawbacks such as long reaction time, low yields, reflux at high temperature and tedious workup procedures.[7] Hence, there is still scope to develop mild and efficient methods in the deacetylation, detetrahydropyranylation and demethoxymethylation of hydroxyl groups.

In the alpha carbonyl carbon (active methyl and methylene) oxidation to dicarbonyl group, various reagents and reaction conditions have been explored that include ammonium chlorochromate,[8a] I_2,[8b] CrO_3-NH_4Cl,[8c] HBr,[8d] MeSSMe-$CuCl_2$-CuO,[8e] $Cu(OAc)_2.H_2O$,[8f] P-Me-sulphonic acid,[8g] SeO_2-DMSO,[8h] KI+O_2-t-BuNH_2.[8i] However, SeO_2 was not reported as reagent for one-pot deprotection of acetyl, THP and MOM ethers and sequel alpha carbonyl carbons oxidation in eco-friendly environment. In continuation of our interest.[9] to develop new methods for the organic synthesis, herein, we report an efficient one-pot protocol for the deprotection of acetyl, tetrahydropyranyl and methoxymethyl ethers and sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon to dicarbonyl functional group using SeO_2 in water as a novel reagent.

Results and Discussion

We screened different oxidizing agents in water for the deprotection and sequel oxidation as CrO_3, DDQ and PCC in H_2O, however failed to give the products (Table 1, entries 1, 3 & 6), OsO_4 and MnO_2 gave a poor yield (5-10%) at 80 ^{0}C after 6h (Table 1, entry 2 & 7), while, SeO_2 gave the optimal yield (85-95%) using substrate:SeO_2 (1:3 ratio) in 1ml H_2O at 80 ^{0}C within 1h (Table 1, entry 5). Under similar conditions, demethoxymethylation and sequel oxidation gave moderate yields (40%) in 1-3h. Therefore,

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Electronic supplementary information (ESI) available:[details of any supplementary information should be available here]. Experimental procedures, characterization data and ^{1}H, ^{13}C NMR spectra associated with this article are available
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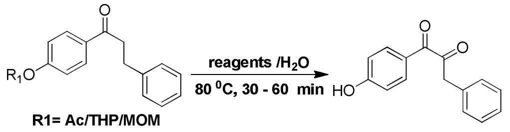
substrate:SeO_2 (1:3 ratio) in 1ml H_2O was selected as an optimized conditions. When, we applied substrate:SeO_2 (1:1 and 1:2 ratios) in 1ml H_2O, got only deprotection product in 95% yields for Ac and THP and demethoxymethylation gave moderate yields (35-40%) at 80 ^{0}C in 1-3h. (Table 1, entry 4 and Table 3). In case of indanone only deprotection was observed no oxidation of alpha hydroxyl to dicarbonyl (Table 3, entry 11). The products were confirmed on the basis of their spectral data (supporting information). For example, product 7, the ^{1}H-NMR spectra showed the characteristic broad peak at δ 5.45 ppm for hydroxyl group. IR value at 3425 cm^{-1} for –OH groups indicates only deprotection without oxidation of methyl/methylene carbons of alpha carbonyl carbon to dicarbonyl group.

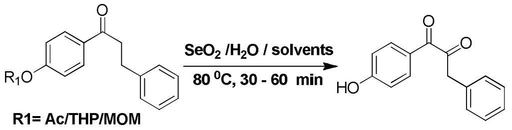
Table 1. Optimization conditions in deprotection of acetate, tetrahydropyranyl and methoxymethyl ethers and sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon.



