



Metal-free selective reduction of acid chlorides to aldehydes using 1-hydrosilatrane

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ABSTRACT

This work uses 1-hydrosilatrane – an accessible and easy-to-handle reducing reagent – to selectively reduce acid chlorides to aldehydes. This metal-free reduction proceeds rapidly at ambient temperature in the presence of *N*-methylpyrrolidine, efficiently producing aldehydes in up to 54% yield and with the balance largely remaining as starting material. No over-reduced alcohol product is observed.

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1. Introduction

Aldehydes are important synthetic building blocks in organic chemistry that can be prepared by selective reduction of readily available or easily prepared carboxylic acid derivatives such as acid chlorides [1]. However, this transformation is challenging due to the reactivity of the resultant aldehyde product, which under most common reducing conditions would be further converted to the alcohol. Given the utility of aldehydes as fine chemicals, chemoselective methods for their preparation from the aforementioned precursors are highly desired.

A classical route from an acid chloride to an aldehyde is the Rosenmund reduction [2], which uses a Pd-BaSO₄ catalyst and requires a careful flow of H₂ to prevent over-reduction. Selective reduction of acid chlorides to aldehydes can also be achieved by using the specialized reagent NaHAL(OtBu)₃ [3]. An alternative, less efficient strategy requires the conversion of the acid chloride to an intermediate such as a Weinreb amide [4] followed by subsequent metal hydride reduction of this species to the aldehyde. Both of the aforementioned metal hydride reductions must be run at -78 °C to produce the aldehyde selectively. These three highlighted methods comprise the practical state of the art, and showcase the challenges associated with this transformation: the reaction conditions must be carefully controlled to prevent over-reduction of the sensitive aldehyde functionality, which results in methods that require spe-

cialized setup and can feature low atom-economy and long reaction times. This provides motivation for designing more innovative methods for this powerful organic transformation.

In recent years, a variety of hydrosilanes have been employed to convert acid chlorides to aldehydes. Hydrosilanes are milder and more stable to air and moisture than metal hydrides, meaning silanes are easier to handle and also allow for better control of chemoselectivity. Dimethylphenylsilane was shown to chemoselectively reduce aromatic and aliphatic acid chlorides to the aldehydes in the presence of a ruthenium catalyst [5]. Triethylsilane can be used to chemoselectively reduce aromatic and aliphatic acid chlorides to aldehydes using a palladium catalyst [6]. While these methods are effective for this transformation, a metal-free hydrosilane-mediated reduction of acid chlorides to aldehydes is more desirable as it would eliminate the cost and toxicity drawbacks associated with using transition metal catalysts. Corriu and co-workers reported such a reaction in 1988, however the widespread adoption of this method is precluded by the boutique nature of the reducing silane reagent [7].

1-Hydrosilatrane (Fig. 1) is a stable hypercoordinate silicon hydride that has recently been applied as a hydride-transfer reagent [8–13]. Its unique reactivity stems from the nitrogen atom donating its lone pair into the σ^* orbital of the silicon atom, thus increasing its inherent Lewis acidity and hydridic capability of the silicon hydride. Additionally, the rigid caged structure stabilises silatrane compared to other pentacoordinate silicon hydrides: it is air- and ambient-moisture-stable, which means that methods that employ it can be done on the benchtop. The combination of these

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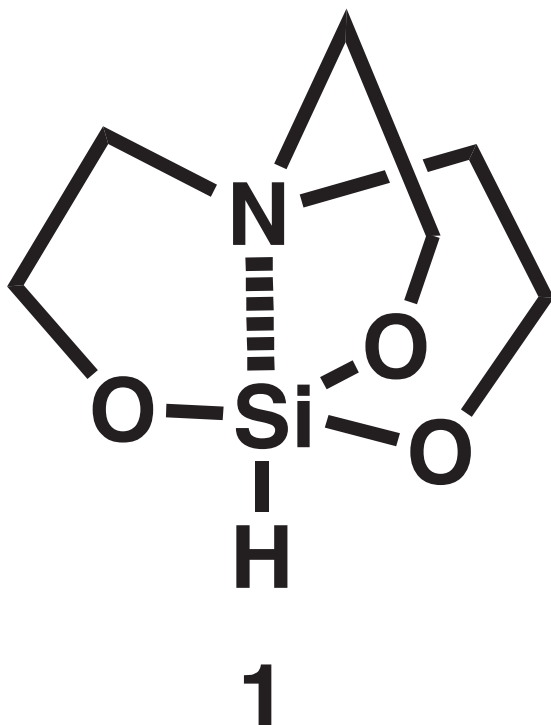


Fig. 1. Structure of 1-hydrosilatrane

two factors (stability, embedded reactivity) make it a versatile and powerful reagent for organic synthesis. Hydrosilatrane is sold commercially and/or can be synthesised from readily available starting materials.

