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The Deoxygenation of Phosphine Oxides under Green Chemical Conditions

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ABSTRACT: *The deoxygenation of a few diarylphenylphosphine oxides, dimethyl-phenylphosphine oxide, and 3-methyl-1-phenyl-3-phospholene 1-oxide was studied by phenylsilane, tetramethyldisiloxane (TMDS), and polymethylhydrosiloxane (PMHS) under conventional or microwave (MW) heating, in toluene or in the absence of any solvent at different temperatures. It was found that the deoxygenation with TMDS or PMHS under MW and solvent-free conditions may be the method of choice and provides a green chemical approach.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–7, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21249

INTRODUCTION

The reduction of tertiary phosphine oxides to phosphines is applied to many syntheses, e.g., in the final step of the preparation of P-ligands [1–5] or during the regeneration of triphenylphosphine from triphenylphosphine oxide formed in the Wittig- or the Appel reaction. It has been a challenge to develop catalytic versions of these reactions involving the recycling of the waste cyclic phosphine oxides in in situ reduction [6]. O'Brian et al. have developed catalytic versions of the Wittig reaction involving in situ reduction, often using diphenylsilane, of a wide range of phosphine oxides including mainly phospholene- and phospholane derivatives [7–10]. In these cases, the phosphoranes were formed in situ by the quaternization of the phosphine by the α-haloacetic ester [7–9] or even an unactivated alkyl halide [8], followed by dehydrohalogenation by Na_2CO_3 [7, 9], diisopropylethylamine [8], or in situ generated ^tBuONa [10].

The most commonly used method for the deoxygenation of phosphine oxides involves the application of silanes [11–14]. Beside the silanes, other reducing agents, such as lithium aluminum hydride [12], sodium borohydride [15], diisobutylaluminum hydride (DIBAL) [16,17], or triphenylphosphine [18] were also described. Phenylsilanes, such as $PhSiH_3$, Ph_2SiH_2, and Ph_3SiH represent an important group within silanes [19, 20]. Phenylsilane ($PhSiH_3$) was used over a temperature range of 26–150°C [19, 20], whereas triphenylsilane (Ph_3SiH) was used at 300°C [19]. The application of $PhSiH_3$ is quite advantageous, as principally 0.33 equiv is enough due to the presence of the three H atoms. However, $PhSiH_3$ is rather expensive. Cl_3SiH is widely used in synthetic organic chemistry [21, 22]. The reduction of phosphine oxides with Cl_3SiH may be performed in an autoclave at 200°C [21], in boiling benzene in the presence of 1 equiv of triethylamine [21], or together with 3 equiv of pyridine [22]. In the latter case, the P-configuration was preserved [22]. Stereochemical retention was also justified by theoretical calculations [23]. It is a disadvantage that Cl_3SiH is quite volatile (bp 31.8°C) and corrosive. Alkyldichlorosilanes ($RSiCl_2H$, where R = C_1–C_4 and C_6 alkyl) and phenyldichlorosilane ($PhSiCl_2H$) were also used,

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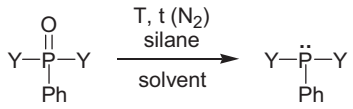


	Y	
1	Ph	**2**
3	4-MePh	**4**
5	4-ClPh	**6**
7	Me	**8**

SCHEME 1

but these reagents have not proved popular [24]. Perchlorosilanes (e.g., Si_2Cl_6) were also applied to deoxygenations [25], but they remained of limited use [25]. The group of user friendly silanes include $(EtO)_3SiH$ [26, 27], $(EtO)_2MeSiH$ [28], 1,1,3,3-tetramethyldisiloxane (TMDS), and polymethylhydrosiloxane (methylpolysiloxane [PMHS]) that has the structure of $[–O–SiH(Me)–]_n$ [19,26,28]. These silanes are not as reactive as, e.g., $PhSiH_3$ or Cl_3SiH. The deoxygenations by TMDS were performed in the presence of a catalytic amount of titanium(IV) isopropoxide [29]. $(EtO)_3SiH$ was also used together with $Ti(O^iPr)_4$ as the catalyst [26,27]. Deoxygenations by TMDS and PMHS were also catalyzed by copper salts and Brønsted acid catalysts (e.g., by $Cu(OTf)_2$ or the diphenyl ester of phosphoric acid, respectively) [28,30]. The authors reported that these catalysts were helpful at 100–110°C in toluene.

