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Note

H_2SO_4-silica-promoted 'on-column' removal of benzylidene, isopropylidene, trityl and *tert*-butyldimethylsilyl groups

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ABSTRACT

H_2SO_4-silica-promoted removal of benzylidene, isopropylidene, trityl and *tert*-butyldimethylsilyl groups from sugar derivatives was accomplished by following an 'on-column' protocol in a virtually waste-free condition.

Protecting group manipulation is an integrated part of synthetic carbohydrate chemistry.[1] Among the other protecting groups, acid-labile groups like benzylidene acetals,[2] isopropylidene ketals,[2] trityl[3] and *tert*-butyldimethylsilyl (TBDMS)[4] are used routinely for the purpose of selective protection and deprotection. Orthodox removal of these groups involves the use of protic[5] or Lewis acids.[6] Common reagents like AcOH, TFA, HCl, and HBr are good enough for the removal of these groups. However, in many cases, these reagents are not compatible with other acid-labile protecting groups and sometime affect the glycosidic linkages. Moreover, use of these reagents leads to rigorous work-up and purification process to get the pure product. Here, we report an H_2SO_4-silica[7]-promoted 'on-column' protocol for the removal of benzylidene, isopropylidene and trityl groups. The method is simple, much less time consuming, devoid of any extraction process, and scalable virtually under waste-free condition.

A glass column (30 cm × 1 cm) was packed with 20 g of silica (60–120 mesh) with a top layer of H_2SO_4-silica (2 g) as the reaction zone for the required hydrolysis. A solution of ethyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (**1**)[8] (500 mg) in CH_2Cl_2 (0.5 mL) was carefully added on the top of the column ensuring that the soaked volume remained within the reaction zone. The column was allowed to stand for 15 min, and was eluted with *n*-hexane–EtOAc (1:1). The resulting compounds were collected and compared by TLC with the hydrolyzed products from a solution-phase reaction. The 'on-column' chemistry resulted in the formation of the desired hydrolyzed product **2** in 76% yield with 20% recovery of the starting compound **1**. No other side product was evident from the TLC. Repeating the experiment by increasing the reaction time to 30 min resulted in 87% formation of the hydrolyzed product **2**, which was satisfactorily characterized by ^1H, ^{13}C NMR, and mass spectrometry. It is worth noting that the same column was used repeatedly and up to 3 cycles of operation, no significant loss of efficiency was observed (see Fig. 1).

A series of benzylidene derivatives with various glycosides and protecting groups were subjected to hydrolysis through this 'on-column' protocol. In all cases, satisfactory yields were obtained including the compound having *p*-methoxybenzylidene group (Table 1, entry 7). The products were characterized by ^1H, ^{13}C NMR, and mass spectrometry. Results of these reactions are summarized in Table 1. A Scale-up reaction (5 g) proved to be accessible by increasing the column size (45 cm × 3 cm). 5 g of compound **1** was converted to hydrolyzed compound **2** in 82% yield using a column.

Similarly, isopropylidene groups were also cleaved successfully from sugar derivative having different types of other protecting groups. Selective deprotection of the terminal isopropylidene group in glucofuranose moiety was achieved in very good yield without affecting the protecting groups (Table 2, entries 1–5). In

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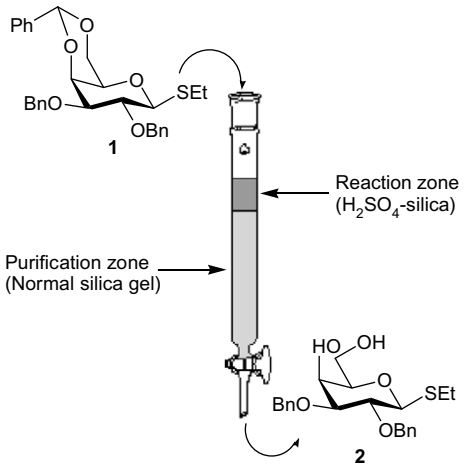


Figure 1. H_2SO_4-silica-promoted 'on-column' removal of benzylidene group.

case of mannopyranose moiety also, the primary isopropylidene group was cleaved successfully in good yield (Table 2, entry 6).

