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RESEARCH ARTICLE

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A study on the deoxygenation of trialkyl-, dialkyl-phenyl- and alkyl-diphenyl phosphine oxides by hydrosilanes

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Abstract

The deoxygenation of 1-alkyl-3-methyl-3-phospholene 1-oxides, which may be regarded as trialkyl phosphine oxides (R_3PO), and the reduction of dialkyl-phenylphosphine oxides (R_2PhPO) and methyl-diphenylphosphine oxide ($MePh_2PO$) have been elaborated by applying user-friendly silanes, such as tetramethyldisiloxane (>SiH–O–HSi<) and polymethylhydrosiloxane ($(O–SiH)_n$) under solvent-free, catalyst-free, and microwave (MW)-assisted conditions. New silanes of type Ar_2SiH_2, $alkyl_2SiH_2$, and Ar_3SiH were also applied in a few cases. The reactivity of the phosphine oxides and the silanes could be mapped on the basis of our experimental data.

1 | INTRODUCTION

These days, the deoxygenation of phosphine oxides is in the focus due to its high importance.[1-6] The resulting phosphines, on the one hand, may be useful intermediates, and on the other hand, they may serve as P-ligands in transition metal complexes. Transformations, such as the Wittig, Appel, and the Mitsunobu reactions, involve the stoichiometric conversion of triphenylphosphine to triphenylphosphine oxide causing an environmental burden and meaning cost. These problems can be eliminated by applying the phosphine in a catalytic amount, and by insuring the in situ reduction of the phosphine oxide formed. This was first elaborated for the Wittig reaction using silanes as the reducing agent by O'Brien.[7-10] Since then, the catalytic Wittig reaction has become a hot topic and found a number of applications.[11-16] It is worth mentioning that P-aryl and alkyl phospholanes and phospholenes are the most suitable phosphines in the catalytic cycles due to the easy reducibility of the related ring phosphine oxides.[7,8] The ring strain is known to significantly aid the deoxygenation of the P=O group.[17]

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Many silanes were described as reducing agents. Trichlorosilane is the most widespread reagent[18-20]; however, its volatile (bp: 32°C) and corrosive properties mean disadvantage. For this, Cl_3SiH is, in most cases, applied together with three equivalents of pyridine or triethylamine that has also an impact on the stereochemistry.[19] Phenylsilane may be the choice of the reagent for the deoxygenation of the P=O function; however, despite the fact that a quantity of 0.33 equivalents is enough, it is rather expensive.[21-23] Tetramethyldisiloxane (TMDS) and polymethylhydrosiloxane (PMHS) are cheap, but not too reactive reducing agents. For this, copper-, titanium- and indium-catalyzed methods,[24-28] along with a phosphoric acid diester-promoted protocol[29] were developed for the deoxygenation of phosphine oxides.

During our earlier work, we studied the deoxygenation of 1-phenyl-3-methyl-3-phospholene 1-oxide (**1**) by different silanes (**3**-**10**) in detail.[30,31] The most important results are summarized in Scheme 1 and Table 1. The expensive phenylsilane ($PhSiH_3$) **3** was found to be the best reagent under solvent-free and microwave (MW)-assisted conditions that could be replaced well by TMDS (**4**) and PMHS (**5**), although somewhat higher temperatures and longer reaction times were necessary (Table 1, entries 2 and 3 vs 1).[30] Later on, other silanes were also tried out.[31] It was found that 1-naphthylsilane ($NaphSiH_3$ **6**), benzylsilane ($BnSiH_3$ **7**), and

bis(4-methylphenyl)silane [$(4\text{-MePh})_2SiH_2$ **8**] were more reactive than PMHS (**5**) and TMDS (**4**) (Table 1, entries 4–6), but tetraphenyl-disilane ($[Ph_2SiH]_2$ **10**) and bis(1-naphthyl) silane ($[1\text{-Naph}]_2SiH_2$ **9**) were less reactive than PMHS (**5**) (Table 1, entries 7 and 8). The reactivity of $(Ph_2SiH)_2$ (**10**) and TMDS (**4**) seemed to be comparable.

The MW-assisted and solvent-free deoxygenation of triarylphosphine oxides (Ar_3PO, where Ar=Ph, 4-MePh, 4-ClPh) requested a higher excess of the silanes (**3**-**5**) and more forcing conditions.[30] Applying $PhSiH_3$ (**3**) in a quantity of nine equivalents, the reductions were complete after a 0.5-hour irradiation at 150°C. Using 10 equivalents of TMDS (**4**) or five equivalents of PMHS (**5**), the deoxygenations were complete after a treatment of 200°C for 6-8 hour and 175°C for 7.5 hour, respectively.[30] Steric hindrance is a limiting factor for P=O deoxygenations.

