

## Conversion of Aldehydes to Acylals Using Acetic Anhydride in Presence of Catalytic Amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Under Solvent-Free Conditions at Room Temperature

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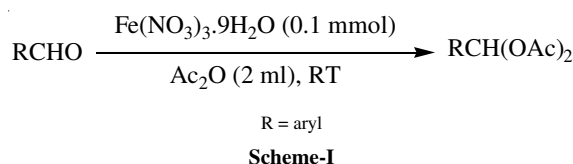
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$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  efficiently catalyzed the conversion of aromatic and aliphatic aldehydes to 1,1-diacetates under solvent-free conditions at room temperature. This study reports the use of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  which is highly efficient, chemoselective, eco-friendly non-toxic and cost effective catalyst for use in the conversion of aldehydes to acylals. Short reaction times and good yields are another advantages of this method. 4-Dimethylaminobenzaldehyde and ketones did not react under the same conditions.

**Key Words:** 1,1-Diacetates, Chemoselective, Efficient, Inorganic catalysts, Solvent-free.

### INTRODUCTION

Acylals have been used as protecting groups for carbonyl compounds because of their stability in neutral and basic media as well as aqueous acids<sup>1,2</sup>. The acylals are important starting materials for the synthesis of valuable intermediates in the Diels-Alder cycloaddition reactions<sup>3</sup>. Acylals have been applied as crosslinking reagents for cellulose in cotton<sup>4</sup>. Hence, there are considerable methods for synthesis of acylals. Some of the catalysts which have been developed for this purpose are including: sulfuric acid<sup>5a</sup>, triflic acid<sup>5b</sup>,  $\text{PCl}_3$ <sup>5c</sup>,  $\text{TMSCl-NaI}$ <sup>5d</sup>,  $\text{ZnCl}_2$ <sup>5e</sup>,  $\text{I}_2$ <sup>5f</sup>, anhydrous ferrous sulfate<sup>5g</sup>,  $\text{FeCl}_3$ <sup>5h</sup>,  $\text{NBS}$ <sup>5i</sup>, zeolites<sup>6a</sup>, sulfated zirconia<sup>6b</sup>, montmorillonite clay<sup>6c</sup>, expansive graphite<sup>6d</sup>, aluminum dodecatungstophosphate<sup>6e</sup>, zeolite HSZ-360<sup>6f</sup>, layered zirconium sulfophenyl phosphonate<sup>6g</sup>,  $\text{Cu}(\text{OTf})_2$  (2.5 mol %)<sup>7a</sup>,  $\text{Sc}(\text{OTf})_3$  (2 mol %)<sup>7b</sup>,  $\text{Bi}(\text{OTf})_3$  (0.1 mol %)<sup>7c</sup>,  $\text{Zn}(\text{BF}_4)_2$ <sup>7d</sup>,  $\text{ZrCl}_4$ <sup>7e</sup>, bismuth nitrate<sup>7f</sup>, ceric ammonium nitrate<sup>8</sup>,  $\text{NH}_2\text{SO}_3\text{H}$ <sup>9</sup>,  $\text{WCl}_6$ <sup>10</sup>,  $\text{LiBF}_4$ <sup>11</sup>,  $\text{LiBr}$ <sup>12</sup>, which are also efficient for this conversion. Many of the reported methods, however, involve strongly acidic or oxidising conditions, corrosive reagents, high temperature, high catalyst loading, longer reaction times. Moreover, some of these are not selective in terms of aldehydes and keto carbonyl functional groups. In view of these, the search for finding a cost effective, mild and simple selective protocol for synthesis of acylals from aldehydes is still relevant. In continuation of our research<sup>13</sup>, we herein report the results of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  catalyzed expedient, simple and cost effective, selective conversion of aldehydes to acylals (**Scheme-I**).



