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An Efficient Approach to Deoximation Using Hexachlorodisilane under Mild Conditions[1]

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Abstract—A simple, facile, and efficient procedure for deoximation of oximes to the corresponding ketones and aldehydes with hexachlorodisilane (Si_2Cl_6) in the presence of SiO_2 from good to high yields is described. Apparently, SiO_2 greatly increases the reaction rate and product yield. The proposed procedure is more advantageous than those described previously due to its higher efficiency, milder reaction conditions, shorter reaction, and easier work-up.

Keywords: deoximation, oximes, hexachlorodisilane, ketones, aldehydes

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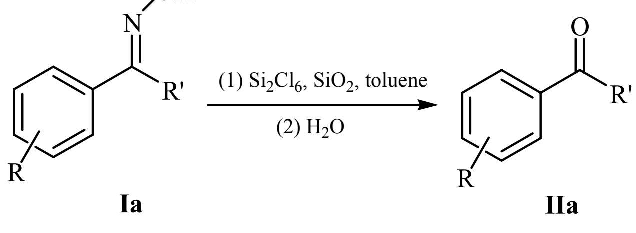
Regeneration of carbonyl compounds from stable and readily obtainable oximes, semicarbazones, and hydrazones has received extensive attention in recent decades [1–7]. Since oximes are prepared from a variety of basic organic compounds such as primary aliphatic amines [8], olefins [9], esters [10], nitriles [10], nitro compounds [11], and alcohols [12], regeneration of carbonyl compounds from oximes may be a convenient alternative method for the preparation of either aldehydes or ketones. Thus far, various deoximation methods based on acid-catalyzed hydrolysis [13–16], reductive cleavage [17], oxidative cleavage [18–28], and photosensitized oxidative deprotection [29–31] have been developed. However, these methods involve either highly poisonous or dangerous reagents, as well as expensive or difficultly accessible metal catalysts. Therefore, development of more appropriate reagents for this kind of reaction is particularly important. Silicon-based reagents have emerged as synthetically useful reagents and intermediates that provide a range of possibilities for the efficient preparation of organic molecules [32–34]. In particular, hexachlorodisilane shows admirable properties in various reactions, most significantly in the reduction of phosphorus–oxygen [35], phosphorus–sulfur [35], sulfur–oxygen [36], carbon–oxygen [37], and nitrogen–oxygen [38] double bonds.

Accordingly, our interest herein is focused on the use of Si_2Cl_6 in combination with SiO_2 for the regeneration of certain aldehydes and ketones from oximes. This work was aimed at developing a simple method for the effective cleavage of the carbon–nitrogen double bond of oximes under mild and heterogeneous conditions (Scheme 1). The results showed that oximes are converted into the corresponding carbonyl compounds in good to excellent yields.

We began our investigation by performing the deoximation of acetophenone oxime (**Ia**, R′ = Me) by the action of Si_2Cl_6 in anhydrous THF in the presence of SiO_2, followed by addition of water. Hexachlorodisilane was added in slight excess to a suspension of **Ia** and SiO_2 in THF. The mixture was refluxed for 8 h, and water was then added. The mixture was stirred for 30 min to obtain acetophenone (**IIa**) in 95% yield. The reaction conditions were optimized with respect to the

Scheme 1.



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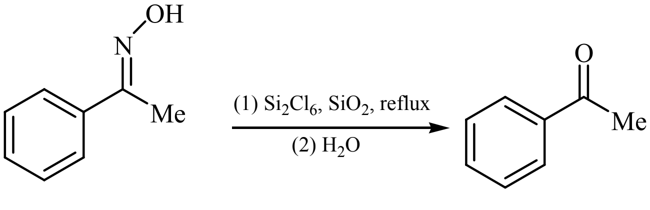
[1] The text was submitted by the authors in English.

Table 1. Optimization of the reaction conditions[a]

