Efficient and Rapid Regioselective Deprotection of Isopropylidene Ketals

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A simple and efficient protocol is described for the regioselective hydrolysis of terminal isopropylidene ketal protection in carbohydrate derivatives **1a** – **11a**. It uses either $CoCl_2 \cdot 2H_2O$ in acetonitrile or $InCl_3$ in methanol at temperatures ranging from 50 to 60 °C. The low cost of $CoCl_2 \cdot 2H_2O$ along with its requirement in catalytic quantities offers a great advantage for the multi-gram scale reaction.

Key words: Isopropylidene Ketals, Regioselectivity, Carbohydrates, Deprotection, Hydrolysis

Isopropylidene ketals, commonly called acetonides, have been extensively used [1], particularly in the domain of carbohydrate chemistry for the protection of 1,2- and 1,3-diols. In a multi-step synthetic sequence, particularly with substrates having multiple acetonide protections, one often needs a selective hydrolysis of one acetonide over the other. Towards this end both Brønsted and Lewis acid based reagents have been reported wherein the less hindered terminal isopropylidene ketals have been selectively hydrolysed in the presence of an internal one. In the Brønsted acid class, aq HCl [2a], aq HBr [2b], aq AcOH [2c], 0.8% H_2SO_4 in MeOH [2d] and Dowex-H^+ in MeOH:H_2O (9:1) [2e] have been the frequent choice of reagents. In contrast to this, the use of Lewis acid based reagents has been scarce and limited to $FeCl_3 \cdot 6H_2O/SiO_2$ [3], $CuCl_2 \cdot 2H_2O$ in ethanol [4], $CeCl_3 \cdot 7H_2O$ [5] and $Zn(NO_3)_2 \cdot 6H_2O$ [6] or $Yb(OTf)_3 \cdot H_2O$ [7] in acetonitrile. While using the Brønsted acids strict control of the reaction parameters like pH of the medium and reaction periods becomes extremely crucial for high regioselectivity. Any negligence in reaction periods leads to further hydrolysis and subsequent problems of purification and diminished yield. In case of Lewis acids the situation is better. Besides the Lewis acidity of the metal ions, apparent *in situ* hydrolysis of the salt also provides the necessary protic medium for a valuable and useful synergistic effect at least in the case of cupric [4] and zinc ions [6].

At few occasions we found that long hours of stirring of substrate **1a** with $Zn(NO_3)_2 \cdot 6H_2O$ in acetonitrile for regioselective hydrolysis also caused hydrolysis of the second ketal function and also some undesired degradation. This could be probably due to higher acidic pH of the medium. At the first instance, this tempted the use of its congener in the same group, namely cadmium. However, the poor solubility of $CdSO_4 \cdot 8H_2O$ in acetonitrile as compared to $Zn(NO_3)_2 \cdot 6H_2O$ possibly precluded any reaction at room temperature. For promoting the solubility of the cadmium salt, it appeared that aqueous condition would be promising. High miscibility of water in THF at low concentration drew our attention to the THF/H_2O (9:1) system. However, once again no hydrolysis occurred at room temperature even with 1 equivalent of $CdSO_4 \cdot 8H_2O$ in THF/H_2O. Interestingly a clean reaction ensued as the temperature was raised to 50 °C. The efficacy of $CdSO_4 \cdot 8H_2O$ in THF/H_2O was general as can be seen from the results in the Table, but the known toxicity of cadmium justified a search for a safer alternative.

In this pursuit our attention was drawn to cobalt chloride. Cobalt(II) chloride in particular has attracted the attention of synthetic organic chemists in the last few years [8] because of the fact that it essentially operates under near neutral conditions. It has been recently used to catalyze acylation [9], tosylation [10], chemoselective acetal formation [11] and thioacetalization of aldehydes [12]. Realizing the fact that mildness of the reaction conditions is extremely important during selective removal of terminal isopropylidene protections particularly in substrates containing other functionalities and obtained through multi-step synthetic sequence, we decided to explore the possible use of cobalt(II) chloride. We found no precedence in the literature towards such an attempt.