The same protocol was used for the selective removal of trityl and TBDMS groups. De-*O*-tritylated products were formed satisfactorily in good yield in the presence of benzyl or benzoyl groups. In a similar fashion, TBDMS group was also cleaved selectively from sugar derivatives. The results from these reactions are summarized in Table 3. In the presence of acetyl groups, obvious acyl migration was observed, and the ratio of the desired product and the migrated product was found to be ~1:1.

It is worth noting that increasing reaction time did not show significant improvement of yields. However, solution-phase reaction with a slurry of H_2SO_4-silica showed 3% increase in yield for entry 1 (Table 1). But to keep it simple, we followed the 'on-column' route. Use of dry solvent or wet solvent did not show any difference on the outcome.

1. Experimental

1.1. General methods

All reagents and solvents were dried prior to use according to standard methods.[20] Commercial reagents were used without further purification unless otherwise stated. Analytical TLC was performed on Silica Gel 60-F_{254} (Merck or Whatman) with detection by fluorescence and/or by charring following immersion in a 10% ethanolic solution of sulfuric acid. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer at 300 and 75 MHz, respectively, using Me_4Si as internal standard, as appropriate.

1.2. Preparation of H_2SO_4-silica

To a slurry of silica gel (10 g, 230–400 mesh) in dry diethyl ether (50 mL) was added commercially available concd H_2SO_4 (1 mL), and the slurry was shaken for 5 min. The solvent was evaporated under reduced pressure resulting in free flowing H_2SO_4-silica, which was dried at 110 °C for 3 h and used for the reactions.

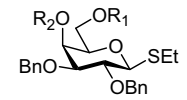
1.3. General procedure for 'on-column' hydrolysis

A glass column (30 cm × 1 cm) was packed with 20 g of silica (60–120 mesh) with a top layer of H_2SO_4-silica (2 g). Now a solution of starting material (500 mg) in 0.5 mL CH_2Cl_2 was charged slowly. The system was allowed to stand for the time mentioned in Tables 1–3. Then, the column was eluted with adequate mixture of *n*-hexane and EtOAc to get the pure product.

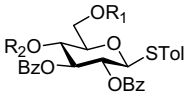
1.4. Propargyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (12)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.34 (t, 1H, $J_{2,3}$, $J_{3,4}$ 9.5 Hz, H-3), 5.25 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 5.14 (dd, 1H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.5 Hz, H-2), 4.42 (m, 2H, CH_2–C≡CH), 4.28 (m, 2H, H-4, H-6a), 4.15 (m, 2H, H-5, H-6b), 2.38 (t, 1H, *J* 1.0 Hz, CH_2–C≡C*H*), 2.23 (br s, 2H,

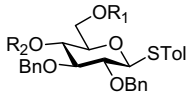
Table 1
Removal of benzylidene acetals from sugar derivatives



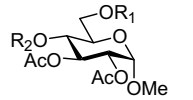
1 R_1,R_2 = benzylidene
2 R_1 = R_2 = H



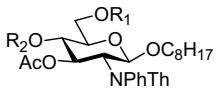
3 R_1,R_2 = benzylidene
4 R_1 = R_2 = H



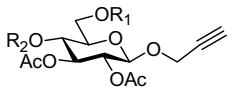
5 R_1,R_2 = benzylidene
6 R_1 = R_2 = H



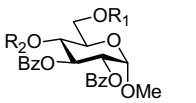
7 R_1,R_2 = benzylidene
8 R_1 = R_2 = H



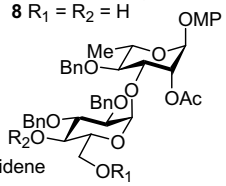
9 R_1,R_2 = benzylidene
10 R_1 = R_2 = H



11 R_1,R_2 = benzylidene
12 R_1 = R_2 = H



13 R_1,R_2 = *p*-MeO-benzylidene
14 R_1 = R_2 = H



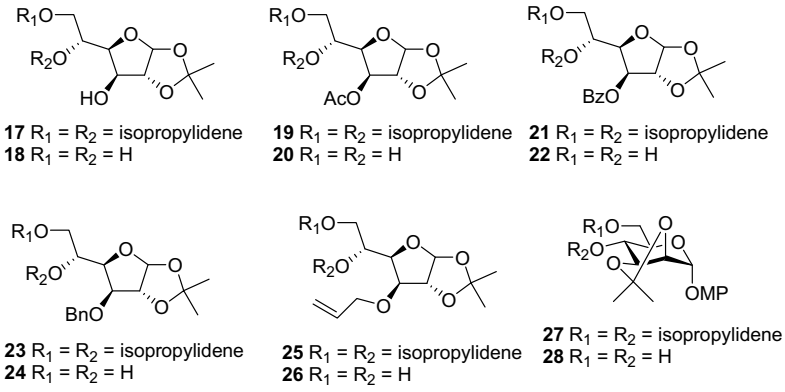
15 R_1,R_2 = benzylidene
16 R_1 = R_2 = H