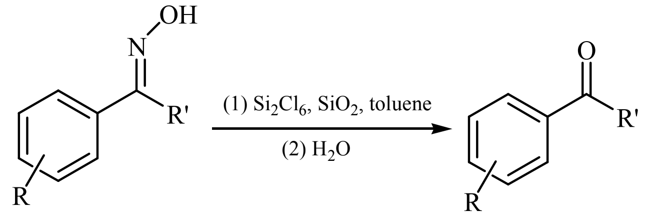


Ia **IIa**

Run no.	Solvent	Si_2Cl_6, mL	SiO_2, g	H_2O, mL	Time, h	Yield,[b] %
1	THF	0.0	5.0	0.5	18	0
2	THF	0.5	5.0	0.5	18	70
3	THF	1.0	5.0	0.5	3	91
4	THF	2.0	5.0	0.5	3	92
5	THF	1.0	2.5	0.5	3	91
6	THF	1.0	1.5	0.5	3	77
7	THF	1.0	0.0	0.5	18	54
8	THF	1.0	2.5	0.2	3	90
9	THF	1.0	2.5	0.1	18	47
10	THF	1.0	2.5	0.0	18	0
11	*n*-Hexane	1.0	2.5	0.2	1	57
12	PhMe	1.0	2.5	0.2	1	95
13	EtOH	1.0	2.5	0.2	1	31
14	DMSO	1.0	2.5	0.2	1	48
15	DCE	1.0	2.5	0.2	1	<10
16	DMF	1.0	2.5	0.2	1	<10

[a] Reaction conditions: **Ia** (2.5 mmol), solvent (5 mL).
[b] Yields of isolated products.

Table 2. Study of the reaction scope[a]



Ia **IIa**

Run no.	R/R′	Time, h	Product[b]	Yield,[c] %
1	H/Me (**Ia**)	1.0	**IIa**	95
2	4-NO_2/Me (**Ib**)	3.0	**IIb**	55
3	3-NO_2/Me (**Ic**)	4.0	**IIc**	>99
4	4-Me/Me (**Id**)	1.0	**IId**	87
5	4-OMe/Me (**Ie**)	0.5	**IIe**	99
6	2-Cl /Me (**If**)	3.0	**IIf**	50
7	3-Cl/Me (**Ig**)	3.0	**IIg**	40
8	4-Cl/Me (**Ih**)	0.5	**IIh**	92
9	4-F/Me (**Ii**)	0.5	**IIi**	90
10	2-F/Me (**Ij**)	8.0	**IIj**	67
11	H/Ph (**Ik**)	8.0	**IIk**	>99
12	4-F/Ph (**Il**)	0.5	**IIl**	>99
13	2-F/Ph (**Im**)	8.0	**IIm**	30
14	H/H (**In**)	0.5	**IIn**	>99
15	4-NO_2/H (**Io**)	1.0	**IIo**	49
16	3-NO_2/H (**Ip**)	4.0	**IIp**	95
17	4-OH/H (**Iq**)	0.5	**IIq**	98
18	4-OMe/H (**Ir**)	0.5	**IIr**	>99
19	4-Me/H (**Is**)	0.5	**IIs**	97
20	4-N(Me)$_2$/H (**It**)	1.0	**IIt**	60

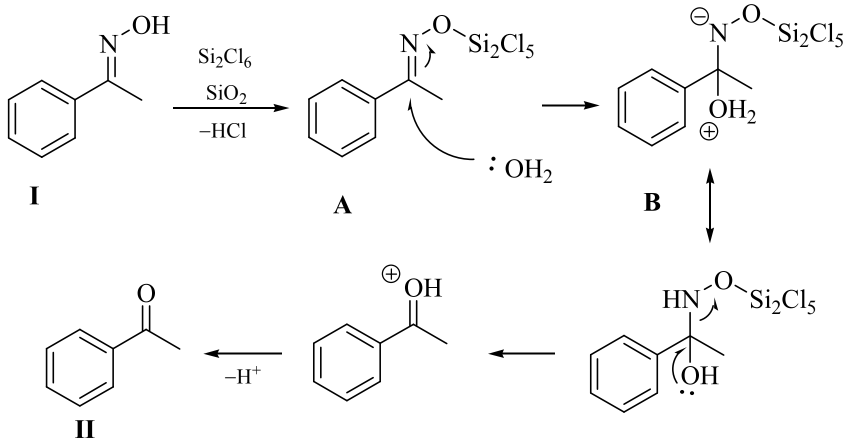
[a] Reaction conditions: **I** (2.5 mmol), Si_2Cl_6 (1 mL), SiO_2 (2.5 g), toluene (5 mL), reflux (110°C), H_2O (0.2 mL).
[b] All products were characterized by ^{1}H NMR spectra and by comparison with published data.
[c] Yields of isolated products.

amounts of Si_2Cl_6, SiO_2, and H_2O (relative to 2.5 mmol of **Ia**), reflux time, and solvent; the results are summarized in Table 1.