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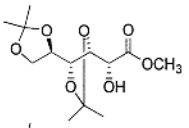
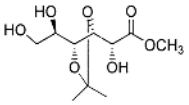
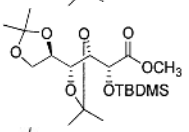
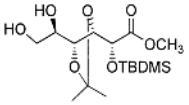
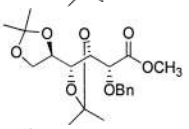
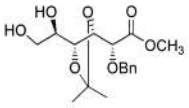
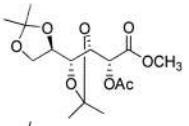
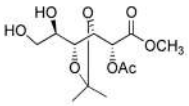
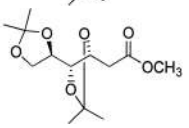
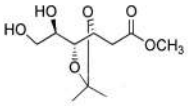
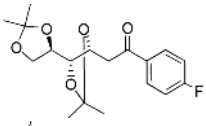
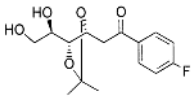
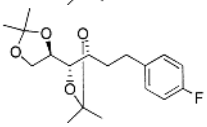
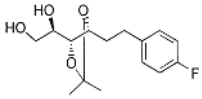
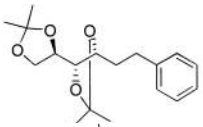
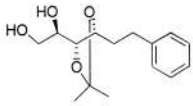
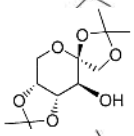
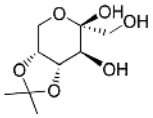
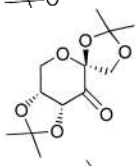
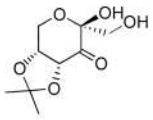
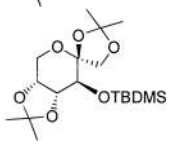
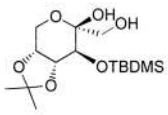
Table 1. Regioselective deprotection of isopropylidene ketals using $CdSO_4 \cdot 8H_2O$, $CoCl_2 \cdot 2H_2O$ and anhydrous $InCl_3$.

Compound	Substrate **1 – 11a**	Product **1 – 11b**	Hydrolysis Condition[a] Method	Time (h)	Yield (%)[b]
1			A	8	80
			B	6	91
			C	10	85
2			A	10	76
			B	8	89
			C	12	85
3			A	6	76
			B	8	91
			C	10	80
4			A	8	75
			B	6	86
			C	12	80
5			A	7	78
			B	6	93
			C	12	82
6			A	8	78
			B	6	90
			C	10	82
7			A	10	78
			B	8	92
			C	12	80
8			A	10	75
			B	8	82
			C	12	78
9			A	8	76
			B	6	90
			C	12	80
10			A	8	75
			B	7	90
			C	12	78
11			A	10	75
			B	7	88
			C	12	76

[a] Method A: $CdSO_4 \cdot 8H_2O$ in THF/H_2O at 50 °C; Method B: $CoCl_2 \cdot 2H_2O$ in acetonitrile at 55 °C; Method C: $InCl_3$ in methanol at 60 °C; [b] isolated yields of pure products with compatible IR, ^1H NMR, ^{13}C NMR and mass spectral data.

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Commercially available magenta colored $CoCl_2 \cdot 6H_2O$ itself was found to be unsuitable for hydrolysis. Thermo-gravimetric analysis (TGA) of this sample reflected loss of the absorbed moisture along with four molecules of H_2O from the crystal lattice when the temperature was around 185 °C. Heating of this commercial hexahydrate sample at 200 °C for 4 h consistently afforded a blue colored salt whose composition was $CoCl_2 \cdot 2H_2O$. The confirmation to this composition comes from the powder XRD pattern [13]. We were delighted to see that 10 mol% of this cobalt(II) chloride dihydrate with respect to substrate in acetonitrile at 55 °C was sufficient for a clean, rapid and efficient regioselective removal of terminal isopropylidene ketal in all the substrates **1a** – **11a** (Table). A solution of $CoCl_2 \cdot 2H_2O$ in acetonitrile (0.033 M) had a pH of 4.4 and this itself was indicative of the mildness of the protocol herein for selective removal of the terminal acetonides, as compared to $Zn(NO_3)_2 \cdot 6H_2O$. In the latter case the solution is more acidic, with pH being 2.76. It was further noted that even anhydrous $CoCl_2$ in commercial grade acetonitrile was excellent for the proposed objective. We speculate that the occluded moisture in the solvent was sufficient for the observed clean removal of the terminal isopropylidene protection.