Entry	Starting material	Product	Time[a] (min)	Yield (%)	Ref.
1	**1**	**2**	30	87	11
2	**3**	**4**	30	83	9
3	**5**	**6**	30	88	10
4	**7**	**8**	30	79	11
5	**9**	**10**	30	85	12
6	**11**	**12**	30	82	
7	**13**	**14**	20	81	14
8	**15**	**16**	45	89	
9[b]	**1**	**2**	30	82	11

[a] Time denotes the standing time (reaction time) between addition of the starting material on the column and column elution.
[b] The reaction performed on 5 g scale.

2 × OH), 2.08 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7 ($COCH_3$), 170.5 ($COCH_3$), 96.1 (C-1), 78.3, 75.3, 70.8, 69.5, 68.0, 67.7, 61.8, 55.3, 20.7 ($COCH_3$), 20.6 ($COCH_3$). HRMS calcd for $C_{13}H_{18}O_8Na$ (M+Na): 325.0899; found *m/z* 325.0896.

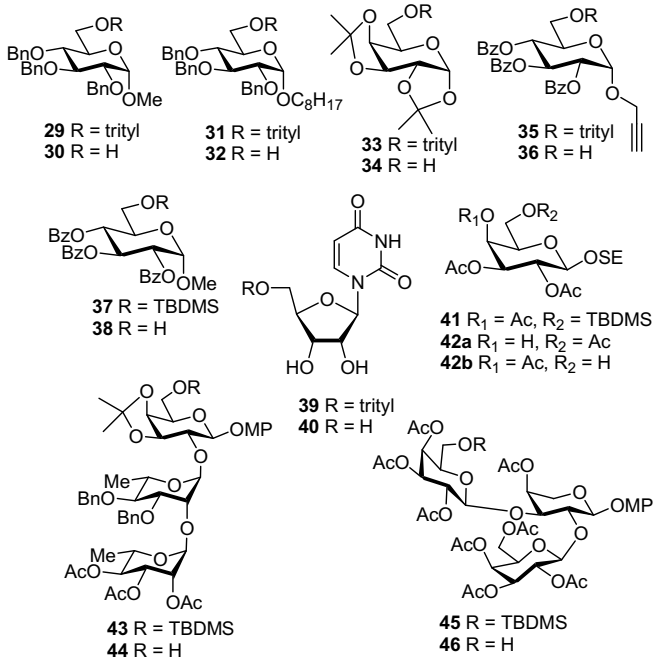
Table 2
Removal of isopropylidene groups from sugar derivatives



Entry	Starting material	Product	Time[a] (min)	Yield (%)	Ref.
1	**17**	**18**	30	83	8c
2	**19**	**20**	30	81	8c
3	**21**	**22**	30	88	8c
4	**23**	**24**	30	86	13
5	**25**	**26**	30	80	8c
6	**27**	**28**	20	73	8c

[a] Time denotes the standing time (reaction time) between addition of the starting material on the column and column elution.

Table 3
Deprotection of trityl and TBDMS groups from sugar derivatives



Entry	Starting material	Product	Time (min)[a]	Yield (%)	Ref.
1	**29**	**30**	20	82	14
2	**31**	**32**	20	80	15
3	**33**	**34**	20	83	16
4	**35**	**36**	20	85	
5	**37**	**38**	30	79	17
6	**39**	**40**	20	81	18
7	**41**	**42a** + **42b**	30	83	19
8	**43**	**44**	30	81	
9	**45**	**46**	30	84	

