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Note

Efficient and selective removal of chloroacetyl group promoted with tetra-*n*-butylammonium fluoride (TBAF)

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ABSTRACT

A practical method for the efficient and selective cleavage of chloroacetyl protecting group using tetra-*n*-butylammonium fluoride (TBAF) in THF solution at rt was disclosed.

The chloroacetyl (ClAc) group was widely used as temporary protecting group in carbohydrate chemistry. It could be orthogonally compatible with other acyl protecting groups, such as acetyl, benzoyl, pivaloyl, and levulinoyl.[1] The frequently-used regent for cleaving chloroacetyl group is thiourea.[2] Other highly selective and efficacious dechloroacetylation regents, such as hydrazine dithiocarbonate (HDTC),[3] diazabicyclo[2.2.2]octane (DABCO),[4] 1-selenocarbamoylpiperidine,[5] and sodium borohydride ($NaBH_4$)[6] were increasingly developed in recent years. Nevertheless, these regents have their own deficiencies which potentially impede its broad application in the dechloroacetylation reaction. For instance, thiourea-promoted cleavage of ClAc group demands relatively harsh reflux conditions and long reaction time, and occasionally gives rise to acyl group migration.[7] The poor chemical stability of HDTC requires its usage immediately after fresh preparation. The application of DABCO was limited by the reaction media which was solely confined to alcoholic solvents. The recently reported 1-selenocarbamoylpiperidine exhibited high chemoselectivity and broad tolerance of reaction solvents in dechloroacetylation, but it is also subject to the laborious preparation of selenourea intermediate and high reaction temperature. The reductive ability of sodium borohydride would potentially hinder its application in carbohydrate chemistry. Thus, mild and easily handling method for highly chemoselective cleavage of chloroacetyl group deserves further exploitation.

Tetra-*n*-butylammonium fluoride (TBAF) has been widely used in organic synthesis[8–11] as an activator for O-acylation and N-alkylation,[12,13] nitro-aldol formation,[14] Dieckmann-type cyclization,[15] and palladium-catalyzed Sonogashira reaction.[16,17] More importantly, it served as a specific regent for the efficient cleavage of various silyl protecting groups, including *tert*-butyldimethylsilyl (TBDMS),[18] *tert*-butyldiphenylsilyl (TBDPS),[19] and triisopropylsilyl (TIPS)[20] groups. TBAF-promoted unusual cleavage of carbamate and benzoyl in THF or DMF solution has also been observed.[21–24] In this study, we present a novel application of TBAF for the efficient and selective cleavage of chloroacetyl protecting group from various organic substrates.

In an attempt to selectively remove TBDMS protecting group from isopropyl 4-*O*-benzoyl-3-*O*-*tert*-butyldimethylsilyl-2-*O*-chloroacetyl-1-thio-α-L-rhamnopyranoside (**1**)[25] with commercially available 1 M TBAF solution in THF at rt, we surprisingly found that the ClAc group on C-2 was also efficiently cleaved and the corresponding 2,3-diol **2** was obtained in 90% isolated yield (Table 1, entry 1). This finding encouraged us to investigate the application and scope of TBAF-promoted dechloroacetylation by utilizing a diverse range of substrates which have ClAc protecting group in different chemical environments (Table 1). The experimental results demonstrated that this new method was effective to most of the substrates and the reaction finished in 2 h. Protecting groups, such as acetyl, benzoyl, benzyl, benzylidene, isopropylidene, and trityl group, were compatible under cleavage reaction conditions; whereas, as previously reported,[18,23] the silyl ether and base-labile fluorenylmethyloxycarbonyl (Fmoc) group were simultaneously removed with ClAc group (entries 1 and 6).