Our group has shown that hydrosilatrane's reactivity can be tuned via simple additives or reaction conditions to selectively reduce functionalities of interest. Ketones and aldehydes can be transformed to their respective alcohols in the presence of oxyanionic Lewis bases [8–10]. Aldehydes can undergo reductive acylation in the presence of acetic acid [11]. Hydrosilatrane can also effect direct reductive amination of ketones and aldehydes [12,13]. Given its versatile reactivity, we envisaged applying hydrosilatrane for the metal-free reduction of acid chlorides to aldehydes chemoselectively. There is some encouraging literature precedence for this transformation: in 1976, Eaborn et al. reported the use of hydrosilatrane to reduce benzoyl chloride in refluxing xylene over 48 h [14]. However, this method was wasteful, employed harsh reaction conditions, and exhibited poor chemoselectivity. Nevertheless, this work confirmed that hydrosilatrane could reduce acid chlorides, and perhaps the chemoselective reduction of acid chlorides could be achieved under different reaction conditions.

2. Results and discussion

We first surveyed various additives that could potentially enhance the electrophilicity of the acid chloride. Activation of acid chlorides can be achieved using tertiary amines such as 4-dimethylaminopyridine (DMAP) [15] or 1,4-diazabicyclo[2.2.2]octane (DABCO) [16] as nucleophilic catalysts.

Their conversion to an acid iodide using KI [17] or a phosphonium ion using Bu_3P [18] have also been reported. Lewis acids such as AlCl_3 may also activate acid chlorides through the acylium ion [19]. We hoped that this activation strategy would facilitate the reaction between the acid chloride and the mildly hydridic silatrane while simultaneously making the reaction conditions milder.

Table 1
Initial screening of additives.^[a]

Entry	Additive	Solvent	Yield ^[b] (%)
1	AlCl_3	Chloroform- <i>d</i>	0
2	AgNO_3	Dichloromethane	0
3	NaI	Dichloromethane	0
4	PPh_3	Dichloromethane	0
5	$(\text{PhO})_3\text{P}$	Dichloromethane	0
6	Pyridine	Dichloromethane	trace
7	NEt_3	Dichloromethane	trace
8	DMAP	Dichloromethane	0
9	DABCO	Chloroform- <i>d</i>	39
10	NMPi	Dichloromethane	49
11	NMPi	Chloroform- <i>d</i>	54
12	NMPi	THF	0
13	NMPi	MeCN	0
14	NMPi	<i>i</i> PrOH	trace

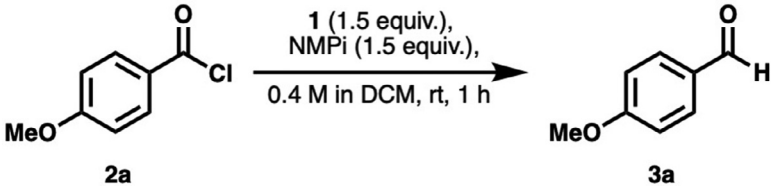
[a] Standard conditions: hydrosilatrane (1, 1.5 equiv.), NMPi (1.5 equiv.), dichloromethane, rt, 1 h. [b] Yield of the aldehyde was determined by ^1H NMR using *p*-tolualdehyde as an internal standard.

Table 1 summarizes the results of some of the additives screened. Lewis acids AlCl_3 and AgNO_3 did not promote any reduction of the acid chloride (Table 1, entries 1–2). Nucleophilic additives such as NaI , PPh_3 , and $(\text{PhO})_3\text{P}$ were tested but the reaction did not proceed under these conditions (Table 1, entries 3–5). While common tertiary amines such as pyridine, NEt_3 , and DMAP afforded trace or no amounts of aldehyde (Table 1, entries 6–8), highly nucleophilic tertiary amines such as *N*-methylpyrrolidine (NMPi) or DABCO promoted reduction of acid chloride to aldehyde. (Table 1, entries 9–10). Importantly, we did not witness any evidence of over-reduction (to produce the alcohol) in any of these trials. Thus, NMPi was chosen as the additive of choice for this chemoselective reduction.

