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Solvent-free benzylation of polyols by phase-transfer catalysis or supported reagent methods

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ABSTRACT

Solvent-free techniques were successfully and efficiently applied under mild conditions to the perbenzylation of methyl α-D-glucopyranoside and methyl 6-bromo(and 6-chloro)-6-deoxy-α-D-glucopyranoside, and to the selective monobenzylation of diethyl (*R*,*R*)-tartrate. Selective 2-*O*- or 3-*O*-benzylation of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside, requiring CH_2Cl_2 as solvent, was observed depending on the nature of the ammonium catalyst.

INTRODUCTION

Benzyl ethers are efficient protecting groups for hydroxyl functions in organic synthesis because they are stable under acidic and basic conditions and readily removable by mild hydrogenolysis[1–3].

Perbenzylation or selective benzylation of primary, secondary, and even tertiary alcohols is frequently used to obtain intermediates in synthetic carbohydrate chemistry. Such alkylations of water-soluble polyols and partially protected hydrophilic sugars have been reported recently using phase-transfer catalysis (PTC) techniques[4–8]. In addition, in numerous alkylations, the advantage of working under solvent-free conditions was shown. Very often better yields and/or milder conditions have been described using solid–liquid PTC in the absence of solvent[9].

We describe herein our results on the benzylation of several models, such as methyl α-D-glucopyranoside (**1**), methyl 6-bromo- and 6-chloro-6-deoxy-α-D-glucopyranoside (**3** and **5**), methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (**8**), and diethyl (*R*,*R*)-tartrate (**12**), by PTC in the absence of organic solvent. In some cases, alkylations have also been studied by performing the reaction in "dry media" with reagents impregnated on alumina[10] and using KOH, KF, or CsF as base.

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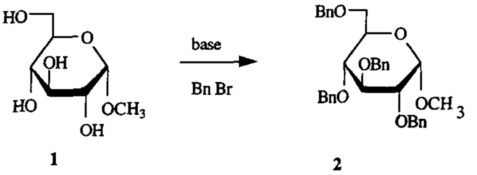
RESULTS AND DISCUSSION

Perbenzylation of methyl α-D-glucopyranoside (**1**).—Perbenzylation of a glycoside usually necessitates the use of a polar solvent, such as DMF or Me_2SO, and a strong base such as NaH, *t*-BuOK, or $NaNH_2$. In the literature, perbenzylation of the glucoside **1** to give methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (**2**) has often been described. The most efficient procedure, reported by Saeki[11], gave a 96% yield using Me_2SO, sodium amide, and benzyl chloride. More recently, crown ether-catalysed alkylation in THF with benzyl bromide and potassium hydroxide was reported (90% yield)[8]. These methods, however, need an inert atmosphere and anhydrous conditions.



Under liquid–liquid PTC conditions, as recommended by Nouguier and coworkers[6,7] (aq NaOH, $Bu_4N^+Br^-$) or with the modifications of Szeja[5] (aq NaOH, $Bu_4N^+HSO_4^-$, in benzene and *tert*-pentyl alcohol), the reported yields (27 and 32%, respectively) were less satisfactory.

Our first objective was to study perbenzylation of **1** under solid–liquid PTC conditions, without solvent, in the presence of Aliquat 336 (methyltrioctylammonium chloride) as transfer agent, a small excess of benzyl bromide (4 to 6 equiv), and different bases, either free or impregnated on solid supports (4 to 12 equiv). The results are summarised in Table I.

The maximum yield (65%) was observed using 6 equiv of benzyl bromide, at 50°C for 48 h in the presence of 6 equiv of KOH and 10% of Aliquat 336, i.e., with a small excess of base and alkylating agent.

In previous reports on the etherification of hydrophilic carbohydrate derivatives under liquid–liquid PTC conditions, it was concluded that alkylation of a substrate can be greatly facilitated by the introduction of a "co-catalyst" (e.g., a tertiary alcohol) and a co-solvent (e.g., Me_2SO) to the mixture[5,7]. In our case, no significant increase in the yield of perbenzyl ether **2** was observed with such modifications (see Table I, entries 1–4).