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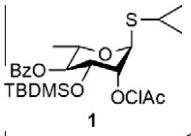
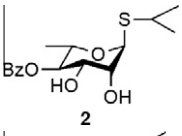
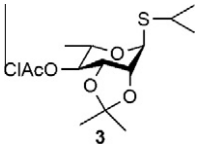
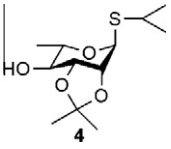
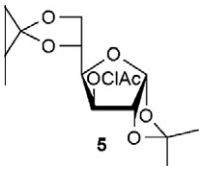
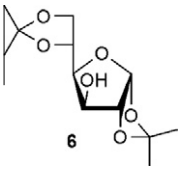
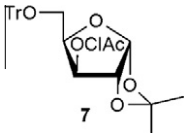
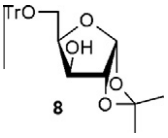
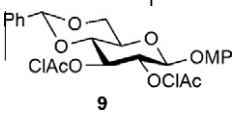
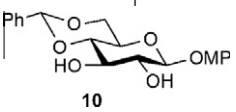
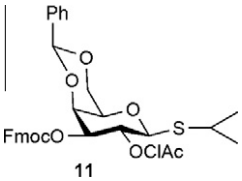
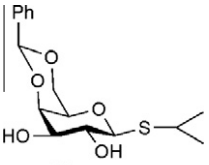
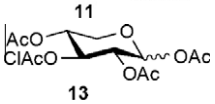
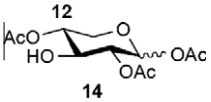
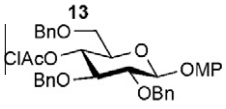
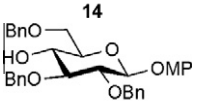
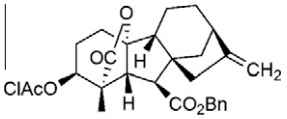
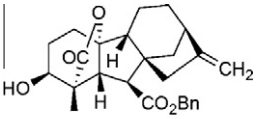
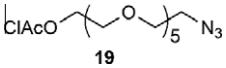
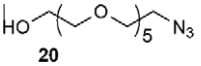
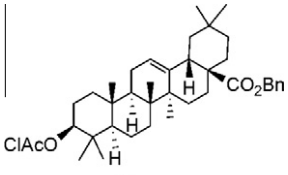
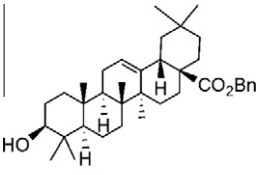
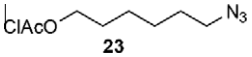
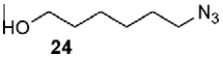
Table 1
TBAF-promoted cleavage of chloroacetyl protection group in THF

Entry	Substrate[a]	Product	Time (h)	Yield[b] (%)
1	 **1**	 **2**	1.0	90
2	 **3**	 **4**	2.0	93
3	 **5**	 **6**	2.0	92
4	 **7**	 **8**	1.0	94
5	 **9**	 **10**	2.0	87
6	 **11**	 **12**	1.5	90
7	 **13**	 **14**	1.0	84
8	 **15**	 **16**	2.0	91
9	 **17**	 **18**	2.5	83
10	 **19**	 **20**	1.0	78
11	 **21**	 **22**	4.0	50[c]
12	 **23**	 **24**	12	38

[a] MP: 4-methoxyphenyl; Tr: triphenylmethyl.
[b] Isolation yield.
[c] Decomposition with prolonged reaction time.

Moreover, subjection of the protected sugar derivatives **1**, **3**, **5**, **7**, **9**,[26] **11**, **13**, and **15** to this method afforded the products **2**, **4**,[27] **6**,[28] **8**,[29] **10**,[30] **12**,[31] **14**,[32] and **16**,[33,34] respectively, in high yields and excellent selectivities (entries 1–8). Furthermore, the different cleavage efficiencies were also observed for the non-carbohydrate derivatives. Dechloroacetylation of gibberellin derivative **17** and

hexaethylene glycol azide derivative **19** afforded the desired product **18**[35] and **20**[36] in the good yields of 83% and 78%, respectively (entries 9 and 10). The 3-*O*-chloroacetyl ursolic acid benzyl ester **21** furnished the product **22**[37] in moderate yield (entry 11), while the chloroacetylated 6-azido-1-hexanol **23** produced **24**[38,39] only in the yield of 38% with prolonged reaction time over 12 h (entry 12). We ascribed this efficiency differences to the substrate solubility effect[40] and/or the inductive electron-attractive effect[41,42] from oxygen atoms in the substrates, and it could be triggered by a nucleophilic attacking of fluoride anion to the carboxyl group.[21]

In summary, a highly efficient method for dechloroacetylation of various sugar substrates with TBAF has been developed. The mild reaction conditions, experimental simplicities, and excellent yields are major advantages of this new method. We believe that this method has potential applications in orthogonal protection–deprotection manipulation for oligosaccharide synthesis.