It is seen that Si_2Cl_6 is necessary for the reaction to occur (Table 1, run no. 1), but the yield increases gradually when redundant Si_2Cl_6 is added (run nos. 3, 4). Addition of SiO_2 dramatically shortens the reaction time and simultaneously improves the product yield (run nos. 3, 5–7). An effort was made to elucidate the origin of the C=O oxygen atom in **IIa**. For this purpose, H_2O was intentionally omitted (run no. 10); in this case, no deoximation was observed. As follows from the results of run nos. 1 and 7, the oxygen atom originates from H_2O, as opposed to SiO_2 or **Ia**. Scheme 2 illustrates a probable reaction mechanism.

Notably, solvent plays a significant role in increaseing the yield (run nos. 8, 11–16). Tetrahydrofuran and toluene ensured similar results, but ultimately we

Scheme 2.



chose toluene as optimum solvent with a view to achieving a shorter reflux time (run nos. 8, 12). To investigate the scope of this reaction, various aromatic oximes **Ia–It** were subjected to deoximation under the optimized reaction conditions (Table 2).

Regarding aromatic oximes **I**, both electronic nature and steric requirements of the substituents on the benzene ring influenced the reaction yield. Notably, aromatic oximes bearing strongly electron-withdrawing (NO_2) and electron-donating groups (OMe) at the *para* position of the benzene ring differed greatly in the yields (Table 2, run nos. 2, 5, 15, 18). However, very good efficiency was achieved in the deoximation of *meta*-nitro derivatives **Ic** and **Ip** (Table 2, run nos. 3, 16). Substituents in the *ortho* position (Table 2, run nos. 2, 6, 10, 13), markedly reduced the yield, which may be due to steric reasons.

In keeping with a plausible mechanism shown in Scheme 2, aromatic oxime **I** initially reacts with Si_2Cl_6 to form intermediate **A**. The subsequent reaction of intermediate **A** with water generates intermediate **B** which undergoes electron and proton transfer to produce final product **II**.

In summary, we have developed a straightforward, facile, and efficient procedure for deoximation of oximes to the corresponding ketones and aldehydes with good to excellent yields. The main advantages of the proposed method are milder reaction conditions, shorter reaction times, and easier workup.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker ACF-400 spectrometer (400 MHz) from solutions in $CDCl_3$; the chemical shifts were measured relative to the residual proton signal of the solvent ($CHCl_3$, δ 7.26 ppm). All solvents were purified and dried according to standard procedures unless otherwise stated.

Typical procedure for the deoximation of oximes. A mixture of 0.378 g (2.5 mmol) of acetophenone oxime (**Ia**), 1.5 g (5.5 mmol) of Si_2Cl_6, and 2.5 g (41.7 mmol) of SiO_2) in 5 mL of toluene was heated for 1 h under reflux (110°C). Water, 0.2 g (11.1 mmol), was then added, and the resulting mixture was stirred for 30 min. When the reaction was complete, the mixture was cooled to room temperature and extracted with methylene chloride (3 × 20 mL). The combined extracts were washed with water (25 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc–petroleum ether, 1 : 50 by volume) to isolate the desired product, acetophenone (**IIa**) [39]. Yield 285 mg (95%), light yellow oil. ^1H NMR spectrum, δ, ppm: 7.97–7.95 m (2H), 7.58–7.54 m (1H), 7.48–7.44 m (2H), 2.61 s (3H).

4-Nitroacetophenone (IIb) [39]**.** Yield 227 mg (55%), light yellow crystals, mp 75–78°C. ^1H NMR spectrum, δ, ppm: 8.33–8.30 m (2H), 8.13–8.10 m (2H), 2.68 s (3H).

3-Nitroacetophenone (IIc) [39]**.** Yield 411 mg (>99%), light yellow solid, mp 76–78°C. ^1H NMR spectrum, δ, ppm: 8.77 d (1H, J = 2.0 Hz), 8.44–8.41 m (1H), 8.30–8.28 m (1H), 7.71–7.67 m (1H), 2.69 s (3H).

4-Methylacetophenone (IId) [39]**.** Yield 291 mg (87%), colorless liquid. ^1H NMR spectrum, δ, ppm:

7.85 d (2H, J = 8 Hz), 7.25 d (2H, J = 8 Hz), 2.57 s (3H), 2.41 s (3H).

4-Methoxyacetophenone (IIe) [39]. Yield 371 mg (99%), colorless crystals, mp 36–38°C. ^{1}H NMR spectrum, δ, ppm: 7.93 d (2H, J = 8.8 Hz), 6.92 d (2H, J = 8.8 Hz), 3.86 s (3H), 2.54 s (3H).