If was a challenge for us to study the deoxygenations of phosphine oxides by TMDS and PMHS that are relatively cheap and user friendly reagents. In this article, the optimum conditions for the reductions by TMDS and PMHS are described. Our preference was to carry out the reductions without the use of any catalyst.

RESULTS AND DISCUSSION

The phosphine oxides selected (diaryl-phenylphosphine oxides, dimethyl-phenylphosphine oxides, and 3-methyl-1-phenyl-3-phospholene 1-oxide) were reduced by phenylsilane (PS), TMDS, and PMHS under different conditions in an aromatic solvent, or without any solvent, using conventional heating or on microwave (MW) irradiation. The reaction mixtures were analyzed by ^{31}P NMR.

The first model reaction was the deoxygenation of triphenylphosphine oxide (**1**) (Scheme 1). Experimental details of the optimizations are listed in Table 1.

The reduction of triphenylphosphine oxide **1** with 9 equiv of PS at 110°C in toluene was slow. After a 12-h reaction time, the conversion to triphenylphosphine (**2**) was only 14% (Table 1, entry 1). At the same time, under solvent-free conditions, the deoxygenation was practically quantitative after 3 h (Table 1, entry 2). On increasing the temperature to 150°C, a 1-h reaction time was sufficient (Table 1, entry 3). The best variation is to carry out the **1** → **2** transformation at 150°C under solvent-free and MW-assisted conditions. In this case, the deoxygenation was complete already after 30 min. The workup involved essentially a filtration via a thin silica layer using hexane–ethyl acetate to give triphenylphosphine (**2**) in a yield of 95% (Table 1, entry 4).

Then, we changed to the less reactive TMDS that was applied to a 10-equiv quantity (that is really a 5 molar equivalent quantity) at 175°C using 1,4-xylene as the solvent, or performing the reduction in the absence of solvent. After a reduction time of 48 and 24 h, the conversion was 53% and 100%, respectively (Table 1, entries 5 and 6). Changing to MW heating, at 175°C/6 h and 200 °C/6 h, the conversion to phosphine **2** was 47% and 93%, respectively (Table 1, entries 7 and 8). In the latter case, the preparative yield of phosphine **2** was 89%.

PMHS was also tried, being applied to a quantity of 5 equiv at 175°C. To carry out the reduction in 1,4-xylene for 48 h, without any solvent for 16 h and under solvent-free MW conditions for 7.5 h, the conversion was 85%, 100%, and 98%, respectively (Table 1, entries 9–11). In the last case, phosphine **2** was isolated with a yield of 90%.

The best experiments were those marked by entries 4, 8, and 11 in Table 1.

The reductive experiments with phenyl-di(4-methylphenyl)phosphine oxide (**3**) led essentially to results similar to those obtained with triphenylphosphine oxide (**1**) (Scheme 1, Table 2). Mostly solvent-free deoxygenations were studied with the three silanes (PS, TMDS, and PMHS). In respect of the MW-assisted variations, the reductions with TMDS at 200°C for 6 h and with PMHS at 175°C for 7.5 h (Table 2, entries 5 and 8) are good alternatives of the accomplishment by PS at 150°C for 0.5 h (Table 2, entry 2). On conventional heating at lower or at the same temperature, the completion required a longer period of time (Table 2, entries 1, 3, and 7). The isolated yields of phenyl-di(4-methylphenyl)phosphine **4** from the best MW-promoted reductions amounted to ca. 87% (Table 2, entries 2, 5, and 8).

