Efficient Acetylation of Carbohydrates Promoted by Imidazole[‡]

Pallavi Tiwari,[a] Rishi Kumar,[b] Prakas R. Maulik,[b] and Anup Kumar Misra*[a]

Dedicated to Professor B. P. Chatterjee[‡‡]

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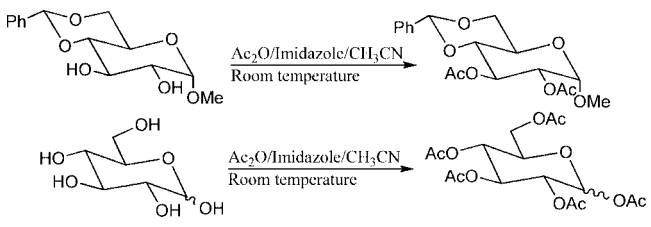
An efficient per-*O*-acetylation of carbohydrate derivatives and unprotected reducing sugars promoted by imidazole is reported. The reaction conditions have been successfully employed to acetylate carbohydrate derivatives containing acid-susceptible functional groups. In most of the cases the yields obtained were excellent.

Introduction

One of the most commonly used techniques for the protection of hydroxy groups in the synthesis of oligosaccharides is acetylation. In carbohydrate chemistry, per-*O*-acetylated sugars are inexpensive and useful intermediates for the synthesis of several natural products containing glycosides, oligosaccharides and other glycoconjugates.[1] The most often used protocol for the acetylation of sugar alcohols employs a large excess of acetic anhydride and pyridine as solvent and activator despite its toxicity and unpleasant odor.[2,3] In some cases, pyridine derivatives, such as, 4-(dimethylamino)pyridine and 4-(pyrrolidino)pyridine have been added to the reaction as co-catalyst to speed up the acetylation reaction.[4,5] Besides some classical reaction protocols for the acetylation of carbohydrates,[6–8] a variety of reagents have been developed for the acetylation of carbohydrate derivatives avoiding the use of pyridine which includes several Lewis acid catalysts[9–14] and a number of heterogeneous catalysts.[15–18] $ZnCl_2$/sodium acetate combination[19] or $InCl_3$[20] with acetic anhydride under microwave conditions have also been reported recently for the acetylation of carbohydrates. Few reports have also appeared on the acetylation of carbohydrates using ionic liquids as solvents and catalysts.[21,22] Considering the fact that solid supported catalysts have extra advantages over homogeneous catalysts in terms of purification of the products, we have recently reported[23] per-*O*-acetylation of carbohydrates using a stoichiometric quantity of acetic anhydride in the presence of $HClO_4/SiO_2$. Although, abovementioned reagents catalyze the acetylation efficiently, most of them are incompatible for the acetylation of carbohydrate derivatives containing acid-sensitive functional groups. In most of the instances, acetic anhydride is being used in an excess quantity, which requires extra efforts for its neutralization in large-scale preparations of acetylated carbohydrate derivatives. Besides this, acetylation of unprotected reducing sugars resulted an isomerized product mixtures of pyranose and furanose in many occasions. Therefore, a search for a new mild, less toxic and efficient catalyst for acetylation of carbohydrates minimizing isomerization and loss of sensitive functional groups is still continuing. Prompted by a recent report[24] on the synthesis of esters of simple alcohols catalyzed by imidazole under microwave conditions, we have explored the catalytic potential of imidazole in the acetylation of carbohydrates particularly with those having acid-sensitive functionalities. In this report we disclose an efficient economical method for the acetylation of carbohydrate derivatives using acetic anhydride promoted by imidazole.

Results and Discussion

Imidazole is well known for its use in several organic reactions.[25–31] It has a relatively lower toxicity than some



Scheme 1.

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[a] Medicinal and Process Chemistry Division, Central Drug Research Institute,
Chattar Manzil Palace, Lucknow 226001, UP, India
[b] Molecular and Structural Biology Division, Central Drug Research Institute,
Chattar Manzil Palace, Lucknow 226001, UP, India
E-mail: akmisra69@rediffmail.com
[‡‡]Indian Association for the Cultivation of Science, Jadavpur, Kolkata, India.