Entry	Substrate: Reagent (equiv)	Time (h)	Yield (%) (deacetylation)	Yield (%) (detetrahydro-pyranylation)
1	Sub.:CrO_3(1:1)	24 h	No reaction	No reaction
2	Sub.:OsO_4(1:1)	6 h	8	5
3	Sub.:DDQ(1:1)	24 h	No reaction	No reaction
4	Sub.:SeO_2(1:1)	1h-3h	Only deprotection	Only deprotection
5	**Sub.:SeO_2(1:3)**	**1 h**	**95**	**94**
6	Sub.:PCC(1:1)	6 h	No reaction	No reaction
7	Sub.:MnO_2(1:1)	6h	10	10

In the case of low soluble or insoluble compounds under optimized conditions, the reaction gave moderate yield (35%). Therefore, 3-4 drops of organic solvents (THF, dioxane, DMF, DEE, ethanol, methanol, $CHCl_3$ and DMSO) were used to improve the solubility, in which THF and dioxane gave the maximum yields (60% and 94%) respectively (Table 2, entries 1-10). However, SeO_2 in any organic solvent failed to give the product without H_2O (Table 2, entry 2). In the MOM ethers deprotection and sequel oxidation of alpha carbon gave only 40% yields even under above conditions.

Table 2. Solvents effects in deprotection of acetate, tetrahydropyranyl and methoxymethyl ethers and sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon.



Entry	H_2O(1ml):Solvents (3-4 drops)	Yield^a (%)	Yield^b (%)
1	H_2O	30	35
2	Organic solvents*	0	0
3	H_2O:THF	65	60
4	**H_2O:Dioxane**	**95**	**94**
5	H_2O:DMF	50	40
6	H_2O:DEE	25	20
7	H_2O:Ethanol	0	0
8	H_2O:methanol	0	0
9	H_2O:$CHCl_3$	0	0
10	H_2O:DMSO	50	40

^{a} Yields of deacetylation. ^{b} Yields of detetrahydropyranylation,

*DMSO, Dioxane, THF, DMF, etc.

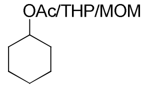
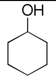
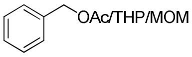
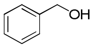
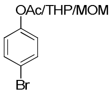
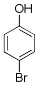
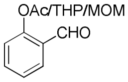
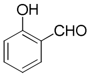
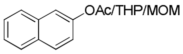
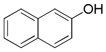
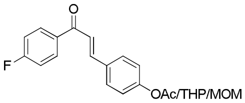
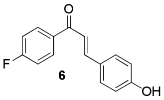
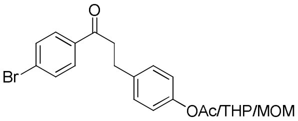
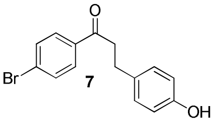
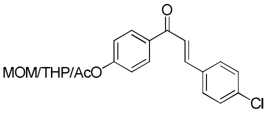
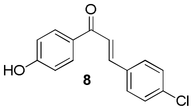
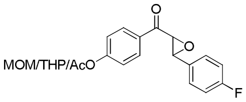
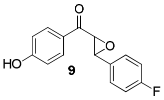
Under optimized reaction conditions using substrate:SeO_2,1:3 ratio, the reaction gave the deprotection and sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon to di-carbonyl group in excellent yield (85-95%) for the deacetylation, detetrahydropyranylation and moderate yield 30-40% for demethoxymethylation (Table 4, entries 3-10) within 30-60 min at 80 ^{0}C. Interestingly, acetyl and THP removal and sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon to di-carbonyl group were observed in the protected hydroxyl acetophenone and dihydrochalcones to give the corresponding hydroxy dicarbonyl derivatives **14**-**21** in excellent yield (85-95%). We further used excess of substrate:SeO_2 in 1:4, 1:5 & 1:6 ratio and prolonging the reaction time (>120 minutes) for the oxidation of another alpha carbon, but failed to give oxidation product (Table 4, entry 11). Similarly, the di-carbonyl compounds were failed to undergo alpha carbon oxidation under optimized condition even prolonging the reaction time (Table 4, entry 12).

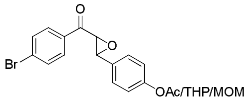
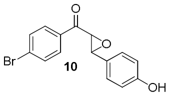
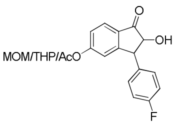
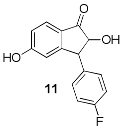
The reagent is also useful for the deprotection of methoxymethyl ether (MOM) of phenolic compounds like, chalcone and chalcone epoxides but the yield of the product was moderate 30-40% (Table 4, entries 3-12). In the case of demethoxymethylation, we performed reaction for longer reaction time (1-3h), but no further conversion was observed. Therefore, the remaining starting material was recovered by column chromatography.