Our next model reaction was the reduction of di(4-chlorophenyl)-phenylphosphine oxide (**5**) (Scheme 1). The experimental data are listed in Table 3. PS could be used as in the deoxygenation of the other diaryl-phenylphosphine oxides **1** and **3**. It can also be seen that in a reaction with TMDS and PMHS, di(4-chlorophenyl)-phenylphosphine

TABLE 1 Deoxygenation of Triphenylphosphine Oxide (**1**) (0.36 mol) by Different Silanes on Conventional Heating or on MW Irradiation

Entry	*Silane*	*Equivalent*	*Mode of Heating*	*T (°C)*	*t (h)*	*Solvent*	*Conversion (%)*	*Yield (%)*	*Comment*
1	$PhSiH_3$	9	Δ	110	12	2 mL toluene	14		
2	$PhSiH_3$	9	Δ	110	3	–	97	86	
3	$PhSiH_3$	9	Δ	150	1	–	100	92	
4	$PhSiH_3$	9	MW	150	0.5	–	99	95	
5	TMDS	10	Δ	175	48	2 mL 1,4-xylene	53		
6	TMDS	10	Δ	175	24	–	100	91	
7	TMDS	10	MW	175	6 (t_{extrap}[a] ~14)	–	47		
8	TMDS	10	MW	200	6	–	93	89	
9	PMHS	5	Δ	175	48	2 mL 1,4-xylene	85		Solid crude mixture
10	PMHS	5	Δ	175	16	–	100		Solid crude mixture
11	PMHS	5	MW	175	7.5	–	98	90	Solid crude mixture

[a] t_{extrap} = Extrapolated reaction time.
Δ = Conventional heating.

TABLE 2 Deoxygenation of Phenyl-di(4-methylphenyl)phosphine Oxide (**3**) by Different Silanes on Conventional Heating or on MW Irradiation

Entry	*Silane*	*Equivalent*	*Mode of Heating*	*T (°C)*	*t (h)*	*Solvent*	*Conversion (%)*	*Yield (%)*	*Comment*
1	$PhSiH_3$	9	Δ	110	3	–	98	91	
2	$PhSiH_3$	9	MW	150	0.5	–	97	89	
3	TMDS	10	Δ	175	24	–	94	85	
4	TMDS	10	MW	175	6 (t_{extrap}[a] ~14)	–	46		
5	TMDS	10	MW	200	6	–	93	86	
6	PMHS	5	Δ	175	48 (t_{extrap}[a] ~60)	2 mL 1,4-xylene	76		
7	PMHS	5	Δ	175	20	–	100	93	Solid crude mixture
8	PMHS	5	MW	175	7.5	–	92	88	Solid crude mixture

[a] t_{extrap} = Extrapolated reaction time.
Δ = Conventional heating.

TABLE 3 Deoxygenation of Di(4-chlorophenyl)-phenylphosphine Oxide (**5**) by Different Silanes on Conventional Heating or on MW Irradiation

Entry	*Silane*	*Equivalent*	*Mode of Heating*	*T (°C)*	*t (h)*	*Conversion (%)*	*Yield (%)*	*Comment*
1	$PhSiH_3$	9	Δ	110	3	97	91	
2	$PhSiH_3$	9	MW	150	0.5	92	87	
3	TMDS	10	Δ	175	24	74		
4	TMDS	10	MW	175	6	36		
5	TMDS	10	MW	200	8	90	86	
6	PMHS	5	Δ	175[a]	24	51		Solid crude mixture
7	PMHS	5	MW	175[b]	7.5	54		Solid crude mixture

[a] 50 μL of toluene was added as a homogenizing additive.
[b] The addition of 50 μL of toluene did not have any impact on the course of the reaction.
Δ = Conventional heating.

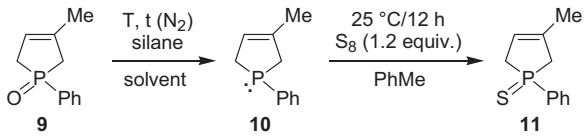
oxide (**5**) is less reactive than the previous model compounds (**1** and **3**). Using TMDS at 175°C, the conversions were lower both on conventional heating (24 h) and under MW (6 h) conditions as compared to the unsubstituted case as shown by the conversions of 74% versus 100% and 36% versus 47%, respectively (Table 3, entry 3 vs. Table 1, entry 6 and Table 3, entry 4 vs. Table 1, entry 7). The MW

variation at 200°C required 8 h to obtain a conversion of 90% (Table 3, entry 5). The yield of phosphine **6** was almost the same (86%), as that obtained in the case, when PS was applied at 150°C for 0.5 h under MW conditions (87%) (Table 3, entries 5 and 2). At the same time, chlorophenyl derivative **5** could not be deoxygenated quantitatively with PMHS due to the heterogeneity of the reaction mixture. There was practically no difference between the outcome of the traditional thermal and the MW-assisted reactions (Table 3, entries 6 and 7). The addition of a small quantity of toluene as a "cosolvent" did not help either.