1. Experimental

1.1. General methods

Optical rotations were determined at 25 °C with a WZZ-2S automatic polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker 400 and 600 spectrometers for solutions in $CDCl_3$. Chemical shifts are given in ppm downfield from internal Me_4Si. Thin-layer chromatography (TLC) was performed on silica gel HF_{254} with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by a UV detector.

1.2. General procedure for TBAF-promoted dechloroacetylation

To a solution of the chloroacetylated substrate (0.1 mmol) in THF (4 mL) was added 1 M TBAF solution in THF (2.0 equiv per ClAc) at rt. The reaction mixture was stirred at conditions mentioned in Table 1, and then concentrated under reduced pressure. The corresponding residue was diluted with EtOAc (15 mL), washed by H_2O and brine. The organic phase was dried over Na_2SO_4, concentrated, and the resulting residue was purified on column chromatography to yield the desired product (see Table 1).

1.3. General procedure for preparation of the chloroacetylated substrates

To a solution of the corresponding hydroxyl group of various substrates (0.2 mmol) in pyridine/CH_2Cl_2 (v/v 1:1, 6 mL) at 0 °C was added chloroacetic anhydride (1.2 equiv). The reaction mixture was stirred under these conditions until TLC indicated the completion of the reaction. The reaction mixture was diluted with CH_2Cl_2 (20 mL), and then washed by 1 M HCl, saturated aqueous $NaHCO_3$ and brine, respectively. The organic phase was dried over Na_2SO_4, concentrated and purified by column chromatography using ethyl acetate–petroleum ether as the eluents to furnish the chloroacetylated product in high yield.

1.4. Characteristic data of new compounds

1.4.1. Isopropyl 4-*O*-benzoyl-1-thio-α-L-rhamnopyranoside (2)

Yield: 90%; $[\alpha]_D$ −135 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz): δ 8.08–7.45 (m, 5H, *Ph*), 5.41 (d, 1H, *J* 1.0 Hz, H-1), 5.04 (t, 1H, *J* 9.4 Hz, H-4), 4.42–4.36 (m, 1H, H-5), 4.11–4.07 (m, 1H, H-2), 4.02–3.96 (m, 1H, H-3), 3.27 (d, 1H, *J* 5.4 Hz, –O*H*), 3.13–3.07 (m, 1H, C*H*$(CH_3)_2$), 2.76 (d, 1H, *J* 3.6 Hz, –O*H*), 1.36, 1.35 (2d, 2 × 3H, *J* 6.8 Hz, CH$(CH_3)_2$), 1.30 (d, 3H, *J* 6.2 Hz, H-6); Anal. Calcd for $C_{16}H_{22}O_5S$: C, 58.87; H, 6.79. Found: C, 58.95; H, 6.58.

1.4.2. Isopropyl 4-*O*-chloroacetyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (3)

Yield: 96%; $[\alpha]_D$ −49 (*c* 4.0, $CHCl_3$); ^{1}H NMR (600 MHz): δ 5.60 (s, 1H, H-1), 4.96 (dd, 1H, *J* 10.0, 7.8 Hz, H-4), 4.20 (d, 1H, *J* 5.2 Hz, H-2), 4.19–4.14 (m, 2H, H-3, H-5), 4.12, 4.09 (2d, 2 × 1H, ClC*H*$_2$CO), 3.09–3.03 (m, 1H, C*H*$(CH_3)_2$), 1.58, 1.34 (2s, 2 × 3H, C$(CH_3)_2$), 1.35, 1.30 (2d, 2 × 3H, *J* 6.8 Hz, CH$(CH_3)_2$), 1.18 (d, 3H, *J* 6.3 Hz, H-6); ^{13}C NMR (150 MHz): δ 166.6, 109.9, 79.3, 77.1, 77.0, 75.2, 64.2, 40.8, 34.9, 27.7, 26.5, 23.4, 23.2, 16.8; Anal. Calcd for $C_{14}H_{23}ClO_5S$: C, 49.62; H, 6.84. Found: C, 49.87; H, 6.75.