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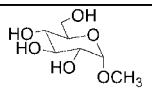
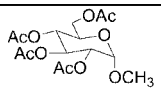
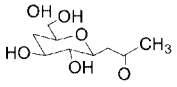
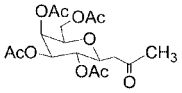
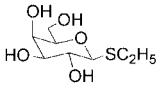
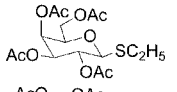
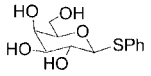
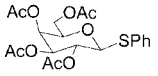
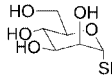
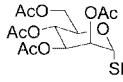
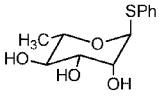
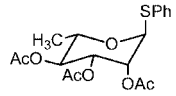
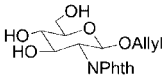
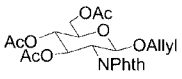
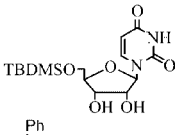
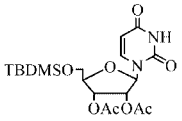
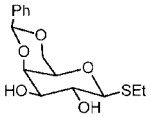
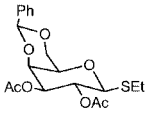
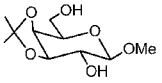
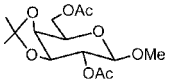
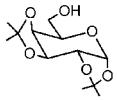
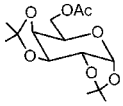
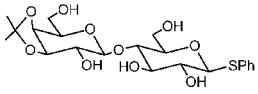
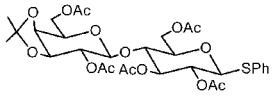
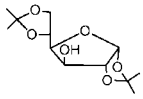
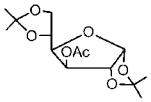
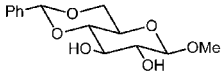
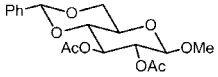
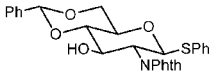
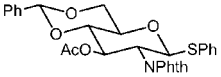
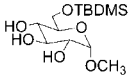
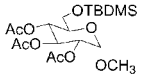
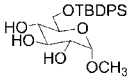
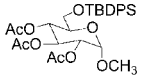
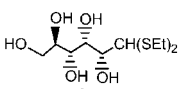
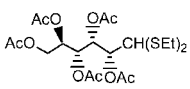
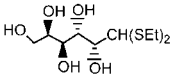
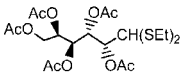
Table 1. Acetylation of carbohydrate derivatives using Ac_2O (1.2 equiv. per OH) and imidazole (0.6 equiv.) at room temperature.

Run	Sugars	Products	Time [h]	Yield [%]	α/β	Ref.
1			6	98	–	[35]
2			6	96	...	...
3			5	98	–	[36]
4			5	96	–	[37]
5			4.5	95	...	[38]
6			4.5	96	–	[39]
7			4.5	95	–	[40]
8			3.5	92	–	–
9			3.5	95	–	[41]
10			3.5	98	–	[42]
11			2	98	–	[13]
12			7	92	–	–
13			1	98	–	[43]
14			3.5	95	–	[44]
15			2	95	–	–
16			3	92	–	[45]
17			3	94	–	–
18			4	98	–	[46]
19			4	96	–	[46]