The concept of transketalization is extremely useful, when aqueous conditions are to be avoided. Towards this end a combination of alcohol or thiol with anhydrous Brønsted acid such as PPTS, or TsOH have been used [14, 15]. Thiols have also been used along with Lewis acid such as $BF_3 \cdot Et_2O$ [16]. Although $InCl_3$ has been used for the same purpose [17], its use for deprotection of acetals in methanol is only a very recent advent [18]. Our present study aiming at regioselective removal of terminal acetonide prompted its exploration and to our satisfaction clean reaction ensued with all the substrates **1a**-**11a** using 10 mol% of $InCl_3$ in methanol at 60 °C.

In conclusion, the use $CoCl_2 \cdot 2H_2O$ and $InCl_3$ has offered a simple, efficient and clean procedure for regioselective removal of terminal isopropylidene protection. The isolated yields are excellent and the reaction is amenable to scale-up. The more attractive among the two is $CoCl_2 \cdot 2H_2O$, due to its extremely low cost and requirement in catalytic quantities. This is of great significance in the light of the fact that $Yb(OTf)_3 \cdot H_2O$ recently used for the same purpose is comparatively very expensive. These new protocols should therefore serve as valuable alternatives, in cases of problematic situations encountered with the other known reagents in the literature.

Experimental Section

The starting substrates **2a** [19], **3a** [20], **4a** [21] and **5a** [22] were prepared from **1a** [23] as described in the literature. The aryl ketone **6a** was prepared by an umpolung strategy [24], wherein the acyl-anion equivalent reacts with diisopropylidene protected arabinitol iodide [25]. Substrate **7a** and **8a** were prepared by sequential reduction and hydrogenation of the corresponding *p*-fluorophenyl ketone **6a** and phenyl ketone [26], respectively. Substrates **9a** and **10a** were prepared from *D*-fructose as described in the literature [27]. Silylation of **9a** using TBDMSiCl/imidazole in DMF afforded **11a**.

General experimental procedure using $CdSO_4 \cdot 8H_2O$: A mixture of isopropylidene ketals (**1 – 11a**) (1 mmol) and $CdSO_4 \cdot 8H_2O$ (1.1 mmol, 0.846 g) in THF/H_2O (9:1) was stirred at 50 °C for 6 – 8 h. After completion of the reaction as indicated by TLC, the THF was evaporated, the oily residue was diluted with water and the crude product was extracted by using CH_2Cl_2 (3 × 10 ml). The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4 and concentrated. The residue obtained was subjected to a quick purification by a short filtration column on silica gel (100 – 200 mesh).

General experimental procedure using $CoCl_2 \cdot 2H_2O$: A mixture of isopropylidene ketals (**1 – 11a**) (1 mmol) and 10 mol% (0.016 g) of $CoCl_2 \cdot 2H_2O$ in acetonitrile (3 ml) [0.33 M with respect to substrate] was stirred at 55 °C for 6 – 8 h. After completion of the reaction as indicated by TLC, the solvent was evaporated, CH_2Cl_2 (3 × 10 ml) was added to the oily residue and this solution was washed with water (5 ml). The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4 and concentrated. The residue obtained was subjected to a quick purification by a short filtration column on silica gel (100 – 200 mesh).

General experimental procedure using $InCl_3$: To a mixture of isopropylidene ketals (**1 – 11a**) (1 mmol) in methanol was added 10 mol% (0.022 g) of anhydrous $InCl_3$ and the solution was heated at 60 °C for 10 – 12 h. After completion of the reaction as indicated by TLC, the solvent was evaporated, the oily residue was diluted with water, the crude product was extracted by using CH_2Cl_2 (3 × 10 ml). The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4 and concentrated. The residue obtained was subjected to a quick purification by a short filtration column on silica gel (100 – 200 mesh).