The supported reagent technique is an interesting tool in organic synthesis. Therefore, we attempted also to impregnate the carbohydrate and/or the base on a solid mineral support (alumina) before the addition of the alkylating agent (entries 7–12). The best result (ca. 60% of **2**) was obtained when KOH or CsF (12 equiv) as base and **1** were preimpregnated on alumina and stirred in the presence of 4 equiv of $C_6H_5CH_2Br$ and 10% of Aliquat 336 as catalyst (entries 9–11).

In terms of yields, our results for the transformation of **1** to **2** were less attractive than the classical benzylation methods. However, besides the obvious

TABLE I

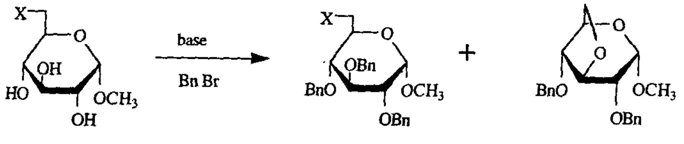
Perbenzylation of **1** by PTC without solvent: **1** + base + $C_6H_5CH_2Br$ + Aliquat 336 (10% mol)

Entry	Base	Relative amounts **1**–base–$C_6H_5CH_2Br$	Reactions conditions		Yield (%)	
			Time (h)	Temp. (°C)	**2**	**2** (in the presence of Me_2SO + *t*-BuOH)
1	KOH	1:6:6	48	50	65 [a]	60
2 [b]	KOH + alumina	1:6:6	48	50	32	37
3 [b]	KF + alumina	1:6:6	48	50	40	35
4 [b]	CsF + alumina	1:6:6	48	50	35	43
5	KOH	1:4:4	48	50	47	
6 [b]	KF + alumina	1:4:4	48	50	22	
7 [c]	KOH/alumina	1:6:4	24	20	30	
8 [c]	KF/alumina	1:6:4	24	20	24	
9 [d]	KOH/alumina	1:12:4	60	20	48	
10	KOH/alumina	1:12:6	48	60	56	
11 [d]	CsF/alumina	1:12:4	60	20	58	
12	CsF/alumina	1:6:4	48	60	44	

[a] Changing Aliquat for $Bu_4N^+HSO_4^-$ or $Hept_4N^+Br^-$ leads to a 38% yield [b] Bases dispersed on alumina. [c] Bases impregnated on alumina via aqueous solutions [d] Bases + **1** impregnated together on alumina via aqueous solutions.

ease of handling, the advantages of the PTC technique over the Me_2SO–$NaNH_2$ procedure include the cost of reagents, safety, and the absence of working up, and use and evaporation of solvents. Our process can be considered as a useful alternative in comparison with the published alkylations.

Perbenzylation of methyl 6-bromo- and 6-chloro-6-deoxy-α-D-glucopyranoside (**3** *and* **5**).—Since perbenzylation of **3** and **5** is a serious challenge, we turned our attention to this problem. Due to the presence of a halogen at position 6 in **3** and **5**, the formation of the 3,6-anhydro derivative **7** might be expected.



3 X = Br
5 X = Cl
4 X = Br
6 X = Cl
7

By treatment of **3** and **5** under the same PTC conditions as for the preparation of **2** (4 equiv $C_6H_5CH_2Br$, 4 equiv KOH, 10% Aliquat 336, over 48 h at 50°C, Table II), the required perbenzyl bromide **4** and perbenzyl chloride **6** were isolated in 25 and 40% yield, respectively. The major product in both cases turned out to be the anhydro derivative **7**.