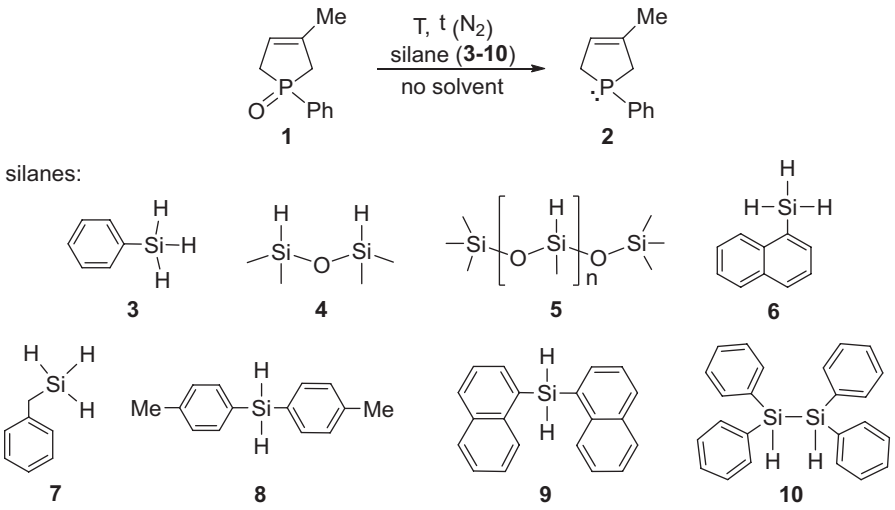
It is a green chemical approach to substitute catalysts by MW irradiation. We experienced that in heterogeneous phase C-alkylations,[32-34] and in Kabachnik-Fields reactions,[35-37] the catalysts could be omitted under MW conditions. It was shown above that this approach was utilized in the TMDS- and PMHS-promoted deoxygenations.[30,31] Due to their lower reactivity, TMDS and PMHS were advised to be applied together with metal-containing or metal-free catalysts.[24-29] We found that under MW irradiation, there is no need for any catalyst (Table 1, entries 2 and 3).[30,31]

In this article, we wish to make a further profit of our finding by extending the method to the reduction of a series of phosphine oxides of type $R_{3-n}PAr_n$ (where n=0, 1, 2). It was also our purpose to set the order of reactivity of the phosphine oxides and also that of the silanes. For this, we planned to test a few more new silanes.

2 | RESULTS AND DISCUSSION

Our first model compounds were 1-alkyl-3-methyl-3-phospholene oxides (**11a**-**d**) that may be important precursors for phosphines in catalytic Wittig reactions, as it was mentioned in the Introduction.[7-10] These trialkyl-like phosphine oxides (**11a**-**d**) were subjected to deoxygenation by $PhSiH_3$, TMDS, and PMHS under solvent-free conditions (Scheme 2). The phosphines (**12a**-**d**) were analyzed as the corresponding phospholene sulfides (**13a**-**d**). Experimental data are summarized in Table 2.

As regards the reduction of 1-ethyl-, 1-propyl-, 1-butyl-, and 1-isopentyl-3-phospholene oxides (**11a**-**d**) with $PhSiH_3$ (**3**), there was practically no observable differences in their

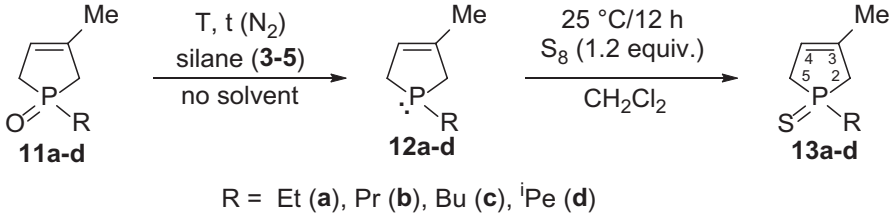


SCHEME 1 Deoxygenation of 3-methyl-1-phenyl-3-phospholene 1-oxide (**1**) by silanes under solvent-free, microwave-assisted conditions[30,31]

TABLE 1 Deoxygenation of 3-methyl-1-phenyl-3-phospholene 1-oxide (**1**) by different silanes under solvent-free, microwave-assisted conditions

Entry	Silane	Equiv.	*T* (°C)	*t*	Conv. (%)[a]	Literature
1	$PhSiH_3$ (**3**)	1	80	40 min	100	[30]
2	TMDS (**4**)	2	110	3 h	100	[30]
3	PMHS (**5**)	2	110	2 h	100	[30]
4	$NaphSiH_3$ (**6**)	1	80	30 min	100	[31]
5	$BnSiH_3$ (**7**)	1	80	50 min	100	[31]
6	$(4\text{-MePh})_2SiH_2$ (**8**)	1	80	1 h	100	[31]
7	$(1\text{-Naph})_2SiH_2$ (**9**)	1	150	1 h	98	[31]
8	$(Ph_2SiH)_2$ (**10**)	1	150	45 min	100	[31]

[a]On the basis of the relative ^{31}P NMR intensities.



