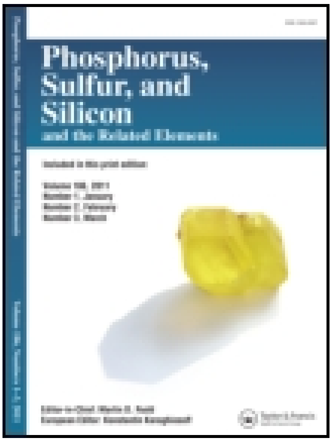

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A New and Efficient Procedure for the Production of 1,1-Diacetate from Corresponding Aldehydes Promoted by Silica Chromate (SiO_2-O-CrO_2-O-SiO_2)

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A NEW AND EFFICIENT PROCEDURE FOR THE PRODUCTION OF 1,1-DIACETATE FROM CORRESPONDING ALDEHYDES PROMOTED BY SILICA CHROMATE (SiO_2-O-CrO_2-O-SiO_2)

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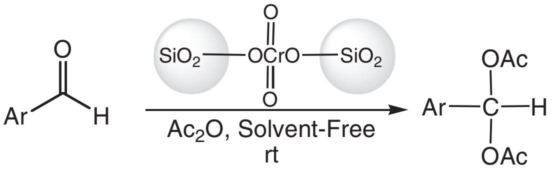
[3]*Department of Chemistry, College of Science, Yazd University, Yazd, Islamic Republic of Iran*

GRAPHICAL ABSTRACT



Abstract *A wide range of aromatic aldehydes has been selectively converted to 1,1-diacetates using silica chromate ($SiO_2—O—CrO_2—O—SiO_2$) under solvent-free conditions at room temperature in moderate to good yields. This protocol is mild and efficient compared to other reported methods.*

Keywords Aldehydes; 1,1-diacetates; silica chromate; solvent-free

INTRODUCTION

Selective protection and deprotection of carbonyl groups are essential steps in synthetic organic chemistry.[1] 1,1-Diacetates are synthetically useful protecting groups for carbonyl compounds due to their stability and also important building blocks for the synthesis of dienes in Diels–Alder reactions.[2,3] Additionally, the (1,1-diacetate) functionality can be converted into other functional groups by reaction with appropriate nucleophiles.[4,5]

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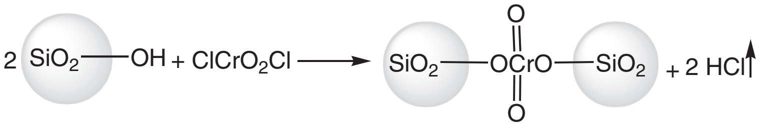
These 1,1-diacetates have several synthetic and industrial applications and are used as cross-linking reagents[6] in cellulose and the cotton industry, and are also used as stain bleaching agents.[7] Usually, 1,1-diacetates are prepared from aldehydes and acetic anhydride in the presence of strong proton acids or Lewis acids as catalyst, such as $RuCl_3.xH_2O$,[7] P_2O_5/montmorillonite K10,[8] zinc(II) perchlorate,[9] $BiCl_3$,[10] methylimidazolium hydrogen sulphate,[11] sodium hydrogen sulfate,[12] PVC-$FeCl_3$,[13] $Zr(HSO_4)_4$,[14] $Cu(NO_3)_2.3H_2O$,[15] Caro's acid supported on silica gel,[16] SO_4^{2-}/SnO_2,[17] copper(II) tetrafluoroborate,[18] $[NO^+Crown- H(NO_3)_2^-]$,[19] $SbCl_3$,[20] and $NbCl_5$.[21] However, some of the reported procedures require the use of harsh conditions, long reaction times, formation of byproducts, laborious work-up, and poor yields of the target products.

RESULTS AND DISCUSSION

In continuation of our investigation on the silica-based reagents,[22–26] we found that silica gel reacts with dichloro chromium oxide to give silica chromate, and it has been used in some organic reactions such as oxidation of 1,4-dihydropyridines,[27] regeneration of carbonyl compounds from oximes,[28] oxidation of alcohols, and deprotection of trimethylsilyl ethers.[29] Silica chromate as a nontoxic and efficient reagent can be easily obtained by the reaction of dichloro chromium oxide with silica gel (Scheme 1).