TABLE II

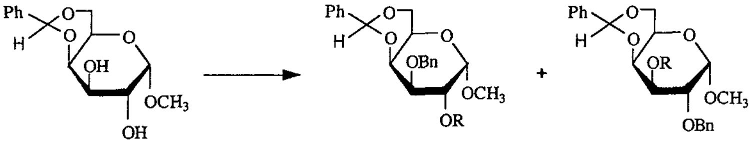
Benzylation of 6-halo derivatives **3** and **5**

Derivative	Relative amounts of **3** (or **5**)-base-$C_6H_5CH_2Br$	Reactions conditions			Yield (%)		
		Solvent or catalyst (10%)	Time (h)	Temp. (°C)	**4**	**6**	**7**
3	1:4(KOH):4	Aliquat 336	48	50	25		60
3	1:4(NaH):4	DMF	12	20	1		90
5	1:4(KOH):4	Aliquat 336	48	50		40	50
5	1:4(NaH):4	DMF	12	20		10	80

The isolation of perbenzyl bromide **4** and chloride **6**, albeit in moderate yields, represents an appreciable improvement when compared with the classical benzylation method using NaH in DMF [1% yield for **4** and 10% for **6** (Table II)].

A classical synthesis of **4** and **6** would require a multistep procedure, as for the perbenzyl iodide[12]: selective tritylation of the 6 position of **1**, then benzylation of the 2, 3, and 4 positions, removal of the 6-*O*-trityl group, and finally halogenation.

*Selective benzylation of 4,6-O-benzylidene-α-*D*-galactopyranoside* (**8**).—It was attractive, along the same lines, to attempt a partial benzylation of diol **8**, using a solvent-free PTC method. In order to obtain monobenzylated methyl 4,6-*O*-benzylidene-α-D-hexopyranosides, several strategies have been employed including complexation with metal chloride[13,14], and the use of stannylene derivatives[15,16]. It was also reported that monobenzylation might be achieved by liquid–liquid PTC techniques[4,17,18,19].



8 **9** R = H **10** R = Bn

11 R = H

In our attempts under solvent-free PTC conditions defined in the two previous cases, yields and regioselectivity of the benzylation of **8** were very low with either Aliquat 336 or TEBA-Cl ($Et_3N^+CH_2C_6H_5,Cl^-$) as transfer agents (Table III, entries 1 and 2). Contrary to the other cases where an excess of benzyl bromide was involved, here 1 equiv of alkylating agent was used thus resulting in a lack of liquid phase to promote efficient reaction. To obtain a heterogeneous solid–liquid mixture, we therefore performed the reaction in the presence of CH_2Cl_2. We then observed good yields either for **9**[20] or**11**, i.e., for the two different regioisomers on the O-3 or O-2 positions of **8**, depending on the nature of the ammonium catalyst (Table III, entries 3 and 4).

TABLE III

Benzylation of **8** by PTC methods: **8** + KOH + $C_6H_5CH_2Br$

Entry	Transfer agent (10% equiv)	Relative amounts of **8**-KOH-$C_6H_5CH_2Br$	Solvent	Yield (%)		
				9	**10**	**11**
1	TEBA-Cl	1:1.5:1.1	none	20	13	18
2	Aliquat 336	1:1.5:1.1	none	10	12	12
3	TEBA-Cl	1:1:5:1.1	CH_2Cl_2	60	8	20
4	Aliquat 336	1:1.5:1.1	CH_2Cl_2	20	9	60
5	Aliquat 336	1:5:5	CH_2Cl_2		90	

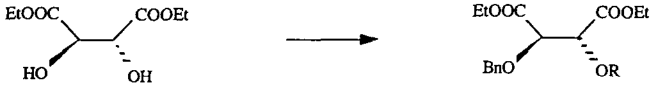
In the presence of 10% of Aliquat 336, 1.5 equiv of powdered KOH, and 1.1 equiv of benzyl bromide in CH_2Cl_2, the 2-*O*-benzyl derivative **11** was isolated in 60% yield together with 20% of the 3-*O*-benzylated product **9** and 9% of the dibenzyl ether **10**[21,22] (Table III, entry 4).

Surprisingly, under the same conditions, the use of TEBA-Cl, instead of Aliquat 336, led to a complete reverse in regioselectivity. The 3-*O*-benzylated regioisomer **9** was now predominant (60%), with small amounts of the 2-benzyl ether **11** (20%) and dibenzyl ether **10** (8%) (Table III, entry 3). The less acidic 3-hydroxyl group was alkylated preferentially, as noted previously, in the presence of $Et_4N^+Br^-$[19] or copper chelates[13].