SCHEME 2 Deoxygenation of 1-alkyl-3-methyl-3-phospholene 1-oxides (**11a-d**) by silanes (**3-5**) under solvent-free conditions

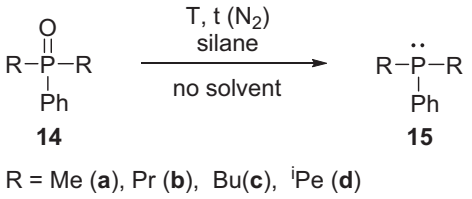
TABLE 2 Deoxygenation of 1-alkyl-3-methyl-3-phospholene 1-oxides (**11a-d**) without solvent by different silanes on conventional heating or microwave irradiation

Entry	Phospholene oxide	Silane	Equiv.	Mode of heating	*T* (°C)	*t*	Conv. (%)[a]	Yield of 13 (%)
1	**11a**	$PhSiH_3$ (**3**)	1	Δ	80	1 h	~100	90 (**13a**)
2	**11a**	$PhSiH_3$ (**3**)	1	MW	80	35 min	100	91 (**13a**)
3	**11a**	TMDS (**4**)	2	Δ	110	5.5 h	99	90 (**13a**)
4	**11a**	TMDS (**4**)	2	MW	110	3 h	90	82 (**13a**)
5	**11a**	PMHS (**5**)	2	Δ	110	3 h	100	90 (**13a**)
6	**11a**	PMHS (**5**)	2	MW	110	2 h	100	93 (**13a**)
7	**11b**	$PhSiH_3$ (**3**)	1	Δ	80	70 min	~100	90 (**13b**)
8	**11b**	$PhSiH_3$ (**3**)	1	MW	80	45 min	100	89 (**13b**)
9	**11b**	TMDS (**4**)	2	Δ	110	9 h	~100	91 (**13b**)
10	**11b**	TMDS (**4**)	2	MW	110	5 h	~100	88 (**13b**)
11	**11b**	PMHS (**5**)	2	Δ	110	4 h	~100	91 (**13b**)
12	**11b**	PMHS (**5**)	2	MW	110	2 h	~100	93 (**13b**)
13	**11c**	$PhSiH_3$ (**3**)	1	Δ	80	1 h	100	94 (**13c**)
14	**11c**	$PhSiH_3$ (**3**)	1	MW	80	40 min	~100	89 (**13c**)
15	**11c**	TMDS (**4**)	2	Δ	110	6 h	98	90 (**13c**)
16	**11c**	TMDS (**4**)	2	MW	110	4 h	91	85 (**13c**)
17	**11c**	PMHS (**5**)	2	Δ	110	3 h	99	91 (**13c**)
18	**11c**	PMHS (**5**)	2	MW	110	2 h	100	93 (**13c**)
19	**11d**	$PhSiH_3$ (**3**)	1	Δ	80	1 h	~100	92 (**13d**)
20	**11d**	$PhSiH_3$ (**3**)	1	MW	80	45 min	100	90 (**13d**)
21	**11d**	TMDS (**4**)	2	Δ	110	6 h	94	89 (**13d**)
22	**11d**	TMDS (**4**)	2	MW	110	4 h	90	88 (**13d**)
23	**11d**	PMHS (**5**)	2	Δ	110	3 h	97	90 (**13d**)
24	**11d**	PMHS (**5**)	2	MW	110	2 h	92	88 (**13d**)

[a]On the basis of relative ^{31}P NMR intensities.

reactivity (Table 2, entries 1, 7, 13, and 19). The MW-assisted accomplishments were significantly faster (Table 2, entries 2, 8, 14, and 20). Using $PhSiH_3$ (**3**), the reactivity of the alkyl-3-phospholene oxides (**11a-d**) was comparable with that of the phenyl derivative (**1**) (Table 1, entry 1). Applying TMDS (**4**) for the series under discussion (**11a-d**), the deoxygenations took somewhat longer than for the 1-phenyl-3-phospholene oxide **1** (Table 2, entries 3/4, 9/10, 15/16, and 21/22 vs Table 1, entry 2 in respect of the MW-assisted accomplishments). Hence, TMDS (**4**) seems to reveal a somewhat lower reactivity toward 1-alkyl-3-phospholene oxides (**11a-d**) than toward the 1-phenyl derivative (**1**). Using PMHS (**5**), it can be said that the reactivity toward the 1-alkyl-3-phospholene oxides (**11a-d**) is more or less the same, as that toward the 1-phenyl substrate (**1**) (Table 2, entries 5/6, 11/12, 17/18, and 23/24 Table 1, entry 3 in respect of the MW-assisted variations).