1.4.3. 3-*O*-Chloroacetyl-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (5)

Yield: 93%; $[\alpha]_D$ −24 (*c* 10, $CHCl_3$); ^{1}H NMR (600 MHz): δ 5.88 (d, 1H, *J* 3.6 Hz, H-3), 5.32 (d, 1H, *J* 1.9 Hz, H-1), 4.52 (d, 1H, *J* 3.6 Hz, H-4), 4.22–4.18 (m, 2H), 4.12–4.06 (m, 3H), 4.00–3.97 (m, 1H), 1.51, 1.39, 1.30 (3s, 4 × 3H, 2C$(CH_3)_2$); ^{13}C NMR (150 MHz): δ 166.0, 112.4, 109.4, 105.0, 83.1, 79.7, 77.6, 72.2, 67.3, 40.6, 26.8, 26.6, 26.2, 25.2; Anal. Calcd for $C_{14}H_{21}ClO_7$: C, 49.93; H, 6.29. Found: C, 49.81; H, 6.44.

1.4.4. 3-*O*-Chloroacetyl-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (7)

Yield: 88%; $[\alpha]_D$ −16 (*c* 10, $CHCl_3$); ^{1}H NMR (600 MHz): δ 7.44–7.27 (m, 15H, *Ph*), 5.91 (d, 1H, *J* 3.6 Hz, H-3), 5.48 (d, 1H, *J* 2.8 Hz, H-1), 4.56 (m, 1H, H-4), 4.53 (d, 1H, *J* 3.6 Hz, H-2), 3.80, 3.66 (2d, 2 × 1H, *J* 14.4 Hz, ClC*H*$_2$CO), 3.55 (dd, 1H, *J* 9.0, 5.2 Hz, H-5a), 3.21 (t, 1H, *J* 9.0 Hz, H-5b), 1.60, 1.35 (2s, 2 × 3H, C$(CH_3)_2$); ^{13}C NMR (150 MHz): δ 165.9, 143.4, 128.6, 127.8, 127.2, 112.3, 104.7, 86.9, 83.1, 77.8, 77.4, 59.9, 40.3, 26.7, 26.2; Anal. Calcd for $C_{29}H_{29}ClO_6$: C, 68.43; H, 5.74. Found: C, 68.57; H, 5.91.

1.4.5. Isopropyl 4,6-*O*-benzylidene-2-*O*-chloroacetyl-3-*O*-fluorenylmethyloxycarbonyl-1-thio-β-D-galactopyranoside (11)

Yield: 90%; $[\alpha]_D$ +33 (*c* 6.0, $CHCl_3$); ^{1}H NMR (400 MHz): δ 7.74–7.20 (m, 13H, *Ph*), 5.55 (t, 1H, *J* 9.9 Hz, H-2), 5.49 (s, 1H, PhC*H*), 4.89 (dd, 1H, *J* 9.9, 3.5 Hz, H-3), 4.56 (d, 1H, *J* 9.9 Hz, H-1), 4.47 (d, 1H, *J* 3.5 Hz, H-4), 4.34–4.28 (m, 3H, H-6a, C*H*$_2$ of Fmoc), 4.24 (t, 1H, *J* 7.4 Hz, C*H* of Fmoc), 4.03 (s, 2H, ClC*H*$_2$CO), 3.99 (d, 1H, *J* 12.5 Hz, H-6b), 3.50 (s, 1H, H-5), 3.31–3.27 (m, 1H, C*H*$(CH_3)_2$), 1.38, 1.27 (2d, 2 × 3H, *J* 6.6 Hz, C$(CH_3)_2$); ^{13}C NMR (100 MHz): δ 165.9, 154.3, 143.1, 141.3, 137.4, 129.2, 128.2, 127.9, 127.3, 127.2, 126.4, 125.3, 125.2, 120.1, 101.1, 82.8, 76.4, 73.4, 70.4, 69.7, 69.0, 68.8, 65.6, 46.6, 40.7, 34.9, 24.8, 23.6; Anal. Calcd for $C_{33}H_{33}ClO_8S$: C, 63.40; H, 5.32. Found: C, 63.67; H, 5.03.