Such an effect of the ammonium salt on the regioselectivity of alkylation is unexpected and difficult to explain. However, there are very few precedents for this effect such as *N*- versus *S*-benzylation of thiocyanate anions[23] and *C*- versus *O*-methylation of an enol[24].

The 2,3-dibenzyl ether **10**, which was produced in ~10% yield in these experiments, can be obtained in 90% yield when 5 equiv of reagents are used in CH_2Cl_2 as solvent.

*Selective benzylation of diethyl (*R,R*)-tartrate* (**12**).—Diesters of 2-*O*-benzyl-(*R*,*R*)-tartrate are interesting four-carbon fragments for the preparation of enantiomerically pure compounds[25–27] due to the presence of a C_2 axis of symmetry in optically active tartaric acids. Dimethyl 2-*O*-benzyl-(*R*,*R*)-tartrate was previously prepared by reductive opening of the benzylidene acetal[25,26] or CsF-catalysed alkylation of the stannylene acetal with benzyl iodide[27].



12

13 R = H

14 R = Bn

The presence of an ester α to the hydroxyl group prohibits the use of strong bases, such as NaH, NaOH, or KOH, for alkylation of **12**. We chose to try potassium carbonate, a weaker base, under PTC conditions without solvent. Selective benzylation of **12** led to the mono-*O*-benzyl derivative **13**, which was isolated in 64% yield by treatment of the diol **12** with 1.25 equiv of potassium carbonate, 1.25 equiv of benzyl bromide, and 10% Aliquat 336 over 6 h at 60°C under vigorous stirring. In this case, the direct alkylation by PTC without solvent appeared to be the method of choice to obtain **13**.

Applying solid–liquid PTC conditions, diethyl 2,3-di-*O*-benzyl-(*R*,*R*)-tartrate (**14**) can also be prepared from the diol **12** in 54% yield if benzyl bromide is transformed in situ into the more reactive benzyl iodide by addition of an excess of potassium iodide to the mixture (5 equiv K_2CO_3, 2.5 equiv BnBr, 2.5 equiv KI, 10% Aliquat 336, 48 h, room temperature). In these conditions, the monobenzyl derivative **13** was also isolated (34%).

The dibenzyl ether **14** could also be obtained in 80% yield from **13**, using 2 equiv K_2CO_3, 2 equiv BnBr, 2 equiv KI, and 10% Aliquat 336 for 48 h at room temperature.

CONCLUSIONS

Solvent-free benzylation appears to be an attractive procedure of great potentiality in carbohydrate chemistry. It permits an increase in yield in several cases examined (**3**, **5**, and **12**), and selective access to monobenzylated products **9** or **11** from **8** (requiring the presence of CH_2Cl_2) and **13** from **12**. In all cases, the method is efficient, inexpensive, and easy to perform under very mild conditions.

EXPERIMENTAL

General methods.—Melting points were determined on a Leitz apparatus and are uncorrected. TLC was performed on silica gel (Schleicher & Schull) with UV detection or by charring with H_2SO_4. Column chromatography was performed on silica gel (SDS 40–60 mesh). ^1H NMR spectra were recorded in $CDCl_3$ with Bruker WM-200 and WM-250 (200 and 250 MHz) spectrometers; chemicals shifts are reported in ppm downfield from Me_4Si. Optical rotations were determined with a Perkin–Elmer 241 polarimeter.

*Perbenzylation of methyl α-*D*-glucopyranoside* (**1**) *to methyl 2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranoside* (**2**).—Powdered KOH (672 mg, 12 mmol), Aliquat 336 (200 mg, 0.5 mmol), and benzyl bromide (1.5 mL, 12 mmol) were added to **1** (390 mg, 2 mmol). The mixture was vigorously stirred during 48 h at 50°C, then MeOH (2 mL) was added. After 1 h, this heterogeneous medium was diluted with EtOAc and filtered through a cake of silica gel. The filtrate was concentrated and the residue submitted to column chromatography (1 : 3 EtOAc–heptane), leading to the tetrabenzyl derivative **2** (720 mg, 65% yield); $[\alpha]_D$ +25° (*c* 1.5, $CHCl_3$); lit.[11] $[\alpha]_D$ +23.8° ($CHCl_3$).