The point is that in the case of 1-alkyl-3-methyl-3-phospholene 1-oxides (**11a-d**), $PhSiH_3$ (**3**) may also be replaced by the cheap and user-friendly TMDS (**4**) and PMHS (**5**). In both variations, MW assistance is advantageous. The corresponding phosphine sulfides (**13a-d**) were prepared in yields of 82%-93%. The 1-alkyl-3-methyl-3-phospholene 1-sulfides (**13a-d**) are new compounds that were characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectral data, as well as HRMS.



SCHEME 3 Deoxygenation of dialkyl-phenylphosphine oxides (**14a-d**) by silanes **3-5**

After the deoxygenation of 1-alkyl-3-phospholene oxides (**11a-d**) that can be regarded as "trialkyl"-like tertiary phosphine oxides, the next model compounds were dialkyl-phenylphosphine oxides and methyl-diphenylphosphine oxide. These tertiary phosphine oxides were reduced by user-friendly silanes $PhSiH_3$ (**3**), TMDS (**4**), and PMHS (**5**) under solvent-free and MW-assisted conditions. In these cases, the products were isolated as phosphines. Comparative thermal experiments were also carried out.

Experimental data on the deoxygenation of dialkyl-phenylphosphine oxides (**14a-d**) (Scheme 3) are found in Table 3. The reducing agents $PhSiH_3$ (**3**), TMDS (**4**), and PMHS (**5**) were used in a one equivalent, two equivalents, and two equivalents quantity, respectively, in the range of 110-175°C.

Reduction of dimethyl-phenylphosphine oxide (**14a**) with $PhSiH_3$ (**3**), TMDS (**4**), and PMHS (**5**) under MW conditions required a reaction time of 0.75, 5, and 2.5 hour, respectively (Table 3, entries 1, 3, and 5), while the thermal variations were complete after 1.75, 8, and 5 hour, respectively (Table 3, entries 2, 4, and 6). Dimethyl-phenylphosphine (**15a**) was isolated in yields of 90%-95%.

Dipropyl-phenylphosphine oxide (**14b**) revealed a similar reactivity toward $PhSiH_3$ (**3**) (Table 3, entries 7 and 8), but in respect of TMDS (**4**) and PMHS (**5**), its reactivity was somewhat lower (Table 3, entries 9-12). Regarding the MW-assisted deoxygenations, reaction times of 0.75, 6, and 4 hour were necessary using $PhSiH_3$ (**3**), TMDS (**4**), and PMHS (**5**), respectively (Table 3, entries 7, 9, and 11). Dipropyl-phenylphosphine (**15b**) could be prepared in yields of 85%-88%.

TABLE 3 Deoxygenation of dialkyl-phenylphosphine oxides (**14a-d**) by different silanes under solvent-free conditions on conventional heating or microwave irradiation

Entry	Phosphine oxide	Silane	Equiv.	Mode of heating	*T* (°C)	*t* (h)	Conv. (%)[a]	Yield (%)
1	**14a**	$PhSiH_3$ (**3**)	1[b]	MW	110	0.75	~100	92
2	**14a**	$PhSiH_3$ (**3**)	1	Δ	110	1.75	~100	95
3	**14a**	TMDS (**4**)	2	MW	175	5	95	90
4	**14a**	TMDS (**4**)	2	Δ	175	8	98	
5	**14a**	PMHS (**5**)	2	MW	175	2.5	92	83
6	**14a**	PMHS (**5**)	2	Δ	175	5	96	
7	**14b**	$PhSiH_3$ (**3**)	1	MW	110	0.75	96	85
8	**14b**	$PhSiH_3$ (**3**)	1	Δ	110	1.75	96	87
9	**14b**	TMDS (**4**)	2	MW	175	6	88	
10	**14b**	TMDS (**4**)	2	Δ	175	10	90	
11	**14b**	PMHS (**5**)	2	MW	175	4	98	88
12	**14b**	PMHS (**5**)	2	Δ	175	6	95	
13	**14c**	$PhSiH_3$ (**3**)	1	MW	110	1	95	88
14	**14c**	$PhSiH_3$ (**3**)	1	Δ	110	2	99	
15	**14c**	TMDS (**4**)	2	MW	175	7	98	90
16	**14c**	TMDS (**4**)	2	Δ	175	10	90	
17	**14c**	PMHS (**5**)	2	MW	175	4	92	84
18	**14c**	PMHS (**5**)	2	Δ	175	6	97	
19	**14d**	$PhSiH_3$ (**3**)	1	MW		1.25	95	87
20	**14d**	$PhSiH_3$ (**3**)	1	Δ	110	2.5	97	
21	**14d**	TMDS (**4**)	2	MW	175	7	94	89
22	**14d**	TMDS (**4**)	2	Δ	175	10	85	
23	**14d**	PMHS (**5**)	2	MW	175	4	90	82
24	**14d**	PMHS (**5**)	2	Δ	175	6	83	

[a]On the basis of relative ^{31}P NMR intensities.