Scheme 1

To investigate the scope and limitation of silica chromate, we decided to apply this reagent for the preparation of 1,1-diacetates. Initially, the results of the preparation of 1,1-diacetoxy-1-(3-nitrophenyl)-methane (as typical example) as a function of the amounts of silica chromate were investigated and listed in Table 1. As the results show, the optimal amount of silica chromate to convert aldehydes to the corresponding 1,1-diacetates is 0.25 g.

In order to investigate the solvent effect on the outcome of the reaction, different solvents were applied for the preparation of 1,1-diacetoxy-1-(3-nitrophenyl)-methane; the

Table 1 Conversion of 3-nitrobenzaldehyde to the corresponding 1,1-diacetate using acetic anhydride and different amounts of silica chromate ($SiO_2{-}O{-}CrO_2{-}O{-}SiO_2$)[a]

Entry	Silica chromate (g)	Time (min)	Yield (%)[b]
1	0.05	50	60
2	0.1	45	70
3	0.15	40	75
4	0.2	35	80
5	0.25	30	90
6	0.3	30	90
7	0.35	25	92

[a] Molar ratio of reagents: aldehyde/acetic anhydride (1 mmol/1 mmol).
[b] Isolated yield.

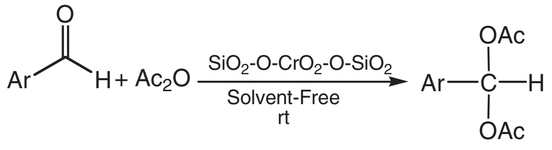
Table 2 Conversion of 3-nitrobenzaldehyde to the corresponding 1,1-diacetate using acetic anhydride and silica chromate ($SiO_2{-}O{-}CrO_2{-}O{-}SiO_2$) in different solvents at room temperature[a]

Entry	Solvent	Time (min)	Yield (%)[b]
1	Acetonitrile	100	75
2	Water	120	40
3	Ethyl acetate	150	45
4	Dichloromethane	100	70
5	Cyclohexane	120	50
6	Ethanol	110	40
7	Solvent-Free	30	90

[a] Molar ratio of reagents: aldehyde/acetic anhydride (1 mmol/1 mmol).
[b] Isolated yield.

results are summarized in Table 2. The protection of 3-nitrobenzaldehyde was performed using a mixture containing 3-nitrobenzaldehyde (1 mmol), acetic anhydride (1 mmol), and silica chromate (0.25 g) at room temperature. It was observed that the solvent-free condition is the most effective media, so it was used in all further reactions.

Consequently, we decided to apply a new heterogeneous protocol for the selective protection of a wide range of aromatic aldehydes (**1**) to the corresponding 1,1-diacetates (**2**) via combination of acetic anhydride and silica chromate under solvent-free conditions at room temperature (Scheme 2 and Table 3).



1 **2**

Scheme 2

1,1-Diacetate products were prepared easily by mixing an aldehyde, acetic anhydride, and silica chromate, then stirring this mixture under solvent-free conditions at room temperature. The pure product can be easily isolated from the reaction media by washing the reaction mixture with diethyl ether, simple filtration, and evaporation of the solvent.

As the results of Table 3 show, the reaction rate for the aromatic rings with electron-withdrawing groups is more than the aromatic rings with electron-donating groups.

The described method for the preparation of 1,1-diacetates has interesting and excellent selectivity. To show the chemoselectivity of the described system, some competitive reactions were designed (Scheme 3).

To the best of our knowledge, silica chromate is the first example of a silica-chromium–based oxidant with covalent linkages. Thus, we hoped that the silica chromate ($SiO_2{-}O{-}CrO_2{-}O{-}SiO_2$) would be superior to the previously reported chromium-based oxidants[30–32] because (i) toxic chromium cations could be collected from the reaction mixture easily; (ii) work up is very simple, and pure products are obtained solely by filtration and removing of solvent; and (iii) there is no need for any chelating agents such as pyridine in pyridinium chlorochromate (PCC). In conclusion, in this article we have developed a simple and efficient procedure for the chemoselective preparation of 1,1-diacetates using

Table 3 Preparation of 1,1-diacetates via combination of aldehydes, silica chromate ($SiO_2{-}O{-}CrO_2{-}O{-}SiO_2$) and acetic anhydride under solvent-free conditions at room temperature[a]