1.5. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (16)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42–7.28 (m, 15H, ArH), 6.97, 6.82 (2d, *J* 7.8 Hz, C_6H_4OMe), 5.55 (dd, 1H, $J_{1,2}$ 1.5, $J_{2,3}$ 1.8 Hz, H-2), 5.34 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 5.20 (d, 1H, $J_{1',2'}$ 3.3 Hz, H-1′), 5.05–4.70 (6d, 6H, *J* 11.4 Hz, 3 × $CH_2C_6H_5$), 4.33 (dd, 1H, *J* 3.3 Hz, 8.4 Hz), 3.91 (dd, 1H, *J* 1.5 Hz, 9.0 Hz), 3.87 (m, 2H), 3.78 (s, 3H, C_6H_4–OCH_3), 3.68–3.61 (m, 4H), 3.55 (dd, 1H, *J* 3.3 Hz, 9.6 Hz), 2.10 (br s, 1H, O*H*), 1.99 (s, 3H, $COCH_3$), 1.70 (br s, 1H, O*H*), 1.34 (d, 3H, *J* 6.3 Hz, C–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.5 ($COCH_3$), 155.1, 150.0, 138.6, 138.0, 137.7, 128.5(2), 128.4(2), 128.3, 128.2(2), 127.9(2), 127.8(2), 127.6(2), 117.8(2), 114.6(2), 96.6 (C-1′), 93.0 (C-1), 96.6, 93.0, 81.0, 79.4, 79.2, 75.7, 75.0, 72.8, 72.2, 71.0, 70.3, 68.5, 67.8, 62.0 (C-6′), 55.6 ($C_6H_4OCH_3$), 20.7 ($COCH_3$), 17.9 (C–CH_3). HRMS calcd for $C_{42}H_{48}O_{12}Na$ (M+Na): 767.3043; found *m/z* 767.3033.

1.6. Propargyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (36)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11–7.26 (m, 15H, ArH), 6.15 (t, 1H, $J_{3,4}$, $J_{4,5}$ 10.0 Hz, H-4), 5.63 (t, 1H, $J_{2,3}$, $J_{3,4}$ 10.0 Hz, H-3), 5.55 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 5.32 (dd, 1H, $J_{1,2}$ 3.5, $J_{2,3}$ 10.0 Hz, H-2), 4.35 (m, 3H, CH_2–C≡CH, H-5), 4.23 (dd, 1H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.14 (dd, 1H, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 12.5 Hz, H-6b), 2.38 (t, 1H, *J* 1.5 Hz, CH_2–C≡C*H*), 2.21 (br s, 1H, O*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.8 (COC_6H_5), 165.7 (COC_6H_5), 165.3 (COC_6H_5), 133.5, 133.4, 133.1, 129.9(2), 129.8(2), 129.7(2), 128.4(2), 128.3(2), 128.2(2) (ArC), 95.1 (C-1), 78.2, 75.4, 71.6, 70.2, 69.1, 68.2, 62.2, 55.7. HRMS calcd for $C_{30}H_{26}O_9Na$ (M+Na): 553.1475; found *m/z* 553.1473.

1.7. *p*-Methoxyphenyl 2,3,4-tri-*O*-acetyl–L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl–L-rhamnopyranosyl-(1→2)-3,4-*O*-isopropylidene-β-D-galactopyranoside (44)