[b]Nine equivalents of $PhSiH_3$ were used in an unoptimized experiment.[30]

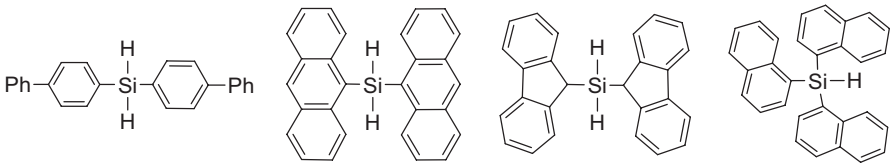


FIGURE 1 New silanes applied by us in deoxygenations

TABLE 4 Deoxygenation of 3-methyl-1-phenyl-3-phospholene 1-oxide (**1**) by silanes **16**-**19** under solvent-free conditions

Entry	Silane	Equiv.	Mode of heating	*T* (°C)	*t* (h)	Conv. (%)[a]
1	$Anth_2SiH_2$ (**17**)	1	Δ[b]	180	3	98
2	$Anth_2SiH_2$ (**17**)	1	MW[b]	180	1.5	96
3	$Fluorenyl_2SiH_2$ (**18**)	1	Δ[b]	150	2	100
4	$Fluorenyl_2SiH_2$ (**18**)	1	MW[b]	150	1	100
5	$(4\text{-}PhPh)_2SiH_2$ (**16**)	1	Δ[b]	150	3	97
6	$(4\text{-}PhPh)_2SiH_2$ (**16**)	1	MW[b]	150	1.5	99
7	$1\text{-}Naph_3SiH$ (**19**)	1	Δ[b]	200	3	0
8	$1\text{-}Naph_3SiH$ (**19**)	1	MW	200	3	0

[a]On the basis of relative ^{31}P NMR intensities.
[b]In the presence of 0.05 mL of PhMe to avoid heterogeneity.

Dibutyl-phenylphosphine oxide (**14c**) behaved rather similarly to the dipropyl analog **14b**. Regarding the MW accomplishments, using $PhSiH_3$ (**3**), TMDS (**4**), and PMHS (**5**), there was a need for a 1-, 7-, and 4-hour reaction time, respectively, to reach almost quantitative conversions (Table 3, entries 13, 15, and 17). Completion of the thermal variations required 2, 10, and 6 hour, respectively (Table 3, entries 14, 16, and 18).

The deoxygenating experiments with diisopentyl-phenylphosphine oxide (**14d**) also matched into the series including the reductions of the propyl and butyl derivatives (Table 3, entries 19-24).

To broaden the scope of the reductive agents, other silanes, such as bis(4-phenylphenyl)silane ($[4\text{-}PhPh]_2SiH_2$ **16**), bis(anthranyl)silane ($Anth_2SiH_2$ **17**), bis(fluorenyl)silane ($Fluorenyl_2SiH_2$ **18**), and tri(1-naphthyl)silane ($1\text{-}Naph_3SiH$ **19**), were also tested (Figure 1). The model reaction was the reduction of 3-methyl-1-phenyl-3-phospholene 1-oxide (**1**) that is an dialkyl-aryl-like phosphine oxide. The results are found in Table 4.

It was found that the fluorenyl and the 4-PhPh bis-silanes (**18** and **16**) could be used in the deoxygenation of phospholene oxide **1** at 150°C (Table 4, entries 3 and 5), and the reactions were faster on MW irradiation (Table 4, entries 4 and 6). However, the application of $Anth_2SiH_2$ (**17**) required a higher temperature of 180°C (Table 4, entries 1 and 2). Trinaphthylsilane **19** remained unreactive even at 200°C (Table 4, entries 7 and 8).

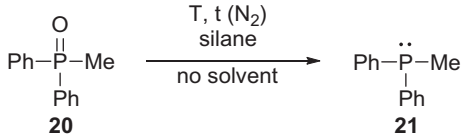
Taking into account also the earlier experiences summarized in Scheme 1,[30,31] the order of reactivity shown in Figure 2 can be set for the silanes (**3**-**10**, **16**-**19**) applied in our study.

Experimental data on the deoxygenation of methyl-diphenylphosphine oxide (**20**) (Scheme 4) are shown in Table 5. It is recalled that triphenylphosphine oxide was reduced by $PhSiH_3$ (**3**) at 150°C.[30] The reactivity of diphenyl derivative **20** allowed a lower temperature of 110°C. Under MW conditions and after an irradiation of 1 hour, phosphine **21** was obtained in a complete conversion and in a yield of 90% (Table 5, entry 1). The comparative thermal experiment required a 2-hour heating (Table 5, entry 2). TMDS (**4**) and PMHS (**5**) were of lower reactivity requesting a reaction temperature of 175°C. Using TMDS (**4**), an irradiation of 7 hour was necessary to obtain phosphine **21** in a yield of 87% (Table 5, entry 3). Measuring in PMHS (**5**), similar results could be obtained after a somewhat shorter (5 hour) reaction time (Table 5, entry 5). In the last two cases, the thermal control experiments required a reaction time of 15 and 9 hour, respectively (Table 5, entries 4 and 6).