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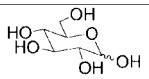
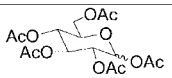
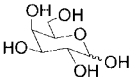
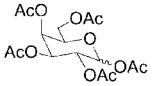
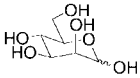
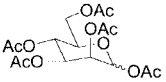
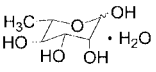
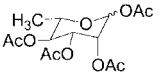
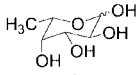
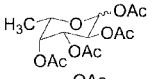
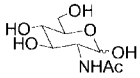
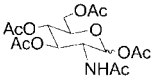
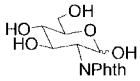
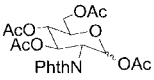
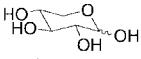
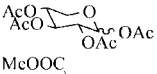
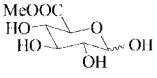
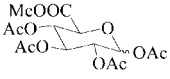
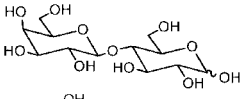
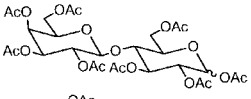
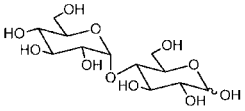
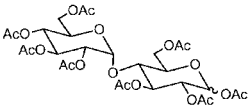
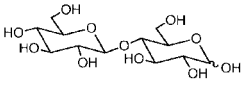
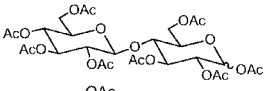
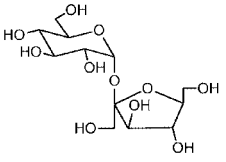
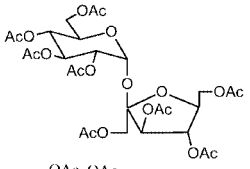
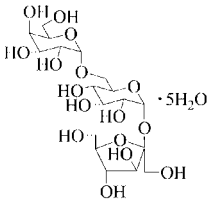
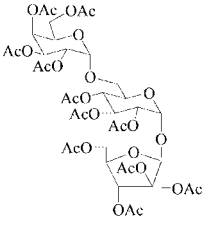
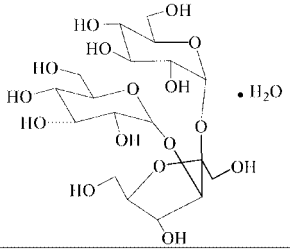
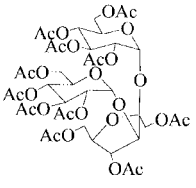
20			5	98	4:1	[11]
21			5	96	6:1	[11]
22			5	96	3:1	[11]
23			5[a]	95	3:1	[11]
24			5	92	5:1	[11]
25			6	95	9:1	[21,22]
26			5	96	1:3	[47]
27			5	96	5:1	[48]
28			5	92	1:9	[49]
29			10	92	1:2.3	[50]
30			10	94	1:4	[20]
31			10	95	1:2.5	[15]
32			10	98	–	[51]
33			12[b]	92	–	[23]
34			12[c]	95	–	[23]

[a] 6.0 equiv. of Ac_2O used. [b] 20 equiv. of Ac_2O used. [c] 15 equiv. of Ac_2O used.

widely used acetylation catalysts, such as pyridine, 4-(dimethylamino)pyridine (DMAP), etc. Earlier, *N*-acylimidazole derivatives have been used for the acylation of simple alcohols and carbohydrates.[32–34] In this endeavor, imidazole has been successfully applied as a catalyst for the acetylation of carbohydrates (Scheme 1). The findings of the acetylation of a variety of carbohydrate derivatives containing both acid-labile and acid-stable functional groups and unprotected reducing sugars are listed in Table 1.