Spectral data for the starting substrates **6a**, **7a**, **8a** *and* **11a**

6a: $[\alpha]_D + 40.2°$ (c = 1, $CHCl_3$). – IR ($CHCl_3$): 1675 cm^{-1}. – ^1H NMR (400 MHz $CDCl_3$): δ = 1.25 (s, 3H), 1.28 (s, 3H), 1.31 (s, 3H), 1.41 (s, 3H), 3.30 (d, J = 8.2 Hz, 1H), 3.61 – 3.83 (m, 4H), 4.54 (dd, J = 8.4,

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4.8 Hz, 1H), 7.0 – 7.1 (m, 2H), 7.91 – 7.99 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.24, 25.31, 25.46, 26.74, 41.27, 71.38, 74.07, 74.98, 78.94, 107.72, 109.61, 113.92, 129.45, 131.38, 165.54, 195.49. – HRMS (ESI): calcd. for $C_{18}H_{23}FO_5$ [M+Na]$^+$: 361.1224; found 361.1216.

7a: $[\alpha]_D$ + 45.2° (c = 1, $CHCl_3$). – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.31 (s, 3H), 1.38 (s, 3H), 1.41 (s, 3H), 1.42 (s, 3H), 1.83 – 1.89 (m, 1H), 1.95 – 2.03 (m, 1H), 2.68 – 2.73 (m, 1H), 2.80 – 2.85 (m, 1H), 3.61 – 3.83 (m, 4H), 3.94 – 4.02 (m, 1H), 6.94 – 7.00 (m, 2H), 7.14 – 7.20 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.46, 26.74, 27.03, 27.36, 31.47, 35.83, 63.82, 72.46, 78.38, 81.04, 107.70, 108.92, 115.176, 129.779, 137.31, 160.05. – HRMS (ESI): calcd. for $C_{18}H_{25}FO_4$ [M+Na]$^+$: 347.1431; found 347.1412.

8a: $[\alpha]_D$ − 27.3° (c = 1, $CHCl_3$). – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.25 (s, 3H), 1.28 (s, 3H), 1.32 (s, 3H), 1.36 (s, 3H), 1.79 – 1.82 (m, 1H), 1.93 – 2.03 (m, 1H), 2.64 – 2.73 (m, 1H), 2.79 – 2.85 (m, 1H), 3.60 – 3.70 (m, 4H), 3.92 – 4.02 (m, 1H), 7.09 – 7.23 (m, 5H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.31, 26.74, 27.06, 27.41, 32.30, 35.79, 63.80, 72.40, 78.48, 81.15, 108.90, 109.61, 125.87, 128.37, 128.42, 141.76. – HRMS (ESI): calcd. for $C_{18}H_{26}O_4$ [M+Na]$^+$ 329.1525; found 329.1053.

11a: $[\alpha]_D$ − 126.5° (c = 1, $CHCl_3$). – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.25 (s, 3H), 1.28 (s, 3H), 1.32 (s, 3H), 0.86 (s, 3H), 0.90 (s, 3H), 1.67 (s, 9H), 2.09 (s, 3H), 2.16 (s, 3H), 3.11 (br s, 1H), 3.37 (br s, 1H), 4.30 – 5.10 (m, 7H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = −3.93, −3.08, 19.02, 25.31, 26.62, 26.74, 27.07, 27.46, 64.40, 70.59, 71.01, 72.36, 72.49, 106.80, 109.42, 112.55. – HRMS (ESI): calcd. for $C_{18}H_{34}O_6Si$ [M+Na]$^+$: 397.1819; found 397.1026.

Data for the new compounds obtained after regioselective deprotection

5b: $[\alpha]_D$ + 57.3° (c = 1, $CHCl_3$). – IR ($CHCl_3$): 3456, 1737 cm^{-1}. – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.31 (s, 3H), 1.33 (s, 3H), 2.58 (dd, J = 15.6, 8.8 Hz, 1H), 2.77 (dd, J = 15.9, 3.25 Hz, 1H), 3.59 (t, J = 7.8 Hz, 1H), 3.72 (s, 3H), 3.95 (dd, J = 8.8, 4.9 Hz, 1H), 4.34 (m, 1H), 4.53 (dd, J = 8.5, 6.1 Hz, 1H), 4.70 (td, J = 8.3, 2.9 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.96, 29.07, 38.97, 52.00, 63.92, 73.04, 76.10, 79.54, 172.0. – HRMS (ESI): calcd. for $C_9H_{18}O_6$ [M+Na]$^+$: 245.1000; found 245.1012.