$$\underset{(\mathbf{3})}{PhSiH_3} \sim \underset{(\mathbf{6})}{NaphSiH_3} > \underset{(\mathbf{7})}{BnSiH_3} > \underset{(\mathbf{8})}{(4\text{-}MePh)_2SiH_2} >> \underset{(\mathbf{5})}{PMHS} > \underset{(\mathbf{4})}{TMDS} \sim \underset{(\mathbf{10})}{(Ph_2SiH)_2} > \underset{(\mathbf{9})}{(1\text{-}Napht)_2SiH_2} \sim$$

$$\underset{(\mathbf{18})}{Fluorenyl_2SiH_2} > \underset{(\mathbf{16})}{(4\text{-}PhPh)_2SiH_2} > \underset{(\mathbf{17})}{Anth_2SiH_2} >>> \underset{(\mathbf{19})}{1\text{-}Naph_3SiH}$$

FIGURE 2 The order of reactivity of different types of silanes in deoxygenation



SCHEME 4 Deoxygenation of diphenyl-methylphosphine oxide (**20**) by silanes **3**-**5**

It can be seen that methyl-diphenylphosphine oxide **20** is significantly less reactive than the dialkyl-phenyl derivatives (**14a**-**d**) are. This may be due to steric factors.

Dialkyl-phenylphosphines **15a**-**c** and methyl-diphenylphosphine (**21**) are known compounds that were identified by comparison of their δ_P chemical shifts with literature data and by HRMS. New phosphine **15d** was identified in a similar way.

The order of reactivity of the phosphine oxides investigated in the present study and earlier[30] is shown in Figure 3.

In summary, a MW-assisted solvent- and catalyst-free method using TMDS and PMHS as user-friendly and cheap silanes was elaborated for the deoxygenation of 1-alkyl-3-methyl-3-phospholene 1-oxides, dialkyl-phenylphosphine oxides, and methyl-diphenylphosphine oxide. The reactivity of the different phosphine oxides and silanes was mapped, and a few new phosphine sulfides were prepared during our work.

3 | EXPERIMENTAL

3.1 | General

^{31}P NMR spectra were registrated in $CDCl_3$ solution on a Bruker AV-300 spectrometer operating at 121.5 MHz. Chemical shifts are downfield relative to 85% H_3PO_4. The spectra used for estimation of the percentage quantity of the components were obtained applying a 30° pulse, d1=2.2 seconds, AQ=0.9 seconds, number of data points=65 536, number of scans: ca. 32. High-resolution molecular weights were obtained using a Q-TOF Premier mass spectrometer in 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 microwave reactor equipped with a pressure controller applying 50-80 W under isothermal conditions. Silanes **3**-**5** and **7** are available commercially, while silanes **6**, **8**-**10**, and **16**-**19** were prepared by $LiAlH_4$ reduction of the corresponding chlorosilanes in accord with literature procedures.[38-41] Compound **9** may also be synthesized by a known procedure.[42] PMHS with an average molecular weight of 1700-3200 was purchased from Sigma-Aldrich.

3.2 | General procedure for the deoxygenation of 1-alkyl-3-methyl-3-phospholene 1-oxides (11) and for the trapping of the phosphines (12) so obtained

A mixture of 0.55 mmol of 1-alkyl-3-methyl-3-phospholene 1-oxides (**11a-d**) (**11a**: 0.08 g, **11b**: 0.09 g, **11c**: 0.10 g, **11d**: 0.10 g) and 0.068 mL (0.55 mmol) of $PhSiH_3$ (**3**), or 0.19 mL (1.1 mmol) of TMDS (**4**), or 0.042 mL (1.1 mmol) of PMHS (**5**), or 0.55 mmol of silanes **6**-**10** and **16**-**19** (**6**: 0.087 mL, **7**: 0.075 mL, **8**: 0.12 mL, **9**: 0.20 g, **10**: 0.19 g, **16**: 0.16 g, **17**: 0.21 g, **18**: 0.20 g, **19**: 0.23 g) was heated under nitrogen atmosphere at the appropriate temperature for the appropriate time in a glass bomb immersed to an oil bath or in a commercial MW vial in the MW reactor

TABLE 5 Deoxygenation of methyl-diphenylphosphine oxide (**20**) by different silanes under solvent-free conditions on conventional heating or microwave irradiation

Entry	Silane	Equiv.	Mode of heating	*T* (°C)	*t* (h)	Conv. (%)[a]	Yield of 21 (%)
1	$PhSiH_3$ (**3**)	1	MW	110	1	98	90
2	$PhSiH_3$ (**3**)	1	Δ	110	2	99	90
3	TMDS (**4**)	2	MW	175	7	90	87
4	TMDS (**4**)	2	Δ	175	15	90	87
5	PMHS (**5**)	2	MW	175	5	93	89
6	PMHS (**5**)	2	Δ	175	9	89	~84

[a]On the basis of relative ^{31}P NMR intensities.