The products were characterized on the basis of their spectral analysis ^{1}H- and ^{13}C-NMR, GC-MS (supporting information). For example, product **16**, the ^{1}H-NMR spectra showed the characteristic singlet peak at δ 3.99 ppm for $–CH_2$ and disappear the charecteristic two triplet peak at δ 2.80 and 2.72 ppm (J = 5.5 - 6.5 Hz) of $-CH_2$-CH_2- and broad peak at δ 5.19 ppm for hydroxyl group, indicates oxidation of alpha carbonyl carbon. In ^{13}C-NMR spectra, the characteristic peak at δ 197.12 and 191.10 ppm for two carbonyl (–CO-CO-) groups and peak at δ 50.89 ppm for $–CH_2$ confirms the oxidation of alpha carbonyl carbon, this confirmation also support by the disappearance of peak at 46.35 and 30.51 ppm of $-CH_2$-CH_2- groups in dihydrochalcone. IR value at 3415 cm^{-1} for –OH groups, 1705 and 1715 cm^{-1} for dicarbonyl indicates the deprotection and sequel oxidation of alpha carbonyl carbon. The structures of all other compounds were further confirmed by GC-MS (supporting information).

Table 3. Examples of deprotection (only) of acetate, tetrahydropyranyl and methoxymethyl ethers in alcohols and phenols.

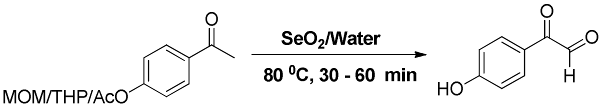
$$\text{ROAc/THP/MOM} \xrightarrow[\mathbf{80\ {}^0C,\ 30\ -\ 60\ \ min}]{\mathbf{SeO_2/Water}} \text{ROH}$$

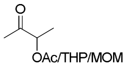
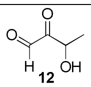
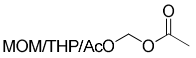
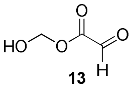
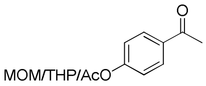
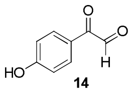
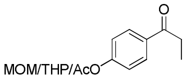
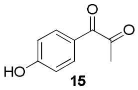
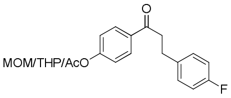
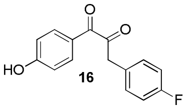
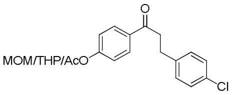
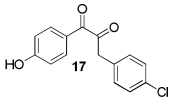
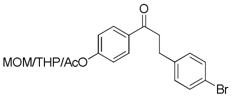
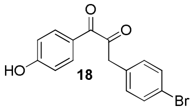
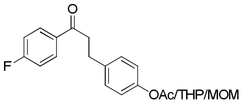
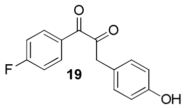
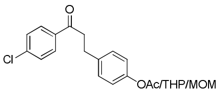
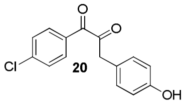
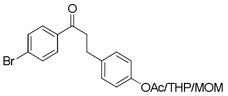
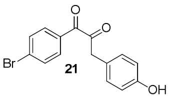
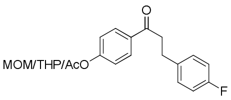
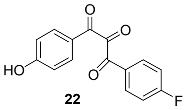
Entry	ROAc/THP/MOM	ROH	Time (min)	Yield^a (%)	Yield^b (%)	Yield^c (%)
1		 **1**	30	92	89	40
2		 **2**	30	92	88	40
3		 **3**	30	95	92	35
4		 **4**	30	93	95	40
5		 **5**	30	95	95	32
6		 **6**	30	96	95	35
7		 **7**	30	90	87	35
8		 **8**	30	96	94	40
9		 **9**	30	95	90	35

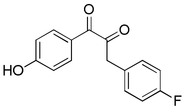
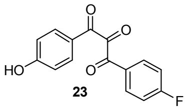
10		 10	30	90	96	35
11		 11	30	92	94	30

[a] Yields of deacetylation, [b] Yields of detetrahydropyranylation, [c] Yields of demethoxymethylation

Table 4. Deprotection of Ac, THP and MOM groups and sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon.