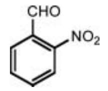
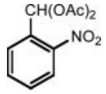
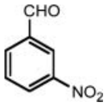
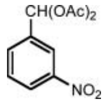
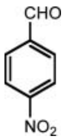
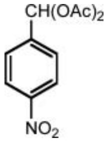
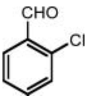
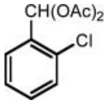
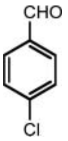
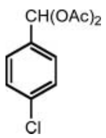
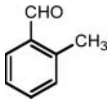
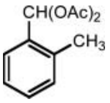
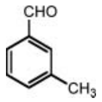
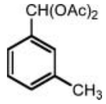
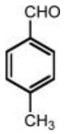
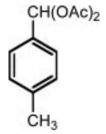
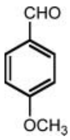
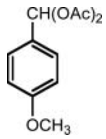
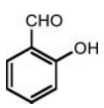
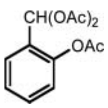
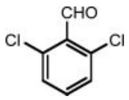
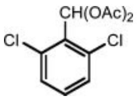
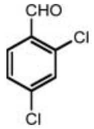
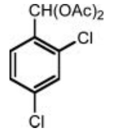
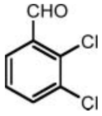
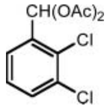
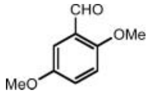
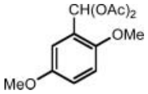
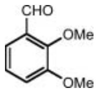
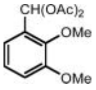
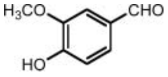
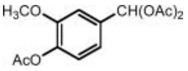
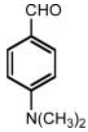
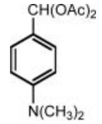
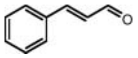
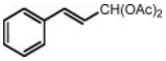
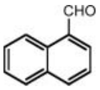
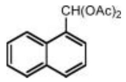
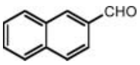
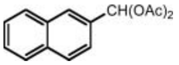
Entry	Substrate	Product	Time (min)	Yield (%)[b]	Mp (°C) found	Mp (°C) reported	Ref.
1			30	85	84–86	85–86	(36)
2			30	95	64–66	65–67	(11)
3			30	90	124	124–126	(11)
4			40	85	51–52	52–53	(11)
5			40	90	81–83	81–82	(11)
6			20	85	68–70	—	—
7			20	80	Gummy	—	—
8			20	85	80–82	80–82	(11)
9			45	75	64–66	65–66	(11)
10			75	75	100–102	101–102	(11)
11			50	80	87–89	89–90	(11)

Table 3 Preparation of 1,1-diacetates via combination of aldehydes, silica chromate ($SiO_2-O-CrO_2-O-SiO_2$) and acetic anhydride under solvent-free conditions at room temperature[a] *(Continued)*

Entry	Substrate	Product	Time (min)	Yield (%)[b]	Mp (°C) found	Mp (°C) reported	Ref.
12			50	80	118–120	—	—
13			50	75	78–79	—	—
14			100	70	108–109	107–108	(11)
15			100	70	103–105	—	—
16			120	80	89–91	90–92	(35)
17			600	65	Gummy	—	—
18			30	85	80–81	84–86	(11)
19			20	85	104–106	105–106	(36)
20			20	90	98–100	99–100	(36)

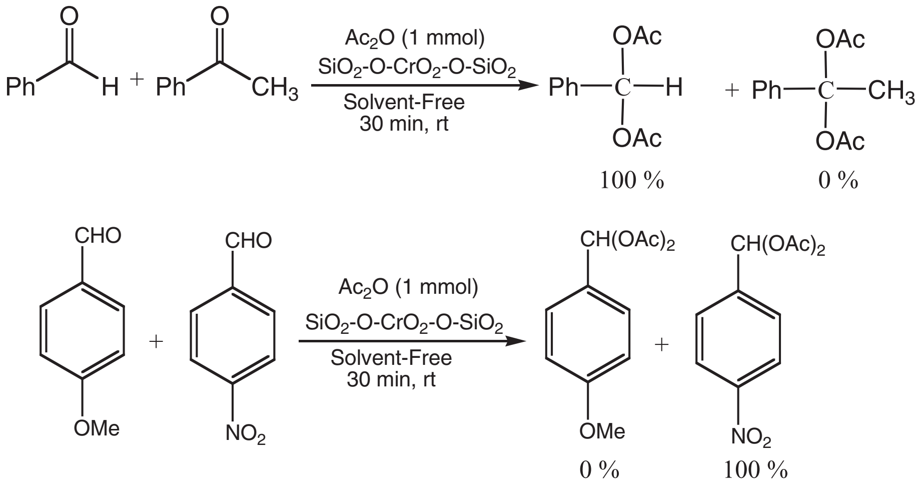
[a] Molar ratio of reagents: aldehyde/silica chromate/acetic anhydride for entries 1–9, 11–15, and 17–20 (1 mmol/0.25 g/1 mmol); for entries 10 and 16 (1 mmol/0.25 g/2 mmol).