In order to ascertain the catalytic potential of imidazole for this transformation, a series of experiments have been carried out at room temperature by varying the quantity of acetic anhydride (2.0–1.0 equiv. per OH) and imidazole (1.0–0.2 equiv.). Under optimized conditions acetic anhydride (1.2 equiv. per OH) and imidazole (0.6 equiv.) in acetonitrile (4.0 mL per mmol of substrate) at room temperature can successfully acetylate carbohydrate derivatives in almost quantitative yield. Use of other commonly used solvents e.g. CH_2Cl_2, $CHCl_3$, THF, DMF, nitromethane could not produce result similar as with acetonitrile. Acid-susceptible functional groups (benzylidene, isopropylidene, TBDMS, TBDPS, dithioacetal, etc.) present in the carbohydrate derivatives remained intact under the reaction condition, which is the most notable advantage of this reaction methodology. In order to extend the scope of this catalyst further, acetylation of unprotected reducing sugars were also investigated under these reaction conditions. In most of the cases clean conversion has been observed and per-*O*-acetylated products were isolated in almost quantitative yield either by two-phase aqueous workup or by simple evaporation of the solvent followed by column chromatography. It is pertinent to note that no formation of per-*O*-acetylated glycofuranose derivatives has been observed, which was reported earlier in heterogeneous catalyst promoted acetylations of unprotected reducing sugars.[15–18] In the case of hydrated sugars a slight excess of acetic anhydride was required with a longer reaction time because of the partial consumption of water present in the starting materials. Products of all known compounds gave acceptable ^{1}H NMR and ^{13}C NMR spectra that matched the data reported in the cited references. In the case of reducing sugars, per-*O*-acetylation gave a mixture of α- and β-acetates, the ratio of which was determined by NMR spectroscopy.

To further establish the efficacy of the present protocol, a comparison study has been carried out to the previously reported methods for acetylation of carbohydrates, which are presented in Table 2. Most of the previously reported protocols take either longer reaction times for completion or require prior preparation of catalysts or use of hazardous chemicals as activators or cannot be used with carbohydrate derivatives containing acid-labile functional groups. From the comparison in Table 2, it is clear that the present protocol is in many aspects more effective than the previously reported methods. Although in some instances, the yield is comparable to the earlier reports, the most notable advantage of the present protocol is that it can acetylate carbohydrate derivatives containing acid-labile functional groups very efficiently without any side reactions.

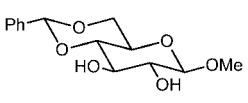
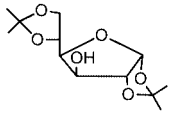
Conclusions

A mild less toxic and efficient protocol for the acetylation of carbohydrates has been devised using imidazole as acetylation activator. This methodology has been further extended to acetylate unprotected reducing sugars to form per-*O*-acetylated glycopyranoses. In most of the cases quantitative yields were obtained. Being operationally so simple, this methodology does not need any aqueous workup and thereby reduces the efforts in purification of the products. Along with these features, this method may be considered as an attractive alternative to the existing methodologies for the acylation of carbohydrates, particularly those containing acid-susceptible functionalities.

Experimental Section

General Experimental Protocol for the Acetylation of Carbohydrates: To a magnetically stirred solution of the carbohydrate

Table 2. Comparative study of acetylation using different reported catalysts at room temperature.

Substrate	Reagent (equiv.)	Catalyst	Time [h]	Yield [%]	Ref.
	Ac_2O (5.0)	pyridine (excess)	3.0	98	[2]
	Ac_2O (4.0)	I_2	0.5	20 (with degraded product)	[9]
	Ac_2O (2.2)	$Cu(OTf)_2$	12.0	92	[11]
	Ac_2O (3.0)	$InCl_3$	30 s	10 (with degraded product)	[20][a]
	Ac_2O (2.2)	$HClO_4/SiO_2$	0.5	10 (with degraded product)	[23]
	Ac_2O (2.4)	imidazole	3.5	95	this work
	Ac_2O (2.5)	pyridine (excess)	1.5	95	[2]
	Ac_2O (2.0)	I_2	0.5	10 (with degraded product)	[9]
	Ac_2O (1.1)	$Cu(OTf)_2$	10.0	90	[11]
	Ac_2O (1.5)	$InCl_3$	30 s	no desired product isolated	[20][a]
	Ac_2O (1.2)	$HClO_4/SiO_2$	20 min	no desired product isolated	[23]
	Ac_2O (1.2)	imidazole	1.0	98	this work

[a] Domestic microwave irradiation.