Methyl 2,3,4-tri-O-benzyl-6-bromo-6-deoxy-α-D-glucopyranoside (**4**) *and methyl 3,6-anhydro-2,4-di-O-benzyl-α-D-glucopyranoside* (**7**).—To **3** (257 mg, 1 mmol) were added powdered KOH (280 mg, 5 mmol), Aliquat 336 (80 mg, 0.2 mmol), and benzyl bromide (0.6 mL, 5 mmol). The mixture was vigorously stirred for 48 h at 50°C, MeOH (1.5 mL) was added, and, after dilution with EtOAc, the solution was filtered through a cake of silica gel. The residue obtained after evaporation was separated on a silica gel column, giving **4** (132 mg, 25%) and **7** (214 mg, 60%).

Bromide **4** was a syrup: $[\alpha]_D$ +30° (c 1.1, $CHCl_3$); ^1H NMR: δ 7.40–7.20 (m, 15 H), 4.96 (m, 2 H), 4.80 (m, 2 H), 4.65 (m, 2 H), 4.63 (d, 1 H, H-1), 4.00 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 3.8 (m, 2 H, H-5,6a), 3.6 (m, 1 H, H-6b), 3.50 (m, 2 H, H-2,4), 3.38 (s, 3 H, CH_3). Anal. Calcd for $C_{28}H_{31}BrO_5$: C, 63.75; H, 5.94; Br, 15.15. Found: C, 63.58; H, 6.00; Br, 15.06.

Oxide **7** crystallised from heptane; mp 107–108°C $[\alpha]_D$ +132° (c 1.03, $CHCl_3$); ^1H NMR: δ 7.50–7.15 (m, 10 H), 4.99 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.98 (d, 1 H), 4.55 (dd, 2 H), 4.39 (t, 1 H, $J_{4,5} = J_{5,6b} = 2.25$ Hz, H-5), 4.32 (t, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 4 Hz, H-3), 4.10 (d, 1 H, $J_{6a,6b}$ 10 Hz, H-6a), 3.82 (dd, 1 H, H-6b), 3.76 (dd, 1 H, H-4), 3.70 (t, 1 H, H-2), 3.60 (s, 3 H, CH_3). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70,76; H, 6.79. Found: C, 70.65; H, 6.81.

Methyl 2,3,4-tri-O-benzyl-6-chloro-6-deoxy-α-D-glucopyranoside (**6**).—From the chloride **5**, under the same conditions, besides the anhydro derivative **7** (50%), **6** was obtained (yield: 40%); $[\alpha]_D$ +56° (c 0.93, CH_2Cl_2); ^1H NMR: δ 7.40–7.20 (m, 15 H), 4.96 (m, 2 H), 4.80 (m, 2 H), 4.82 (m, 2 H), 4.65 (m, 2 H), 4.62 (d, 1 H, H-1), 4.05 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 3.85 (m, 2 H, H-5,6a), 3.73 (m, 1 H, H-6b), 3.55 (m, 2 H, H-2,4), 3.38 (s, 1 H, CH_3). Anal. Calcd for $C_{28}H_{31}ClO_5$: C, 69.63; H, 6.47; Cl, 7.34. Found: C, 69.53; H, 6.71; Cl, 7.24.

Benzylation of methyl 4,6-O-benzylidene-α-D-galactopyranoside (**8**): *methyl 3-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside* (**9**), *methyl 2-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside* (**11**), *and methyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside* (**10**).—(*a*) To a solution of the diol **8** (13 g, 46.1 mmol) in CH_2Cl_2 (40 mL) were added powdered KOH (3.9 g, 69.1 mmol), benzyl bromide (6 mL, 50.7 mmol), and Aliquat 336 (1.86 g, 4.6 mmol). The mixture was vigorously stirred at room temperature during 12 h, before addition of MeOH (5 mL). After 2 h, the solution was filtered through a cake of silica gel, and the cake was washed with EtOAc. The filtrate was evaporated and the residue submitted to column chromatography (19:1 $CHCl_3$–heptane).