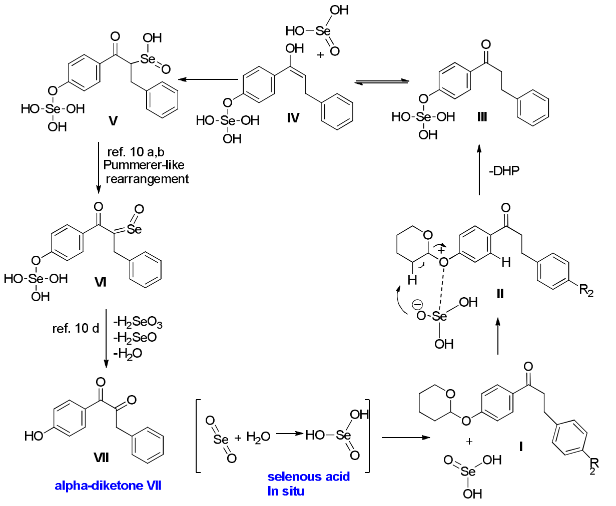
Entry	compounds with alpha carbonyl carbon	Dicarbonyl	Time (min)	Yield[a] (%)	Yield[b] (%)	Yield[c] (%)
1		 12	60	92	95	32
2		 13	60	90	88	32
3		 14	60	93	95	40
4		 15	30	94	94	35
5		 16	60	91	85	40
6		 17	60	93	88	40
7		 18	60	90	87	30
8		 19	60	95	85	35
9		 20	60	94	82	35
10		 21	60	95	80	30
11[d]		 22	>120	-	-	-

12^e		 **23**	>60	-	-	-

^{a} Yields of deacetylation, ^{b} Yields of detetrahydropyranylation, ^{c} Yields of demethoxymethylation, ^{d} Used substrate:SeO$_2$ ratio: 1:4, 1:5 & 1:6 , with prolonging reaction time but no further oxidation was observed, ^{e} Under optimized condition, di-carbonyl compound failed to give alpha carbon oxidation product.

A plausible mechanism was proposed (scheme 1). First, selenium dioxide and water reacts to form the selenous acid in *situ* which reacted with tetrahydropyranyl dihydrochalcone **I** to make complex **II**. Selenous acid ligated with oxygen of tetrahydropyranyl dihydochalcone II , followed by removal of DHP via intramolecular abstraction of proton by selanolate ion to give compound **III**.

Further, complex **III** undergoes keto-enol tautomerization to getcompound **IV**. The key step is the beta-ketoseleninic acid **V** formation by the dihydrochalcone followed by Pummerer -like[10 a, b] reaction to obtain compound **VI**. Then, the hydrolysis gave the deprotected alpha-diketone **VII** of THP dihydochalcone.[10c]



Scheme 1. Propose mechanism for the deprotection of tetrahydropyranyl ethers and sequel oxidation of methyll/methylene carbons of alpha carbonyl carbon to di-carbonyl group in SeO$_2$/water.

Conclusions

In conclusion, we have developed an efficient one-pot protocol for the deprotection of acetyl, tetrahydropyranyl and methoxymethyl ethers and sequel oxidation sequel oxidation of methyl/methylene carbons of alpha carbonyl carbon to di-carbonyl functional group using substrate: SeO$_2$ (1:3 ratio) in H$_2$O. The reaction gave excellent yield (85-95%) for acetyl and THP ethers and moderate yield (30-40%) at 80 ^{0}C in 30-60 min. However, a selective deprotection of acetyl, tetrahydropyranyl and methoxymethyl was afforded using substrate:SeO$_2$ (1:1 ratio) in H$_2$O. This methodology has advantages such as short reaction time, high yields, and easy workup procedures

Experimental Section

General methods

Organic solvents were dried by standard methods; the reagents (chemicals) were purchased from commercial sources, and used withoutfurther purification. All reactions were monitored by TLC using precoated silica gel aluminum plates. Visualization of TLC plates was accomplished with an UV lamp. Column chromatography was performed using silica gel 60–120 mesh size (RANKEM Limited) with EtOAc–hexanes as eluent. Melting points were recorded on Perfit apparatus and are uncorrected. All products were characterized by NMR, IR and MS spectra. 1H and 13C NMR spectra were recorded in deuterated chloroform (CDCl$_3$) on a 500 MHz and 125 MHz spectrometer (Bruker), respectively. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br).