(1.0 mmol) and acetic anhydride (1.2 equiv. per OH) in acetonitrile (2.0 mL) was added imidazole (0.6 mmol) at room temperature and the reaction mixture was stirred at ambient temperature for the appropriate time as mentioned in Table 1. After completion of the reaction (TLC; hexane/EtOAc, 1:1), the reaction mixture was poured in water and extracted with CH_2Cl_2. The organic layer was washed with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. Column chromatography of the crude product on SiO_2 using hexane/EtOAc (4:1) as an eluent furnished pure acetylated carbohydrate derivatives (Table 1). In some cases, direct evaporation of the solvent under reduced pressure avoiding two-phase partition of the reaction mixture followed by column chromatography furnished pure acetylated products. Spectral data for compounds, which were not reported earlier follow below.

5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-1,3-dideoxy-D-glycero-L-gluclononulose [1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)acetone]: Yield: 96%; white solid; m.p. 91–92 °C. $[a]_D^{25}$ = +5.6 (*c* = 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.34 (br. s, 1 H, 7-H), 5.01–4.98 (m, 2 H, 5-H and 6-H), 4.05–3.98 (m, 2 H, 9-H_{ab}), 3.96–3.85 (m, 2 H, 4-H and 8-H), 2.74 (dd, *J* = 16.3 and 8.5 Hz, 1 H, 3-H_a), 2.45 (dd, *J* = 16.4 and 3.4 Hz, 1 H, 3-H_b), 2.16, 2.15, 2.02, 2.01, 1.96 (5 s, 15 H, 5 COCH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 Hz): δ = 204.5, 169.9 (2 C), 169.7, 169.6, 74.4, 74.3, 71.9, 69.3, 67.9, 61.6, 45.6, 30.9, 20.7, 20.6 (2 C), 20.5 ppm. IR (KBr): ṽ = 2960, 1741, 1713, 1598, 1439, 1386, 1220, 1030, 726 cm^{-1}. ESI-MS: *m*/*z* = 411 [M + Na]. $C_{17}H_{24}O_{10}$ (388): calcd. C 52.57, H 6.23; found C 52.30, H 6.50.

2,3-Di-*O*-acetyl-5-*O*-*tert*-butyldimethylsilyluridine: Yield: 92%; white solid; m.p. 84 °C. $[a]_D^{25}$ = –2.5 (*c* = 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.18 (br. s, 1 H, N*H*), 7.72 (d, *J* = 9.0 Hz, 1 H), 6.15 (d, *J* = 6.0 Hz, 1 H), 5.62 (d, *J* = 9.0 Hz, 1 H), 5.20–5.18 (m, 2 H), 4.09 (br. s, 1 H), 3.85–3.73 (m, 2 H), 2.04, 1.98 (2 s, 6 H, 2 COCH_3), 0.85 [s, 9 H, C(CH_3)$_3$], 0.06 (s, 6 H, 2 CH_3Si) ppm. ^{13}C NMR ($CDCl_3$, 75 Hz): δ = 169.3, 169.0, 163.0, 150.6, 139.0, 103.0, 85.0, 83.4, 73.1, 71.4, 63.0, 25.7 (2 C), 25.4, 20.4, 20.1, 18.1, –5.8 (2 C) ppm. IR (KBr): ṽ = 3202, 3072, 2929, 2858, 1749, 1715, 1460, 1380, 1241, 1125, 1101, 1046, 834, 813, 778, 757 cm^{-1}. ESI-MS: *m*/*z* = 465 [M + Na]. $C_{19}H_{30}N_2O_8Si$ (442): calcd. C 51.57, H 6.83; found C 51.28, H 7.08.