1.4.6. 1,2,4-Tri-*O*-acetyl-3-*O*-choroacetyl-D-xylopyranose (13)

Yield: 95%; $[\alpha]_D$ +21 (*c* 5.0, $CHCl_3$); ^{1}H NMR (400 MHz): δ 6.27 (d, 0.5H, *J* 3.6 Hz, H-1α), 5.72 (d, 0.5H, *J* 7.1 Hz, H-1β), 5.51 (t, 0.5H, *J* 9.9 Hz, H-3α), 5.27 (t, 0.5H, *J* 8.5 Hz, H-3β), 5.11–4.99 (m, 2H, H-2, 4), 4.16 (dd, 0.5H, *J* 12.0, 5.1 Hz, H-5aα), 4.02 (s, 2H, ClC*H*$_2$CO), 3.95 (dd, 0.5H, *J* 11.2, 6.0 Hz, H-5aβ), 3.72 (t, 0.5H, *J* 11.2 Hz, H-5bβ), 3.54 (dd, 0.5H, *J* 12.0, 8.7 Hz, H-5bα), 2.19, 2.11, 2.07, 2.06, 2.05, 2.03 (6s, 6 × 1.5H, 3Ac); ^{13}C NMR (100 MHz): δ 169.7, 169.6, 169.3, 169.0, 168.9, 168.8, 166.8, 166.5, 92.0, 89.1, 73.1, 71.4, 69.4, 69.1, 68.4, 68.1, 62.8, 60.5, 40.4, 20.8, 20.7, 20.6, 20.5, 20.4, 20.3; Anal. Calcd for $C_{13}H_{17}ClO_9$: C, 44.27; H, 4.86. Found: C, 44.11; H, 5.04.

1.4.7. 4-Methoxyphenyl 2,3,6-tri-*O*-benzyl-4-*O*-chloroacetyl-β-D-glucopyranoside (15)

Yield: 84%; $[\alpha]_D$ −13 (*c* 9, $CHCl_3$); ^{1}H NMR (600 MHz): δ 7.41–7.27 (m, 15H, *Ph*), 7.08, 6.86 (2d, 2 × 2H, *J* 9.0 Hz, *Ph*), 5.12 (t, 1H, *J* 9.6 Hz, H-4), 5.07, 4.87 (2d, 2 × 1H, *J* 10.9 Hz, C*H*$_2$Ph), 4.93 (d, 1H, *J* 7.8 Hz, H-1), 4.90, 4.67 (2d, 2 × 1H, *J* 11.6 Hz, C*H*$_2$Ph), 4.53, 4.50 (2d, 2 × 1H, *J* 11.9 Hz, C*H*$_2$Ph), 3.81–3.78 (m, 4H), 3.71 (t,

1H, *J* 9.0 Hz), 3.69–3.63 (m, 2H), 3.62–3.58 (m, 3H); ^{13}C NMR (150 MHz): δ 166.2, 155.5, 151.3, 118.5, 114.6, 102.7, 81.9, 75.3, 75.2, 73.7, 73.0, 72.5, 69.6, 65.5, 55.6; Anal. Calcd for $C_{36}H_{37}ClO_8$: C, 68.29; H, 5.89. Found: C, 68.06; H, 5.73.