### EXPERIMENTAL

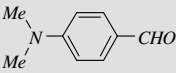
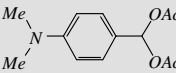
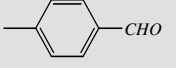
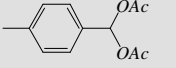
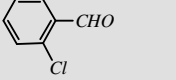
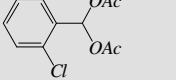
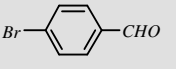
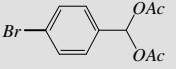
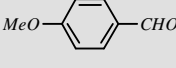
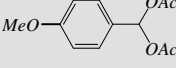
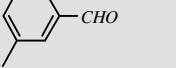
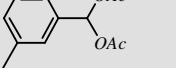
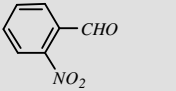
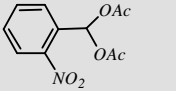
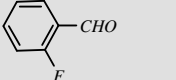
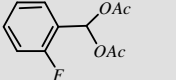
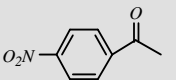
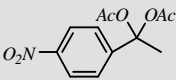
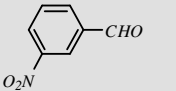
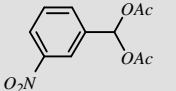
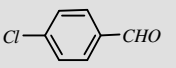
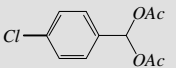
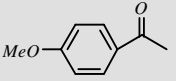
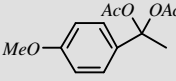
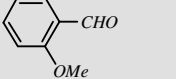
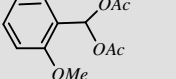
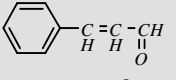
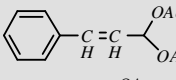
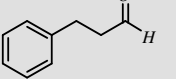
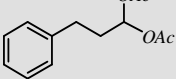
All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopy data (IR, <sup>1</sup>H NMR spectra). The spectra were measured in  $\text{CDCl}_3$  unless otherwise stated, relative to TMS (0.00 ppm).

**General procedure:** A mixture of aldehyde (1 mmol),  $\text{Ac}_2\text{O}$  (2 mL) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.1 mmol) was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was washed with a 10 % aqueous solution of NaOH, then washed with  $\text{Et}_2\text{O}$  and dried over  $\text{Na}_2\text{SO}_4$  and solvent was removed under reduced pressure. The resultant product was filtered through a column of silica gel to afford pure acylals.

### RESULTS AND DISCUSSION

The conversions of various aldehydes to their corresponding 1,1-diacetates (acylals) are presented in Table-1.

TABLE-1  
PREPARATION OF ACYLALS IN THE PRESENCE  
OF  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.1 mmol) AND ACETIC ANHYDRIDE  
(2 mL) UNDER SOLVENT-FREE CONDITIONS  
AT ROOM TEMPERATURE

| No. | Substrate   | Time (min) | Yield (%) <sup>a,b</sup> | Product   |
|-----|---|------------|--------------------------|---|
| 1   |    | 2880       | –                        |    |
| 2   |    | 420        | 70                       |    |
| 3   |    | 480        | 76                       |    |
| 4   |    | 90         | 86                       |    |
| 5   |    | 1440       | –                        |    |
| 6   |    | 5          | –                        |    |
| 7   |    | 1440       | –                        |    |
| 8   |   | 660        | 78                       |   |
| 9   |  | 2880       | –                        |  |
| 10  |  | 2880       | –                        |  |
| 11  |  | 180        | 66                       |  |
| 12  |  | 1440       | –                        |  |
| 13  |  | 960        | 79                       |  |
| 14  |  | 240        | 76                       |  |
| 15  |  | 5          | 79                       |  |

<sup>a</sup>Products were characterized by their physical constants, comparison with authentic samples and by their IR and NMR spectra. <sup>b</sup>Isolated yields.