Phenyl (2,6-Di-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside: Syrup. $[a]_D^{25}$ = +5.5 (*c* = 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.52–7.20 (m, 5 H, aromatic H), 5.23 (dd, *J* = 10.8 and 8.1 Hz, 1 H, 2-H), 4.92 (t, *J* = 9.5 Hz each, 1 H, 2′-H), 4.87–4.80 (m, 1 H), 4.67 (d, *J* = 9.8 Hz, 1 H, H-1), 4.47 (d, *J* = 11.2 Hz, 1 H, 1-H), 4.35–4.20 (m, 3 H), 4.19–4.02 (m, 3 H), 3.95–3.90 (m, 1 H), 3.80–3.55 (m, 2 H), 2.08, 2.04 (2 s, 15 H, 5 COCH_3), 1.52, 1.31 [2 s, 6 H, C(CH_3)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 75 Hz): δ = 170.5, 170.4, 170.0, 169.4, 169.3, 133.2–128.4 (aromatic C), 111.0, 100.6 (C-1′), 85.7 (C-1), 78.1, 77.2, 76.2, 73.8, 73.4, 72.9, 71.2, 70.6, 63.4, 62.7, 27.7, 26.5, 21.0 (3 C), 20.9 (2 C) ppm. IR (neat): ṽ = 2923, 2855, 2363, 1730, 1461, 1218, 769 cm^{-1}. ESI-MS: *m*/*z* = 707 [M + Na]. $C_{31}H_{40}O_{15}S$ (684): C 54.38, H 5.89; found C 54.75, H 6.12.

Phenyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside: White solid; m.p. 115 °C. $[a]_D^{25}$ = +18.3 (*c* = 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.85–7.71 (m, 4 H, aromatic H), 7.42–7.25 (m, 10 H, aromatic H), 5.85 (t, *J* = 9.5 and 9.0 Hz, 1 H, 3-H), 5.80 (d, *J* = 10.6 Hz, 1 H, 1-H), 5.50 (s, 1 H, PhC*H*), 4.41 (d, *J* = 5.9 Hz, 1 H, 4-H), 4.30 (t, *J* = 10.2 and 10.1 Hz, 1 H, 2-H), 3.82–3.70 (m, 3 H, 5-H and 6-H_{ab}), 1.87 (s, 3 H, COCH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 Hz): δ = 170.5, 168.2, 167.6, 137.3–124.1 (aromatic C), 102.1, 84.3, 79.4, 70.9, 69.0, 54.7, 20.9 ppm. IR (KBr): ṽ = 2934, 2829, 2367, 1715, 1595, 1366, 1228, 1105, 1030, 966, 719 cm^{-1}. ESI-MS: *m*/*z* = 554 [M + Na]. $C_{29}H_{25}NO_7S$ (531): C 65.52, H 4.74; found C 65.68, H 5.0.

Methyl 2,3,4-Tetra-*O*-acetyl-6-*O*-di-*tert*-butyldiphenylsilyl-α-D-glucopyranoside: Syrup. $[a]_D^{25}$ = +124 (*c* = 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.65–7.64 (m, 4 H, aromatic H), 7.42–7.32 (m, 6 H, aromatic H), 5.38 (t, *J* = 9.6 and 9.9 Hz, 1 H, 2-H), 5.03 (t, *J* = 9.9 and 9.3 Hz, 1 H, 3-H), 4.92 (d, *J* = 3.0 Hz, 1 H, 1−H), 4.82 (dd, *J* = 10.2 and 2.4 Hz, 1 H, 4-H), 3.85–3.80 (m, 1 H, 5-H), 3.71–3.63 (m, 2 H, 6-H_{ab}), 3.39 (s, 3 H, OCH_3), 2.07, 1.98, 1.86 (3 s, 9 H, 3 COCH_3), 1.05 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 Hz): δ = 169.8, 169.7, 169.0, 135.7–127.7 (aromatic C), 96.5, 71.0, 70.6, 69.9, 68.9, 62.6, 55.0, 26.8 (3 C), 20.7 (2 C), 20.5, 19.3 ppm. IR (neat): ṽ = 2390, 1715, 1580, 1366, 719 cm^{-1}. ESI-MS: *m*/*z* = 581 [M + Na]. $C_{29}H_{38}O_9Si$ (558): C 62.34, H 6.86; found C 62.10, H 7.05.

Acknowledgments

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