One can see that the more reactive, but expensive PS can be replaced well by the less reactive, but cheaper TMDS or, with the exception of the case of the chlorophenyl derivative, PMHS. The preparative yields of triarylphosphines (**1–5**) were around 90%. It is also noteworthy that the deoxygenations were accomplished under solvent-free and MW-assisted conditions, providing an advantage from the point of view of green chemistry techniques.

Then, reduction of an obviously more reactive phosphine oxide, dimethyl-phenylphosphine oxide **7** was investigated (Scheme 1). As can be seen from Table 4, all the three kinds of silanes could be used at somewhat milder conditions, than in the case of triarylphosphine oxides (**1**, **3**, and **5**). The deoxygenation of phosphine oxide **7** by PS at 110°C required 2 h on conventional heating and 1 h under MW irradiation (Table 4, entries 1 and 2). In the presence of only 3 equiv of PS, quantitative deoxygenation was achieved at 130°C after a 1 h of MW irradiation (Table 4, entry 3). Using TMDS at 150°C, completion of the thermal and the MW-assisted variation required 15 and 9 h, respectively (Table 4, entries 4 and 5). On increasing the temperature of the MW-promoted reaction to 175°C, the deoxygenation was complete after 4 h even in the presence of only 4 equiv of TMDS (Table 4, entry 6). Applying PMHS at 150°C and depending on whether conventional or MW heating was used, completion of the reaction required 10 and 4.5 h, respectively (Table 4, entries 7 and 8). At 175°C, the MW variation completed after 2 h even in the presence of only 2 equiv of PMHS (Table 4, entry 9). The best experiments were again the MW-promoted deoxygenations giving dimethyl-phenylphosphine **8** in 88–94% yield after a filtration through a thin silica gel layer (Table 4, entries 3, 6, and 9) and, for these reactions, the cheaper TMDS and PMHS may well replace the more expensive PS. MW irradiation made it possible to shorten reduction times, and there was no need for a solvent.

Finally, the deoxygenation of 3-methyl-1-phenyl-3-phospholene 1-oxide (**9**) was studied in silane



SCHEME 2

reductions. In this case, the phosphine (**10**) was quite sensitive to air oxidation, and so this was prevented by an in situ reaction with sulfur to give the corresponding phospholene sulfide (**11**) for identification (Scheme 2).

Earlier, the reduction of 3-methyl-1-phenyl-3-phospholene 1-oxide **9** by silanes was studied in toluene solutions [31]. Applying PS, TMDS, and PMHS in boiling toluene, completion of the deoxygenation required 6–8 h. The experimental details of the present study are listed in Table 5. The enhanced reactivity of the phospholene oxide (**9**) and the oily consistency made possible the use of the silanes in a smaller quantity. Hence, PS, TMDS, and PMHS were applied to a quantity of 3, 4, and 2 equiv, respectively. Using PS at 80°C without any solvent, the completion of the deoxygenation required 2 h (Table 5, entry 1). Under solvent-free MW conditions, the reaction time was 1 h (Table 5, entry 2).

Changing to TMDS and selecting 110°C, under thermal and MW conditions, the reaction time was 5 and 3 h, respectively (Table 5, entries 3 and 4). Finally, the experiments with PMHS performed at 110°C showed that the thermal deoxygenation took 4 h, whereas the MW variation only 2 h (Table 5, entries 5 and 6).

The yields of the MW-assisted reactions amounted to 91–92%, and TMDS along with PMHS were again fully comparable with PS. MW activation, together with solvent-free conditions, providing an attractive alternative for the deoxygenations with silanes.

On the basis of our experiences, the order of reactivity of the phosphine oxides tested is as follows:

$(4\text{-ClPh})_2P(O)Ph < Ph_3P(O) \sim (4\text{-MePh})_2P(O)Ph < Me_2P(O)Ph <$ 

The trialkylphosphine oxides are less reactive as a consequence of the steric hindrance around the P=O moiety. 3-Phospholene 1-oxide **9** may be more reactive than $PhP(O)Me_2$, as on the one hand, the ring system results in some decrease in the steric hindrance. On the other hand, unsaturation may also promote reactivity.