### Spectral data

**Compound 2:** <sup>1</sup>H NMR (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta$  7.32 (s, 1H), 6.98-7.08 (dd, 4H), 2.05 (s, 3H), 1.79 (s, 6H). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3033, 2926, 1770, 1367, 1244, 1207, 1068, 1006, 959, 815, m.p. 80-82 °C, reported<sup>9</sup> m.p. 81-82 °C.

**Compound 3:** <sup>1</sup>H NMR (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta$  7.54-7.85 (m, 5H), 2.11 (s, 6H). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3055, 3025, 1767, 1621, 1495, 1201, 1012, 804, 762, 604, m.p. 51-52 °C, reported<sup>14</sup> m.p. 52-53 °C.

**Compound 4:** <sup>1</sup>H NMR (90 MHz, acetone- $d_6/\text{TMS}$ ):  $\delta$  7.61 (m, 5H), 2.10 (s, 6H). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3094, 1758, 1592, 1488, 1373, 1234, 1206, 942, 828, m.p. 94-96 °C, reported<sup>15</sup> m.p. 93-95 °C.

**Compound 8:** <sup>1</sup>H NMR (90 MHz, acetone- $d_6/\text{TMS}$ ):  $\delta$  7.91 (s, 1H) 7.19-7.54 (m, 4H), 2.11 (s, 6H). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2987, 2781, 1769, 1620, 1594, 1495, 1371, 1245, 1200, 1011, 805, 765.

**Compound 11:** <sup>1</sup>H NMR (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta$  7.33-7.55 (m, 5H), 2.03 (s, 6H). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3055, 2934, 1761, 1600, 1492, 1373, 1207, 1013, 943, 832, m.p. 81-83 °C, reported<sup>9</sup> m.p. 82-83 °C.

**Compound 13:** <sup>1</sup>H NMR (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta$  7.86 (s, 1H), 7.41 (d, 1H), 7.26 (t, 1H), 6.91 (t, 1H), 6.82 (d, 1H), 3.74 (s, 3H), 2.05 (s, 6H). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3010, 2967, 1761, 1602, 1495, 1372, 1238, 1200, 1021, 950, 758, m.p. 66-73 °C, reported<sup>16</sup> m.p. 73-74 °C.

**Compound 14:** <sup>1</sup>H NMR (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta$  7.20-7.80 (m, 6H), 6.92 (d, 1H), 6.33 (dd, 1H), 2.18 (s, 6H). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3083, 2972, 1750, 1678, 1380, 1248, 1198, 1058, 940, 747, 692, m.p. 84-85 °C, reported<sup>11</sup> m.p. 84-86 °C.

**Compound 15:** <sup>1</sup>H NMR (90 MHz, acetone- $d_6/\text{TMS}$ ):  $\delta$  7.23 (m, 5H), 6.78 (t, 1H), 2.73 (m, 2H), 2.01 (q, 8H). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3029, 2932, 2865, 1763, 1549, 1455, 1497, 1375, 1245, 1208, 1111, 1011, 946, 879, 756, 701.

Aldehydes having both electron withdrawing and electron-donating groups were acetylated without formation of any oxidative side products with 0.1 mmol of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as a catalyst (entry 2, 3, 4, 8, 11, 13). An unsaturated aldehyde (entry 14) was converted to the corresponding unsaturated acylal without affecting the double bond. Some aromatic ketones were also checked for the reaction: 4-nitroacetophenone and 4-methoxy acetophenone, they have not reacted under the described experimental conditions. Likewise, 4-dimethylaminobenzaldehyde failed to give the expected 1,1-diacetate. These reactions, in comparison with similar reactions, which have been performed in an autoclave at 150-200 °C in the presence of expensive and toxic catalysts, were occurred under milder reaction conditions. All the yields were calculated from crystallized products.

### Conclusion

An efficient and selective method is reported for the preparation of 1,1-diacetate from aldehyde under solvent free conditions using catalytic amounts of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The selectivity, cheapness, availability, low cost and no toxicity of the catalyst, easy and clean workup and good to high yields are noteworthy features of the reported method.

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