The 2,3-di-*O*-benzyl derivative **10** was eluted first (1.54 g, 9%), and recrystallised from EtOAc–heptane; mp 170–172°C; $[\alpha]_D$ +80° (c 0.3, $CHCl_3$); lit.[21] mp 176–177°C; $[\alpha]_D$ +77° ($CHCl_3$).

Then, the 2-*O*-benzylglycoside **11** was isolated (10.5 g, 60%) and recrystallised from EtOAc–heptane; mp 174–176°C; $[\alpha]_D$ +92° (c 1.47; CH_2Cl_2); ^1H NMR: δ 7.6–7.2 (m, 10 H), 5.55 (s, 1 H), 4.76 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.76 (dd, 2 H), 4.32 (m, 3 H, H-5,6a,6b), 4.16 (dd, 1 H, $J_{3,4}$ 3 Hz, H-3), 3.83 (dd, 1 H, H-2), 3.35 (s, 3 H, CH_3). Anal. Calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.93; H, 6.61.

The 3-benzyl ether **9** was eluted as the third product (3.5 g, 20%); mp 187–188°C; $[\alpha]_D$ +193° (*c* 1.1, CH_2Cl_2); lit.[20] mp 194°C; $[\alpha]_D$ +186° ($CHCl_3$).

(*b*) If TEBA-Cl was used instead of Aliquat 336, under the same conditions, a mixture of **9**, **10**, and **11** was obtained. By silica gel column chromatography (19:1 $CHCl_3$–heptane), the dibenzyl ether **10** was isolated in 8% yield, then the 2-benzyl ether **11** (20%), followed by the 3-benzyl ether **9** (60%).

(*c*) The use of 5 equiv of KOH and benzyl bromide with 0.2 equiv of Aliquat 336, under the same conditions as (*a*), led to the 2,3-di-*O*-benzyl derivative **10** (90% yield).

*Diethyl 2-O-benzyl-(*R,R*)-tartrate* (**13**).—Under vigorous shaking, diethyl (*R*,*R*)-tartrate (**12**; 4.12 g, 20 mmol) was added to a mixture of K_2CO_3 (3.45 g, 25 mmol), benzyl bromide (2.97 mL, 25 mmol), and Aliquat 336 (840 mg, 2 mmol). After 6 h at 60°C followed by addition of MeOH (3 mL), the mixture was diluted with EtOAc, filtered on Florisil, and evaporated; **13** was isolated by flash chromatography on silica gel (5:6 EtOAc–heptane) in 64% yield (12.8 mmol); $[\alpha]_D$ +72° (*c* 1, $CHCl_3$); lit.[25] $[\alpha]_D$ +73° ($CHCl_3$).

*Diethyl 2,3-di-O-benzyl-(*R,R*)-tartrate* (**14**).—(*a*) A mixture of **12** (412 mg, 2 mmol), K_2CO_3 (1.4 g, 10 mmol), benzyl bromide (0.6 mL, 5 mmol), Aliquat 336 (84 mg, 0.2 mmol), and KI (830 mg, 5 mmol) was vigorously stirred for 48 h at 20°C. After addition of MeOH (1 mL), the mixture was diluted with EtOAc, filtered on Florisil, and evaporated. By flash chromatography on silica gel (1:4 EtOAc–heptane), **13** and **14** were isolated in 34 and 54% yield, respectively; **14** was distilled: $bp_{0.5}$ 160°C; $[\alpha]_D$ +105° (*c* 0.98, $CHCl_3$). Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.36; H, 6.87.

(*b*) *From* **13**. By the same procedure as described above, **14** was prepared in 80% yield from **13**, using 2 mol equiv of K_2CO_3, BnBr, and KI, and 0.1 equiv of Aliquat 336.

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