In summary, the deoxygenation of phosphine oxides by the cheaper reagents TMDS and PMHS

TABLE 4 Deoxygenation of Dimethyl-phenylphosphine Oxide (**7**) by Different Silanes on Conventional Heating or on MW Irradiation

Entry	*Silane*	*Equivalent*	*Mode of Heating*	*T (°C)*	*t (h)*	*Conversion (%)*	*Yield (%)*	*Comment*
1	$PhSiH_3$	9	Δ	110	2	100	93	
2	$PhSiH_3$	9	MW	110	1	97	90	
3	$PhSiH_3$	3	MW	130	1	99	94	
4	TMDS	10	Δ	150	15	97	89	
5	TMDS	10	MW	150	6 (t_{extrap}[a] ~9)	70		
6	TMDS	4	MW	175	4	98	88	
7	PMHS	5	Δ	150	10	100	95	Solid crude mixture
8	PMHS	5	MW	150	4 (t_{extrap}[a] ~4.5)	87		Solid crude mixture
9	PMHS	2	MW	175	2	100	93	Solid crude mixture

[a] t_{extrap} = Extrapolated reaction time.
Δ = Conventional heating.

TABLE 5 Deoxygenation of 3-Methyl-1-phenyl-3-phospholene 1-Oxide (**9**) without a Solvent by Different Silanes on Conventional Heating or MW Irradiation

Entry	*Silane*	*Equivalent*	*Mode of Heating*	*T (°C)*	*t (h)*	*Conversion. (%)*	*Yield (%)*[a]
1	$PhSiH_3$	3	Δ	80	2	100	95
2	$PhSiH_3$	3	MW	80	1	100	91
3	TMDS	4	Δ	110	5	100	92
4	TMDS	4	MW	110	3	100	92
5	PMHS	2	Δ	110	4	100	91
6	PMHS	2	MW	110	2	100	92

[a]The phosphine (**10)** was identified as its sulfide (**11**).
Δ = Conventional heating.

may offer a good alternative under MW and solvent-free conditions to replace the more expensive and more reactive PS. This is the first case that TMDS and PMHS turned out to be generally usable deoxygenation agents. The application of MW and solvent-free conditions offers a greener chemical approach.

EXPERIMENTAL

General

^1H, ^{13}C, and ^{31}P NMR spectra were obtained in a $CDCl_3$ solution on a Bruker AV-300 spectrometer operating at 300, 75.5, and 121.5 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 and TMS. Couplings are given in hertz. High-resolution molecular weights were obtained using a Q-TOF Premier mass spectrometer in the positive electrospray mode. PMHS with an average molecular weight 1700–3200 was used. The reactions were carried out in a 300-W CEM Discover focused MW reactor equipped with a pressure controller applying 50–80 W under isothermal conditions.

General Procedure for the Deoxygenation of the Phosphine Oxides **1**, **3**, **5**, *and* **7**

Using PS in a Quantity of 9 Equiv. A mixture of 0.36 mmol of phosphine oxide (**1**: 0.10 g, **3**: 0.11 g, **5**: 0.098 g, **7**: 0.13 g) and 1.1 mmol (0.13 mL) of PS was heated under nitrogen atmosphere using an oil bath or a MW oven at the appropriate temperature in a glass bomb (a thick-wall glass tube that can be closed) or in a commercial MW vial, respectively, for the appropriate time. Then, the reaction mixture was cooled to room temperature and after taking up the oily mixture in some ethyl acetate, it was absorbed on a 2-cm layer of silica gel. Then, the phosphine was washed off using hexane–ethyl acetate, 9:1 to afford the corresponding phosphine (**2**: as a white solid, or **4, 6**, and **8**: as colorless oils). (For the details, see Tables 1–4.) As a matter of fact, the main fraction was collected after a smaller prefraction.