[b] Isolated yield.

silica chromate ($SiO_2-O-CrO_2-O-SiO_2$) under mild and solvent-free conditions with moderate to good yields.

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The oxidation products were characterized by comparison of their spectral (IR, ^1H NMR, or ^{13}C NMR) and physical data with authentic samples.



Scheme 3

Preparation of Silica Chromate

A 500-mL suction flask was used. It was equipped with a constant pressure dropping funnel containing dichloro chromium oxide (23.2 g, 0.15 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution, i.e., water. It was charged with silica gel (100 g). Dichloro chromium oxide was added dropwise over a period of 20 min at room temperature. HCl gas evolved from the reaction vessel immediately (Scheme 1). After the addition was complete, the mixture was shaken for 90 min. A brown solid (silica chromate) was obtained quantitatively.[29]

Typical Procedure: Preparation of 1,1-Diacetoxy-1-(3-methylphenyl)-methane

In a round bottom flask, 3-methylbenzaldehyde (0.120 g, 1 mmol), acetic anhydride (0.102 g, 1 mmol), and silica chromate (1 mmol) were added. The mixture was stirred at room temperature for 20 min. The progress of the reaction was monitored by TLC using n-hexane and ethyl acetate (7:3) as an eluent. After completion of the reaction, diethyl ether was added to the mixture and filtered. The organic layer was washed with saturated $NaHCO_3$ (2 × 25 mL) and water (30 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated to give the pure 1,1-diacetoxy-1-(3-methylphenyl)-methane in 80% yield (0.177 g); colorless gummy oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 1H), 7.12 (m, 3H), 7.01 (s, 1H), 2.19 (s, 3H), 1.93 (s, 6H) ppm; IR (KBr): $\bar{\upsilon}$ = 2926, 1757, 1609, 1490, 1370, 1242, 1205, 791 cm^{-1}.

1,1-Diacetoxy-1-(2-methylphenyl)-methane. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 1H), 7.31 (d, 1H, J = 8 Hz), 7.05 (m, 3H), 2.26 (s, 3H) 1.93 (s, 6H) ppm; IR (KBr): $\bar{\upsilon}$ = 3100, 2890, 1750, 1619, 1442, 1371, 1247, 1215, 972, 967, 768 cm^{-1}.

1,1-Diacetoxy-1-(2,4-dichlorophenyl)-methane. Crystalline white solid, mp 118–120°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.32 (m, 3H), 1.95 (s, 6H) ppm; IR (KBr): $\bar{\upsilon}$ = 3010, 2883, 1751, 1609, 1373, 1196, 1017, 890 cm^{-1}.

1,1-Diacetoxy-1-(2,3-dichlorophenyl)-methane. Crystalline white solid, mp 78–79°C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.72$ (s, 1H), 7.07–7.59 (m, 3H), 1.95 (s, 6H) ppm; IR (KBr): $\bar{\upsilon} = 3012, 2893, 1748, 1429, 1375, 1219, 1031, 780$ cm^{-1}.

1,1-Diacetoxy-1-(2,3-dimethoxyphenyl)-methane. Crystalline white solid, mp 103–105°C ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.78$ (s, 1H), 6.75–6.91 (m, 3H), 3.70 (s, 6H), 3.67 (s, 6H), 1.91 (s, 6H) ppm; IR (KBr): $\bar{\upsilon} = 2938, 1753, 1602, 1488, 1452, 1369,1242, 1208, 1054, 1018, 964, 804$ cm^{-1}.

1,1-Diacetoxy-1-(4-N,N-dimethylaminophenyl)-methane. Colorless gummy oil; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.48$ (s,), 6.94–7.26 (m, 4H), 2.12 (s, 6H) 1.93 (s, 6H) ppm; IR (KBr): $\bar{\upsilon} = 3021, 2989, 1761, 1602, 1448, 1372, 1203, 1059, 1011, 805, 698$ cm^{-1}.

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