$[\alpha]_D^{25}$ +81 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55–7.47 (m, 10H, ArH), 7.19, 6.99 (2d, 4H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.65 (dd, 1H, $J_{1'',2''}$ 1.8 Hz, $J_{2'',3''}$ 3.3 Hz, H-2″), 5.56 (dd, 1H, $J_{2'',3''}$ 3.3 Hz, $J_{3'',4''}$ 9.9 Hz, H-3″), 5.49 (d, 1H, $J_{1'',2''}$ 1.8 Hz, H-1″), 5.26 (t, 1H, $J_{3'',4''}$, $J_{4'',5''}$ 9.9 Hz, H-4″), 5.13, 4.94, 4.85, 4.79 (4d, 4H, *J* 11.7 Hz, 2 × CH_2Ph), 5.10 (d, 1H, $J_{1,2}$ 6.3 Hz, H-1), 4.95 (d, 1H, $J_{1',2'}$ 1.5 Hz, H-1′), 4.46–4.35 (m, 4H, H-2′, H-3, H-5″, H-6a), 4.24 (dd, 1H, $J_{1,2}$ 6.3 Hz, $J_{2,3}$ 9.9 Hz, H-2), 4.19–4.12 (m, 4H, H-4, H-5, H-5′, H-6b), 4.04 (dd, 1H, $J_{2',3'}$ 2.7 Hz, $J_{3',4'}$ 9.3 Hz, H-3′), 3.99 (s, 3H, $C_6H_5OCH_3$), 3.79 (t, 1H, $J_{3',4'}$, $J_{4',5'}$ 9.6 Hz, H-4′), 2.36 (s, 3H, $COCH_3$), 2.31 (s, 3H, $COCH_3$), 2.26 (s, 3H, $COCH_3$), 1.82 (s, 3H, isopropylidene-CH_3), 1.57 (s, 3H, isopropylidene-CH_3), 1.57 (d, 3H, $J_{5'',6''}$ 6.0 Hz, C–CH_3), 1.45 (d, 3H, $J_{5',6'}$ 6.3 Hz, C–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.6 ($COCH_3$), 169.5 ($COCH_3$), 169.4 ($COCH_3$), 155.4, 151.5, 139.0, 138.5, 128.3(2), 128.2(2), 127.8(2), 127.4(2), 127.3(2), 117.9(2), 114.7(2) (ArC), 110.6 [$C(CH_3)_2$], 100.3 (C-1), 99.5 (C-1″), 97.5 (C-1′), 80.1(2), 79.4, 75.1, 75.0, 73.8, 73.7, 72.3, 71.2, 69.9, 69.2, 68.4, 66.8, 62.2 (C-6), 55.5 ($C_6H_4OCH_3$), 28.1 (isopropylidene-CH_3), 26.6 (isopropylidene-CH_3), 20.9 ($COCH_3$), 20.8 ($COCH_3$), 20.7 ($COCH_3$), 18.1 (C–CH_3), 17.2 (C–CH_3). HRMS calcd for $C_{48}H_{60}O_{18}Na$ $(M+Na)^+$: 947.3677; found 947.3675.

1.8. *p*-Methoxyphenyl 2,3,4-tri-*O*-acetyl-β-D-galactopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-L-arabinopyranoside (46)

$[\alpha]_D^{25}$ +107 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.81 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.43 (bd, 1H, $J_{3',4'}$ 3.0 Hz, H-4′), 5.36 (d, 1H, $J_{3'',4''}$ 3.3 Hz, H-4″), 5.26 (d, 1H, $J_{3,4}$ 3.3 Hz, H-4), 5.23–5.11 (m, 2H, H-2′, H-2″), 5.05 (dd, 1H, $J_{2',3'}$ 9.3 Hz, $J_{3',4'}$ 3.0 Hz, H-3′), 5.03 (m, 2H, H-1, H-3″), 4.95 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.67 (d, 1H, $J_{1'',2''}$ 7.8 Hz, H-1″), 4.29 (m, 1H, H-3), 4.09–3.91 (m, 5H, H-2, H-5a, H-6a′, H-6a″, H-6b′), 3.76 (s, 3H, $C_6H_4OCH_3$), 3.57–3.48 (m, 4H, H-5′, H-5″, H-5b, H-6b″), 3.18 (br s, 1H, O*H*), 2.21 (s, 3H, $COCH_3$), 2.20 (s, 3H, $COCH_3$), 2.16 (s, 3H, $COCH_3$), 2.11 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8 ($COCH_3$), 169.7 ($COCH_3$), 169.7 ($COCH_3$), 169.5 ($COCH_3$), 169.5 ($COCH_3$), 169.1 ($COCH_3$), 169.1 ($COCH_3$), 168.9 ($COCH_3$), 154.8, 149.5, 118.2(2), 114.1(2) (ArC), 100.3 (C-1′), 100.1 (C-1″), 97.9 (C-1), 78.0, 76.8, 76.4, 75.7, 74.5, 73.8, 73.2, 70.7, 68.8, 68.4, 66.9, 66.4, 62.5, 60.6, 55.0 ($C_6H_4OCH_3$), 20.9 ($COCH_3$), 20.9 ($COCH_3$), 20.4 ($COCH_3$), 20.4 ($COCH_3$), 20.2 ($COCH_3$), 20.2 ($COCH_3$), 20.1 ($COCH_3$), 20.1 ($COCH_3$). HRMS calcd for $C_{40}H_{56}O_{24}N$ ($M+NH_4$): 934.3192; found 934.3193.

Acknowledgments

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