Using TMDS in a Quantity of 10 Equiv. The reductions were carried out as those with PS shown above using 1.8 mmol (0.32 mL) of TMDS. The phosphines (**2**, **4**, **6**, and **8**) were obtained as a white solid (**2**) or as colorless oils (**4**, **6**, and **8**). (For the details, see Tables 1–4.)

Using PMHS in a Quantity of 5 Equiv. The reductions were carried out as those with PS shown above using 1.8 mmol (0.068 mL) of PMHS. The phosphines (**2**, **4**, **6**, and **8**) were obtained as a white solid (**2**) or as colorless oils (**4**, **6**, and **8**). (For the details, see Tables 1–4.)

The following phosphines were prepared:

Triphenylphosphine (**2**). Based on the experimental details presented in Table 1 (entry 3), yield: 95%; white solid, mp: 81–82°C; mp. [32]: 79–81°C; ^{31}P NMR ($CDCl_3$) δ: –5.0, δ: ($CDCl_3$) [32]: –5.1; $[M + H]^+_{found} = 263.0980$, $C_{18}H_{16}P$ requires: 263.0984.

Phenyl-di(p-tolyl)phosphine (**4**). Based on the experimental details presented in Table 2 (entry 8), yield, 92%; colorless oil; ^{31}P NMR ($CDCl_3$) δ: –6.8, δ ($CDCl_3$) [33]: –6.2; $[M + H]^+_{found} = 291.1304$, $C_{20}H_{20}P$ requires: 291.1297.

Bis(4-chlorophenyl)-phenylphosphine (**6**). Based on the experimental details presented in Table 3 (entry 1), yield: 91%; colorless oil; ^{31}P NMR ($CDCl_3$) δ: –7.4, δ ($CDCl_3$); ^{13}C NMR ($CDCl_3$) δ: 128.8 (J = 8.4, $C_{2'}$),[a] 128.9 (J = 7.2, C_2),[b] 129.2 ($C_{4'}$),[c] 133.7 (J = 19.8, $C_{3'}$),[a] 135.0 (J = 20.3, C_3),[b] 135.1 (C_4),[c] 135.5 (J = 106.0, $C_{1'}$),[d] 135.7 (J = 96.0, C_1)[d], [a–d] may be reversed; ^{1}H NMR ($CDCl_3$) δ: 6.90–7.80 (m, ArH); $[M + H]^+_{found} = 331.0212$, $C_{18}H_{14}Cl_2P$ requires: 331.0205.

Dimethyl-phenylphosphine (**8**). Based on the experimental details presented in Table 4 (entry 8), yield: 95%; colorless oil; ^{31}P NMR ($CDCl_3$) δ: –43.2, δ ($CDCl_3$) [34]: –42.4; $[M + H]^+_{found} = 139.0682$, $C_8H_{12}P$ requires: 139.0677.

*General Procedure for the Deoxygenation of 1-Phenyl-3-methyl-3-phospholene 1-Oxide (**9**), and for the Trapping of the Phosphine (**10**) so Obtained*

A mixture of 0.11 g (0.55 mmol) of 1-phenyl-3-methyl-3-phospholene 1-oxide (**9**) and 0.068 mL (0.55 mmol) of PS or 0.19 mL (1.1 mmol) of TMDS or 0.042 mL (1.1 mmol) of PMHS was heated under nitrogen atmosphere at the appropriate temperature in a glass bomb immersed in an oil bath or in a commercial MW vial in the MW oven for the appropriate time. Then, the reaction mixture was cooled to room temperature to afford phosphine **10** that was reacted further immediately to form the corresponding sulfide (**11**).

To the ~0.55 mmol of the corresponding phosphine (**10**) in 2 mL of toluene, 20.7 mg (0.65 mmol) of powdered sulfur was added under nitrogen. The mixture was stirred at 26°C overnight and then evaporated to dryness. Column chromatography (hexane–ethyl acetate, 9:1 as an eluent) of the residue afforded the sulfide (**11**) as a dense oil. (For the details, see Table 5.)

3-Methyl-1-phenyl-3-phospholene 1-sulfide (**11**). ^{31}P NMR ($CDCl_3$) δ: 55.3, δ ($CDCl_3$) [35]: 55.3; $[M + H]^+_{found} = 209.0554$, $C_{11}H_{14}PS$ requires $[M + H]^+ = 209.0554$.

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