1.4.8. Compound 17

Yield: 87%; $[\alpha]_D$ +8 (*c* 5.0, $CHCl_3$); ^{1}H NMR (400 MHz): δ 7.36–7.33 (m, 5H, *Ph*), 5.16, 5.12 (2d, 2 × 1H, *J* 12.2 Hz, C*H*$_2$Ph), 5.02 (br s, 1H), 4.96 (s, 1H), 4.80 (s, 1H), 4.08, 4.04 (2d, 2 × 1H, *J* 14.4 Hz, ClC*H*$_2$CO), 3.15 (d, 1H, *J* 10.8 Hz), 2.72 (d, 1H, *J* 10.8 Hz), 2.62 (br t, 1H, *J* 6.4 Hz), 1.02 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz): δ 176.4, 172.1, 166.6, 156.5, 135.4, 128.6, 128.5, 107.5, 93.5, 73.6, 66.8, 53.7, 53.2, 51.9, 51.6, 51.5, 44.3, 40.8, 38.8, 36.7, 31.3, 27.6, 25.4, 16.1, 14.6; Anal. Calcd for $C_{28}H_{31}ClO_6$: C, 67.40; H, 6.26. Found: C, 67.58; H, 6.21.

1.4.9. 17-Azido-3,6,9,12,15-pentaoxaheptadecyl 2-chloroacetate (19)

Yield: 93%; ^{1}H NMR (600 MHz): δ 4.31 (t, 2H, *J* 5.0 Hz), 4.08 (s, 2H, ClC*H*$_2$CO), 3.70 (t, 2H, *J* 4.6 Hz), 3.66–3.54 (m, 18H), 3.35 (t, 2H, *J* 5.0 Hz); ^{13}C NMR (150 MHz): δ 167.3, 70.6 (5C), 70.5 (3C), 70.0, 68.7, 65.1, 50.6, 40.8; Anal. Calcd for $C_{14}H_{26}ClN_3O_7$: C, 43.81; H, 6.83; N, 10.95. Found: C, 43.68; H, 6.98; N, 10.70.

1.4.10. Compound 21

Yield: 82%; $[\alpha]_D$ +52 (*c* 4.0, $CHCl_3$); ^{1}H NMR (400 MHz): δ 7.35–7.32 (m, 5H, *Ph*), 5.28 (t, 1H, *J* 3.6 Hz), 5.10, 5.05 (2d, 2 × 1H, *J* 12.6 Hz, C*H*$_2$Ph), 4.57 (t, 1H, *J* 6.5 Hz, H-3), 4.07, 4.03 (2d, 2 × 1H, *J* 14.6 Hz, ClC*H*$_2$CO), 2.90 (dd, 1H, *J* 13.9, 4.1 Hz), 1.14, 0.92, 0.91, 0.89, 0.88, 0.87, 0.84, 0.61 (7s, 7 × 3H, 7C*H*$_3$); ^{13}C NMR (100 MHz): δ 177.4, 167.1, 143.7, 136.4, 128.4, 128.0, 127.9, 12.3, 65.9, 55.3, 47.5, 46.7, 45.8, 41.7, 41.4, 41.2, 39.3, 38.0, 37.9, 36.9, 33.9, 33.1, 32.6, 32.4, 30.7, 28.0, 27.6, 25.8, 23.6, 23.4, 23.0, 18.2, 16.9, 16.6, 15.3; Anal. Calcd for $C_{39}H_{55}ClO_4$: C, 75.15; H, 8.89. Found: C, 75.38; H, 8.71.

1.4.11. 6-Azidohexyl 2-chloroacetate (23)

Yield: 90%; ^{1}H NMR (600 MHz): δ 4.16 (t, 2H, *J* 6.6 Hz), 4.04 (s, 2H, ClC*H*$_2$CO), 3.24 (t, 2H, *J* 6.9 Hz), 1.68–1.62 (m, 2H), 1.60–1.55 (m, 2H), 1.42–1.36 (m, 4H); ^{13}C NMR (150 MHz): δ 167.3, 66.0, 51.3, 40.8, 28.6, 28.3, 26.2, 25.3; Anal. Calcd for $C_8H_{14}ClN_3O_2$: C, 43.74; H, 6.42; N, 19.13. Found: C, 43.88; H, 6.57; N, 18.85.

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