6b: $[\alpha]_D$ + 12.2° (c = 1, $CHCl_3$). – IR ($CHCl_3$): 3456, 1676 cm^{-1}. – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.28 (s, 3H), 1.31 (s, 3H), 3.30 (d, J = 8.2 Hz, 1H), 3.61 – 3.83 (m, 4H), 4.54 (dd, J = 8.4, 4.8 Hz, 1H), 7.0 – 7.1 (m, 2H), 7.91 – 7.99 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.24, 25.46, 41.27, 71.38, 74.07, 74.98, 78.94, 107.72, 113.92, 129.45, 131.38, 165.54, 195.49. – HRMS (ESI): calcd. for $C_{15}H_{19}FO_5$ [M+Na]$^+$: 321.1224; found 321.1216.

7b: $[\alpha]_D$ + 15.2° (c = 1, $CHCl_3$). – IR ($CHCl_3$): 3425 cm^{-1}. – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.38 (s, 3H), 1.42 (s, 3H), 1.83 – 1.89 (m, 1H), 1.95 – 2.03 (m, 1H), 2.68 – 2.73 (m, 1H), 2.80 – 2.85 (m, 1H), 3.61 – 3.83 (m, 4H), 3.94 – 4.02 (m, 1H), 6.94 – 7.00 (m, 2H), 7.14 – 7.20 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.03, 27.36, 31.47, 35.83, 63.82, 72.46, 78.38, 81.04, 108.92, 115.176, 129.779, 137.31, 160.05. – HRMS (ESI): calcd. for $C_{15}H_{21}FO_4$ [M+Na]$^+$: 307.1431; found 307.1412.

8b: $[\alpha]_D$ − 27.3° (c = 1, $CHCl_3$). – IR ($CHCl_3$): 3424 cm^{-1}. – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.32 (s, 3H), 1.36 (s, 3H), 1.79 – 1.82 (m, 1H), 1.93 – 2.03 (m, 1H), 2.64 – 2.73 (m, 1H), 2.79 – 2.85 (m, 1H), 3.60 – 3.70 (m, 4H), 3.92 – 4.02 (m, 1H), 7.09 – 7.23 (m, 5H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.06, 27.37, 32.30, 35.79, 63.80, 72.40, 78.48, 81.15, 108.92, 125.87, 128.37, 128.42, 141.76. – HRMS (ESI): calcd. for $C_{15}H_{22}O_4$ [M+Na]$^+$: 289.1525; found 289.1053.

9b: $[\alpha]_D$ − 103.5° (c = 1, $CHCl_3$). – IR ($CHCl_3$): 3440 cm^{-1}. – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.36 (s, 3H), 1.41 (s, 3H), 3.10 (br s, 1H), 3.46 (br s, 1H), 3.67 – 4.12 (m, 7H), 4.44 (br s, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.23, 26.41, 64.15, 68.75, 69.34, 71.82, 71.89, 105.79, 111.95. – HRMS (ESI): calcd. for $C_9H_{16}O_6$ [M+Na]$^+$: 243.0954; found 243.0284.

10b: $[\alpha]_D$ − 35.30° (c = 1, $CHCl_3$). – IR ($CHCl_3$): 3392, 1744 cm^{-1}. – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.32 (s, 3H), 1.47 (s, 3H), 3.10 (br s, 1H), 3.46 (br s, 1H), 3.75 – 4.81 (m, 6H), 4.44 (br s, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.13, 26.28, 63.27, 69.50, 73.54, 74.16, 104.33, 113.52, 198.95. – HRMS (ESI): calcd. for $C_9H_{14}O_6$ [M+Na]$^+$: 241.0797; found 241.0147.

11b: $[\alpha]_D$ − 106.5° (c = 1, $CHCl_3$). – ^{1}H NMR (400 MHz $CDCl_3$): δ = 1.32 (s, 3H), 0.86 (s, 3H), 0.90 (s, 3H), 1.67 (s, 9H), 2.09 (s, 3H), 2.16 (s, 3H), 3.11 (br s, 1H), 3.37 (br s, 1H), 4.30 – 5.10 (m, 7H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = −3.93, −3.08, 19.02, 26.62, 27.07, 27.46, 64.40, 70.59, 71.01, 72.36, 72.49, 106.80, 112.55. – HRMS (ESI): calcd. for $C_{15}H_{30}O_6Si$ [M+Na]$^+$: 357.1819; found 357.1026.

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