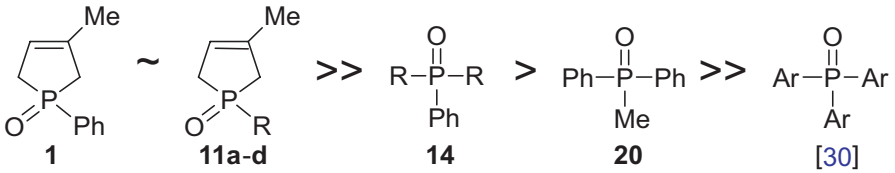


FIGURE 3 The order of reactivity of different tertiary phosphine oxides in deoxygenations by silanes

(Table 2). Then, the reaction mixture containing phosphine **12** was cooled to 26°C, and the crude product was reacted further immediately to form the corresponding sulfide (**13**).

To ~0.55 mmol of the corresponding phosphine (**12**) in 2 mL of dichloromethane, 20.7 mg (0.65 mmol) of powdered sulfur was added under nitrogen. The mixture was stirred at 25°C for overnight, and then the solvent was evaporated. Column chromatography of the residue using hexane-ethyl acetate 9:1 as the eluent afforded the sulfide (**13**) as a dense oil. For the details, see Table 2.

The following phospholene sulfides were prepared:

*1-Ethyl-3-methyl-3-phospholene 1-sulfide (***13a***).* ^{31}P NMR ($CDCl_3$) δ: 65.1; ^{13}C NMR ($CDCl_3$) δ: 6.7 ($^2J_{P\text{-}C}$=4.6, $C_{2'}$), 19.6 ($^3J_{P\text{-}C}$=10.3, C_3-Me), 26.0 ($^1J_{P\text{-}C}$=48.7, $C_{1'}$), 37.8 ($^1J_{P\text{-}C}$=50.1, C_2*), 41.0 ($^1J_{P\text{-}C}$=52.6, C_5*), 121.2 ($^2J_{P\text{-}C}$=5.2, C_4), 137.2 ($^2J_{P\text{-}C}$=9.6, C_3), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 1.24 (dt, J_1=7.6, J_2=19.5, 3H, CH_2CH_3), 1.81 (bs, 3H, C_3-CH_3), 1.88-2.08 (m, 2H, CH_2CH_3), 2.54-2.91 (m, 4H, CH_2PCH_2), 5.49 (d, J=30.5, 1H, CH=); $[M+H]^+_{found}$=161.0551, $C_7H_{14}PS$ requires $[M+H]^+$=161.0548.

*3-Methyl-1-propyl-3-phospholene 1-sulfide (***13b***).* ^{31}P NMR ($CDCl_3$) δ: 62.4; ^{13}C NMR ($CDCl_3$) δ: 15.1 ($^3J_{P\text{-}C}$=15.9, $C_{3'}$), 16.2 ($^2J_{P\text{-}C}$=3.6, $C_{2'}$), 19.4 ($^3J_{P\text{-}C}$=10.3, C_3-Me), 34.7 ($^1J_{P\text{-}C}$=47.5, $C_{1'}$), 38.4 ($^1J_{P\text{-}C}$=50.0, C_2*), 41.6 ($^1J_{P\text{-}C}$=52.5, C_5*), 121.0 ($^2J_{P\text{-}C}$=5.2 C_4), 137.1 ($^2J_{P\text{-}C}$=9.6, C_3), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 1.07 (*t*, J=7.3, 3H, CH_2CH_3), 1.63-1.77 (m, CH_2CH_3) overlapped by 1.80 (bs, C_3-CH_3), total int. 5H, 1.89-2.02 (m, CH_2Et, 2H), 2.60-2.92 (m, 4H, CH_2PCH_2), 5.48 (d, J=31.2, 1H, CH=); $[M+H]^+_{found}$=175.0711, $C_8H_{16}PS$ requires $[M+H]^+$=175.0705.

*1-Butyl-3-methyl-3-phospholene 1-sulfide (***13c***).* ^{31}P NMR ($CDCl_3$) δ: 62.9; ^{13}C NMR ($CDCl_3$) δ: 13.4 ($C_{4'}$), 19.5 ($^3J_{P\text{-}C}$=18.2, C_3-Me), 23.7 ($^3J_{P\text{-}C}$=15.5, $C_{3'}$), 24.7 ($^2J_{P\text{-}C}$=3.8, $C_{2'}$), 32.6 ($^1J_{P\text{-}C}$=47.7, $C_{1'}$), 38.4 ($^1J_{P\text{-}C}$=50.1, C_2*), 41.7 ($^1J_{P\text{-}C}$=52.6, C_5*), 121.2 ($^2J_{P\text{-}C}$=5.2, C_4), 137.2 ($^2J_{P\text{-}C}$=9.6, C_3), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.95 (*t*, J=7.3, 3H, CH_2CH_3), 1.38-1.52 (m, 2H, CH_2), 1.57-1.72 (m, 2H, CH_2), 1.80 (bs, 3H, C_3-CH_3), 1.89-2.04 (m, 2H, CH_2Pr), 1.91-2.04 (m, 4H, CH_2PCH_2), 5.48 (d, J=31.3, 1H, CH=); $[M+H]^+_{found}$=189.0867, $C_9H_{18}PS$ requires $[M+H]^+$=189.0861.