Screening of solvents showed that performing the reaction in either dichloromethane or chloroform-*d* resulted in the best yield (Table 1, entries 10–11). When tetrahydrofuran, acetonitrile, or isopropanol were used, only a small amount of aldehyde was detected (Table 1, entries 12–14). This may be due simply to the poor solubility of silatrane in these solvents.

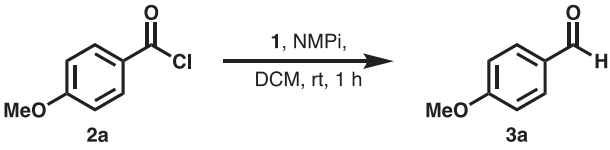
We then turned our attention to optimizing the concentration of reactants and reagents (Table 2). We observed a 54% yield of the aldehyde at a concentration of 0.2 M of acid chloride (Table 2, entry 2). Conducting the reaction at more dilute reaction conditions yielded only trace amounts of aldehyde (Table 2, entries 3–4). Doubling the equivalents of both silatrane and NMPi had no beneficial effect on the yield (Table 2, entry 5), while using a substoichiometric amount of NMPi decreased the yield significantly (Table 2, entry 6).

Under the standard conditions in dichloromethane (0.40 M acid chloride, 1.5 equiv. silatrane, NMPi), we observed 49% aldehyde formation with the remainder of the material as a single product with NMR signature nearly identical to our starting acid chloride. We devised a number of experiments in an effort to understand why the reaction was not proceeding to completion (Table 3). We needed to first confirm that the non-aldehyde material was not the carboxylic acid, which would result as a consequence of hydrolysis of the acid chloride as a competing reaction. We found that the addition of 1 equiv. of H_2O (7.2 μL) to a reaction mixture containing *p*-anisoyl chloride, silatrane, and dichloromethane, followed by the addition of NMPi did not afford any aldehyde (Table 3, entry 1).

Table 2
Concentration and equivalents optimization.


Entry	Deviation from standard conditions	Yield [a] (%)
1	None	49
2	0.20 M with respect to 2 [b]	54
3	0.05 M with respect to 2 [b]	trace
4	0.01 M with respect to 2 [b]	trace
5	3.0 equiv. NMPi + hydrosilatrane (1)	43
6	0.5 equiv. NMPi	14

[a] Yield of the aldehyde was determined by ^1H NMR using *p*-tolualdehyde as an internal standard.
 [b] Benzoyl chloride (R = H) was used as the substrate in this reaction due to ease of handling liquid substrate via microsyringe at small scale.

Table 3
Impact of air/moisture on the reaction.^[a]


Entry	Conditions	Yield [b] (%)
1	With 1 equiv. of water	0
2	Open to air [c]	54
3	Anhydrous (with 4 Å mol. sieves) [c]	50
4	Anhydrous (without 4 Å mol. sieves)	49

[a] Standard conditions: hydrosilatrane (**1**, 1.5 equiv.), NMPi (1.5 equiv.), dichloromethane, rt, 1 h. [b] Yield of the aldehyde was determined by ^1H NMR using *p*-tolualdehyde as an internal standard. [c] Chloroform-*d* was used as the solvent in this reaction.

This suggests that hydrolysis outcompetes the reduction reaction if an appreciable amount of water is present. However, we observed no discernible difference in the yields whether the reaction was run under anhydrous conditions (either with or without molecular sieves) or open to air in a dram vial with no extra efforts to exclude moisture (Table 3, entries 2-4). This demonstrates that any residual water that was potentially in the reaction mixture did not affect the reaction.