General procedure for deprotection of acetyl, tetrahydropyranyl and methoxymethyl ethers of alcohol and phenol: SeO$_2$ (1 mmol) was added to a stirred solution of Esters and ethers (1 mmol) in a water (1ml) and 3-4 drops of dioxane, suspension obtained, applied heating to 80°C. After TLC monitoring, the resulting reaction mixture was poured in cold water and extracted with EtOAc. The organic layer was washed with brine, dried with anhyd.Na$_2$SO$_4$, and concentrated in *vacuo* to give the corresponding product which was purified by silica gel column chromatography with hexane- EtOAc eluent to obtain the products **1** to **11** (table 3) in excellent yield 85-95% and 30-40% for deacetylation, detetrahydropyranylation and demethoxymethylation respectively. Similarly, *1-(4-bromophenyl)-3-(4-hydroxyphenyl)propan-1-one (7):* ^{1}H NMR (CDCl$_3$, 500 MHz) δ ppm 8.02 (d, J = 7.5 Hz, 2H), 7.74 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H) , 7.39 (d, J = 8.5 Hz, 2H), 5.45 (s, 1H), 2.80 (t, J = 6.5 Hz, 2H), 2.73 (t, J = 6.0 Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 199.12, 157.13, 136.27, 133.63, 131.54, 130.78, 129.62, 129.30, 115.19, 45.81, 30.17; IR ν$_{max}$ (KBr, cm^{-1}): 3425 (OH str), 2928, 2885 (aromatic C-H str), 1705 (C=O str), 1599 (aromatic, C=C str), 1265, 1079, 862, 725; GC-MS (m/z): 304, 306 [M$^{+\cdot}$, C$_{15}$H$_{13}$BrO$_2$].

General procedure for deprotection of acetyl, tetrahydropyranyl and methoxymethyl ethers in alcohols and phenols and sequel oxidation of *methylene carbon alpha carbonyl carbon to carbonyl functional groups*: SeO$_2$ (3 mmol) was added to a stirred solution of Esters and ethers (1 mmol) in a water (1ml) and 3 to 4 drops of dioxane, suspension obtained, applied heating to 80°C, gave products **12** to **21** (table 4) in excellent yield 85-95% and 30-40% for deacetylation, detetrahydropyranylation and demethoxymethylation followed by sequel oxidation of *methylene carbon alpha carbonyl carbon to carbonyl groups* respectively. *3-(4-fluorophenyl)-1-(4-hydroxyphenyl)propane-1,2-dione (16):* ^{1}H NMR (CDCl$_3$, 500 MHz) δ ppm 7.73(d, J = 9.0 Hz, 1H), 7.57 (d, J = 7.5 Hz, 2H), 7.53 (d, J = 9.0 Hz, 1H), 7.38 (d, J = 8.5 Hz, 2H) , 6.98 (d, J = 8.5 Hz, 2H), 5.19 (s, 1H), 3.99 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 197.12, 191.10, 166.42, 163.17, 131.54, 130.71, 129.62, 129.30, 122.38, 117.19, 116.11, 50.89; IR ν$_{max}$ (KBr, cm^{-1}): 3415 (OH str), 2935, 2879 (aromatic C-H str), 1705, 1715 (C=O str), 1593 (aromatic, C=C str), 1268, 1087, 865, 731; GC-MS (m/z): 258 [M$^{+\cdot}$, C$_{15}$H$_{11}$FO$_3$].

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Keywords: SeO_2-water system/ deacetylation/detetrahydropyranylation/Demethoxymethylation/ oxidation of methyl/methylene carbons of alpha carbonyl carbon

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