2-Chloroacetophenone (IIf) [39]. Yield 193 mg (50%), colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 7.56–7.53 m (1H), 7.41–7.30 m (3H), 2.64 s (3H).

3-Chloroacetophenone (IIg) [39]. Yield 154 mg (40%), colorless oil. ^{1}H NMR spectrum, δ, ppm: 7.93–7.92 m (1H), 7.84–7.82 m (1H), 7.55–7.52 m (1H), 7.43–7.39 m (1H), 2.59 s (3H).

4-Chloroacetophenone (IIh) [39]. Yield 355 mg (92%), colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 7.88 d (2H, J = 8.8 Hz), 7.42 d (2H, J = 8.8 Hz), 2.58 s (3H).

4-Fluoroacetophenone (IIi) [39]. Yield 310 mg (90%), colorless liquid. ^{1}H NMR spectrum, δ, ppm: 8.00–7.96 m (2H), 7.15–7.11 m (2H), 2.58 s (3H).

2-Fluoroacetophenone (IIj) [39]. Yield 231 mg (67%), colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 7.89–7.85 m (1H), 7.53–7.49 m (1H), 7.24–7.20 m (1H), 7.16–7.11 m (1H), 2.64 d (3H, J = 5 Hz).

Benzophenone (IIk) [40]. Yield 452 mg (>99%), colorless crystals, mp 47–49°C. ^{1}H NMR spectrum, δ, ppm: 7.81–7.79 m (4H), 7.61–7.57 m (2H), 7.50–7.46 m (4H).

4-Fluorobenzophenone (IIl) [40]. Yield 496 mg (>99%), colorless crystals, mp 46–48°C. ^{1}H NMR spectrum, δ, ppm: 7.86–7.83 m (2H), 7.78–7.76 m (2H), 7.62–7.57 m (1H), 7.50–7.47 m (2H), 7.18–7.15 m (2H).

2-Fluorobenzophenone (IIm) [40]. Yield 151 mg (30%), colorless liquid. ^{1}H NMR spectrum, δ, ppm: 7.85–7.83 m (2H), 7.58–7.45 m (5H), 7.28–7.25 m (1H), 7.18–7.14 m (1H).

Benzaldehyde (IIn) [41]. Yield 264 mg (>99%), colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 7.51 t (2H, J = 7.6 Hz), 7.61 t (1H, J = 7.2 Hz), 7.86 d (2H, J = 7.6 Hz), 9.99 s (1H).

4-Nitrobenzaldehyde (IIo) [41]. Yield 185 mg (49%), light yellow crystals, mp 104–107°C. ^{1}H NMR spectrum, δ, ppm: 8.09 d (2H, J = 7.2 Hz), 8.41 d (2H, J = 6.8 Hz), 10.18 s (1H).

3-Nitrobenzaldehyde (IIp) [41]. Yield 359 mg (95%), light yellow solid, mp 55–58°C. ^{1}H NMR spectrum, δ, ppm: 10.19 s (1H), 8.73 s (1H), 8.50 s (1H), 8.27 s (1H), 7.80 s (1H).

4-Hydroxybenzaldehyde (IIq) [41]. Yield 299 mg (98%), light yellow crystals, mp 114–117°C. ^{1}H NMR spectrum, δ, ppm: 9.87 s (1H), 7.82 d (2H, J = 6.8 Hz), 6.97 d (2H, J = 7.2 Hz), 6.73 br s (1H).

4-Methoxybenzaldehyde (IIr) [41]. Yield 339 mg (>99%), colorless liquid. ^{1}H NMR spectrum, δ, ppm: 9.85 s (1H), 7.81 d (2H, J = 8.8 Hz), 6.98 d (2H, J = 8.4 Hz), 3.86 s (3H).

4-Methylbenzaldehyde (IIs) [41]. Yield 291 mg (97%), colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 9.94 s (1H), 7.76 d (2H, J = 7.6 Hz), 7.31 d (2H, J = 8.4 Hz), 2.42 s (3H).

4-(Dimethylamino)benzaldehyde (IIt) [41]. Yield 224 mg (60%), light yellow solid, mp 72–75°C. ^{1}H NMR spectrum, δ, ppm: 9.72 s (1H), 7.72 d (2H, J = 8.8 Hz), 6.68 d (2H, J = 8.8 Hz), 3.06 s (6H).

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