We next tracked the reaction by NMR to look for intermediates that may be impacting reaction progress (Table 4). ^1H NMR spectra of the reaction in progress (Table 4 entry 1) showed a dynamic peak at ~5.8 ppm integrating to one proton with a corresponding set of aromatic protons. A 2-day time-lapse ^{29}Si NMR of the same reaction revealed three distinct signals (see SI, page 40-41). The disappearance of the signal at ~5.8 ppm on the ^1H NMR after two days in chloroform-*d* matched the disappearance of one of the signals (at -98.1 ppm) in the ^{29}Si NMR, suggesting that the signal at ~5.8 ppm observed in the ^1H NMR is a silicon-containing species. The other two signals appear to belong to hydrosilatrane (at -83.5 ppm) and an unidentified silicon byproduct (at -88.3 ppm).

To gain partial mechanistic insight, we investigated whether there is coordination between 1) hydrosilatrane and NMPi or 2) hydrosilatrane and acid chloride (see SI, pages 42-43) by mixing the components individually and looking for either a shift in the hydrosilatrane peak or the presence of an additional new signal in the ^{29}Si NMR spectrum. However, we did not observe any new signals or shifts when hydrosilatrane is singularly mixed with

just one of the two reaction components (NMPi or acid chloride). Only when the three reaction components (hydrosilatrane, NMPi, and acid chloride) are present together do we see new ^{29}Si NMR signals appear, with concurrent reduction taking place. Based on these observations, we propose that the reaction is proceeding by NMPi-initiated nucleophilic activation of the acid chloride, followed by reaction with hydrosilatrane to yield a meta-stable silyl ether intermediate **4a**. The NMR signal at ~5.8 ppm disappears after a silica plug workup (in dichloromethane) or simply over time (in chloroform-*d*) (Table 4, entries 1-2). An aqueous workup was also attempted to cleave **4a** to afford the aldehyde in comparable yields (Table 4, entry 3). Carrying out the reaction at an elevated temperature did not push the reaction further forward, rather it resulted in many side reactions including the formation of the alcohol product (Table 4, entry 4).

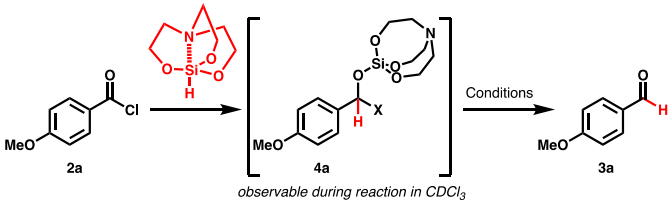
As an explanation for the achievement of only moderate product yield, we considered the possibility of inhibition of the intended reaction by the product aldehyde. Aromatic aldehydes and aromatic acid chlorides can undergo spontaneous reaction to form the α -chlorobenzoyl benzoate [20]. We hypothesized that by running a reaction at 0 °C we could reduce the rate of conversion of **4a** to **3a**, resulting in a build-up of **4a** which could then be cleaved all at once to form **3a** in the presence of tetrabutylammonium fluoride (TBAF). This methodological construct would circumvent the possibility of reaction progress inhibition by products of the reaction. Unfortunately, when this reaction was conducted the yield of **3a** remained nearly the same (44%) (Table 4, entry 5). A more direct attempt to observe an aldehyde/acid adduct was pursued by mixing equimolar amounts of *p*-anisoyl chloride, *p*-anisaldehyde, and NMPi in chloroform-*d*. No reaction was observed under these conditions (Fig. 2a), therefore the aldehyde formed is seemingly not interfering with product formation.

We also investigated whether this reaction is equilibrating under the conditions. Addition of 1 equiv. of *p*-anisaldehyde to a standard reaction mixture in chloroform-*d* after 1 hour did not increase the proportion of acid chloride or the silyl ether; an additional equivalent of aldehyde was simply observed unchanged in the final product mixture. This suggests that the transformation of acid chloride to aldehyde (via the silyl ether or otherwise) is not reversible under these conditions (Fig. 2b).