*1-Isopentyl-3-methyl-3-phospholene 1-sulfide (***13d***).* ^{31}P NMR ($CDCl_3$) δ: 63.4; ^{13}C NMR ($CDCl_3$) δ: 19.4 ($^3J_{P\text{-}C}$=10.3, C_3-Me), 21.9 (2× $CHCH_3$), 28.5 ($^3J_{P\text{-}C}$=15.0, $C_{3'}$), 30.6 ($^1J_{P\text{-}C}$=47.9, $C_{1'}$), 31.1 ($^2J_{P\text{-}C}$=3.8, $C_{2'}$), 38.1 ($^1J_{P\text{-}C}$=50.1, C_2*), 41.4 ($^1J_{P\text{-}C}$=52.6, C_5*), 130.0 ($^2J_{P\text{-}C}$=5.2, C_4), 137.0 ($^2J_{P\text{-}C}$=9.6, C_3), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.71-0.81 (m, 6H, 2× $CHCH_3$), 1.26-1.40 (m, 2H, CH_2CH), 1.41-1.53 (m, 1H, CH), 1.62 (bs, 3H, C_3-CH_3), 1.71-1.84 (m, 2H, PCH_2CH_2), 2.39-2.69 (m, 4H, CH_2PCH_2), 5.30 (d, J=30.3, 1H, CH=); $[M+H]^+_{found}$=203.1029, $C_{10}H_{20}PS$ requires $[M+H]^+$=203.1023.

3.3 | General procedure for the deoxygenation of the phosphine oxides 14a-d and 20 using phenylsilane, TMDS, and PMHS

A mixture of 0.50 mmol of phosphine oxide (**14a**: 0.08 g, **14b**: 0.11 g, **14c**: 0.12 g, **14d**: 0.12 g, **20**: 0.12 g), 0.50 mmol (0.062 mL) of phenylsilane or 1.0 mmol (0.18 mL) of TMDS or 1.0 mmol (0.040 mL) of PMHS was heated under nitrogen atmosphere using an oil bath or a microwave 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 **14a-d** and **20** (as colorless oils). As a matter of fact, the main fraction was collected after a smaller pre-fraction. For the details, see Tables 3 and 5.

The following phosphines were prepared:

*Dimethyl-phenylphosphine (***15a***).* From the experiment marked in Table 3, entry 5. Yield: 83%, colorless oil; ^{31}P NMR ($CDCl_3$) δ: −43.2, δ ($CDCl_3$)[43]: −42.4; $[M+H]^+_{found}$=139.0682, $C_8H_{12}P$ requires: 139.0677.

*Dipropyl-phenylphosphine (***15b***).* From the experiment marked in Table 3, entry 11. Yield: 88%, colorless oil; ^{31}P NMR ($CDCl_3$) δ: −26.3, δ ($CDCl_3$)[44]: −27.7; $[M+H]^+_{found}$=195.1316, $C_{12}H_{20}P$ requires: 195.1297.

*Dibutyl-phenylphosphine (***15c***).* From the experiment marked in Table 3, entry 17. Yield: 84%, colorless oil; ^{31}P NMR ($CDCl_3$) δ: −24.2, δ ($CDCl_3$)[45]: −24.6; $[M+H]^+_{found}$=223.1618, $C_{14}H_{24}P$ requires: 223.1610.

*Diisopentyl-phenylphosphine (***15d***).* From the experiment marked in Table 3, entry 23. Yield: 82%, colorless oil; ^{31}P NMR ($CDCl_3$) δ: −22.8, δ ($CDCl_3$); $[M+H]^+_{found}$=251.1929, $C_{16}H_{28}P$ requires: 251.1923. On oxidation by 30% H_2O_2, the starting phosphine oxide (**14d**) was regenerated; ^{31}P NMR ($CDCl_3$) δ: 42.5, $[M+H]^+_{found}$=267.1880, $C_{16}H_{28}PO$ requires: 267.1872.

*Diphenyl-methylphosphine (***21***).* From the experiment marked in 5, entry 5. Yield: 89%, colorless oil; ^{31}P NMR ($CDCl_3$) δ: −26.4, δ ($CDCl_3$)[46]: −26.1; $[M+H]^+_{found}$=201.0840, $C_{13}H_{14}P$ requires: 201.0833.

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