Subsequently, we sought further confirmation that it was our starting acid chloride that remained and not an unreactive, spectroscopically similar product of a deleterious side reaction. A standard reaction was set up and, after one hour, benzylamine (5

Table 4

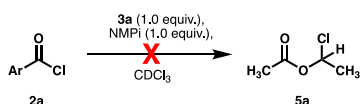
The reaction pathway going through possible silyl ether intermediate and NMR yields using various workups ^[a]



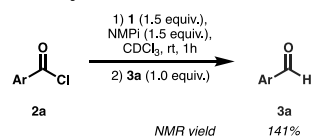
Entry	Conditions	Yield ^[b] (%)
1	2 days (in chloroform- <i>d</i>)	47
2	Filtered through silica plug	49
3	Aqueous workup	49
4	Heat to 60 °C ^[c,d]	13
5	TBAF (0 °C) ^[c,e]	44

[a] Standard conditions: hydrosilatane (**1**, 1.5 equiv.), NMPi (1.5 equiv.), dichloromethane, rt, 1 h. [b] Yield of the aldehyde was determined by ¹H NMR using *p*-tolualdehyde as an internal standard. [c] The reaction was run using chloroform-*d* as the solvent. [d] The reaction was run in a sealed microwave vial and heated to 60 °C for 1 h. [e] The reaction was run at 0 °C for 1 hour then TBAF (0.6 equiv.) was added and the reaction was stirred for 1 hour at rt.

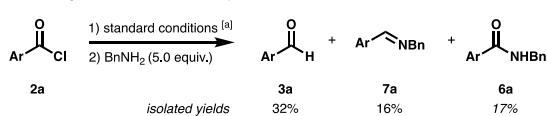
a) Determining if product aldehyde reacts with acid chloride



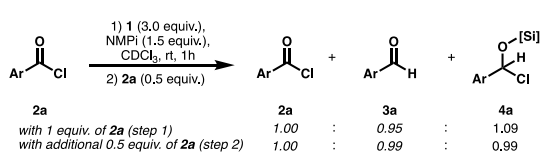
b) Determining if the reaction is reversible under the reaction conditions



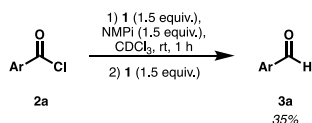
c) Determining if leftover acid chloride is present



d) Determining if leftover hydrosilatane is available



e) Determining the effects of adding more silatrane at the reaction end point



[a] Standard conditions: hydrosilatane (1.5 equiv.), NMPi (1.5 equiv.), dichloromethane, rt, 1 h. [b] Ar = *p*-OMePh.

Fig. 2. Experiments to probe factors that may be contributing to incomplete conversion ^[a,b] [a] Standard conditions: hydrosilatane (1.5 equiv.), NMPi (1.5 equiv.), dichloromethane, rt, 1 h. [b] Ar = *p*-OMePh.

equiv.) was added to the reaction mixture (Fig. 2c). The next day, *p*-anisaldehyde **3a**, its imine **7a**, and amide **6a** were the prominently visible species in the ¹H NMR spectrum (see SI, pages 59–63). This confirmed that a considerable amount of material remaining from the reduction was the acid chloride, or another acylating agent.

In reactions run in chloroform-*d* we observed what we believed to be unreacted hydrosilatane in both the ¹H NMR and ²⁹Si spec-

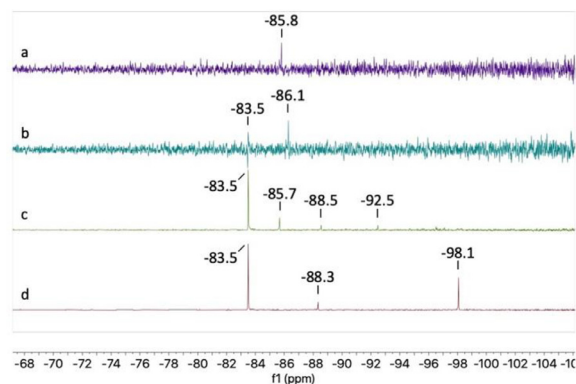
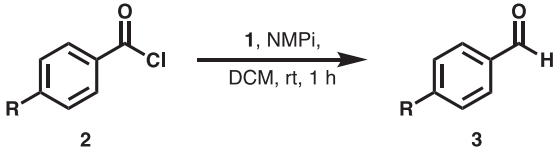


Fig. 3. Stacked ²⁹Si NMR (CDCl₃, referenced to hydrosilatane at -83.5 ppm) spectra for the investigation of the final silicon-containing byproduct. a) ²⁹Si NMR (CDCl₃) of chlorosilatane. b) ²⁹Si NMR (CDCl₃) of chlorosilatane and hydrosilatane. c) ²⁹Si NMR (CDCl₃) of a reaction of *p*-anisoyl chloride **2a**, hydrosilatane (**1**, 1 equiv.), chlorosilatane (1 equiv.), NMPi (1.5 equiv.), in CDCl₃, rt, 1 h. d) ²⁹Si NMR (CDCl₃) of a typical reduction reaction in CDCl₃: *p*-anisoyl chloride **2a**, hydrosilatane (**1**, 1.5 equiv.), NMPi (1.5 equiv.), rt, 1 h.

tra at the reaction endpoint. We wanted to confirm its persistence and ability to act as a reducing agent under the final reaction conditions. To probe this, we added an additional 0.5 equiv. of acid chloride to a reaction mixture following the stalling of the reaction; the additional acid chloride was converted to product with the same efficiency as the original reaction, resulting in a final ratio that mirrored the initial product ratio (Fig. 2d). Addition of further hydrosilatane to the reaction mixture following stalling of the reaction failed to increase of the amount of final aldehyde product (Fig. 2e). These results suggest that hydrosilatane is indeed persisting in the reaction, but something is preventing the unreacted hydrosilatane from reacting with the remaining acid chloride.

Consequently, we returned to investigate the identity of the silicon species observed at -88.3 ppm in the ²⁹Si NMR of a typical reduction reaction in CDCl₃ to determine if it is the species preventing complete conversion in our reactions. Initially, this species was presumed to be chlorosilatane. However, when chlorosilatane was prepared [21], we observed that its chemical shift was distinctly different (Fig. 3a).

Table 5
Reduction of substituted acid chlorides using 1-hydrosilatane (1) ^[a]


Entry	R	Yield of 3 ^[b] (%)
1	OMe (2a)	49 (3a)
2	H (2b)	52 (3b)
3	<i>t</i> -Bu (2c)	55 (3c)
4	CF ₃ (2d)	31 (3d)
5	CN (2e)	0 (3e)
6 ^[c]	NO ₂ (2f)	0 (3f)
7 ^[d]	Myristoyl chloride	0 (3g)

[a] Standard conditions: hydrosilatane (**1**, 1.5 equiv.), NMPi (1.5 equiv.), dichloromethane, rt, 1 h. [b] Yield of the aldehyde was determined by ¹H NMR using *p*-tolualdehyde as an internal standard. [c] Aliquot ¹H NMR taken after 1 hour showed no aldehyde present. [d] The reaction was run using myristoyl chloride as the substrate.

As a control, we ran a ²⁹Si NMR of a mixture of chlorosilatane and hydrosilatane (Fig. 3b) and confirmed that the chemical shift of chlorosilatane does not vary significantly in the presence of hydrosilatane, and that the observed chemical shift of chlorosilatane is accurate when referenced to hydrosilatane. We then considered that this species resonating at -88.3 ppm arose from a reaction between chlorosilatane formed *in-situ* and a substrate over the course of the reduction reaction, and that its build-up over time is what prevents further conversion of acid chloride to aldehyde. However, when chlorosilatane was added to a reaction mixture of acid chloride, hydrosilatane, and NMPi, the reduction of acid chloride still took place (Fig. 3c). Of further interest, the inclusion of chlorosilatane promoted side reactions as evidenced by the presence of novel aromatic species in the ¹H NMR spectrum (See SI, page 69). The difference in the ²⁹Si NMR signals seen in this experiment (Fig. 3c) compared to a typical reduction reaction (Fig. 3d) also seem to suggest the occurrence of previously unobserved side reactions. The results imply that chlorosilatane is not formed over the course of the reduction reaction, and the identity of the silicon-containing byproduct remains unknown.

Finally, we subjected a variety of acid chlorides to the reaction conditions to probe the scope and potentially provide further insight into the seemingly limited effectiveness of this method (Table 5). Electron-donating groups favour the formation of **3** (Table 5, entries 1 & 3), and electron-withdrawing groups hinder the formation of **3** (Table 5, entries 4-6). The reaction was not effective for the single investigated aliphatic acid chloride (Table 5, entry 7). These findings suggest that the Lewis basicity of the carbonyl is a crucial factor in the reaction. In all cases, the reduction was selective for the acid chloride as no alcohol product was observed.

3. Conclusions

We have demonstrated a method for the chemoselective reduction of acid chlorides to aldehydes using 1-hydrosilatane. The reaction requires a nucleophilic tertiary amine additive such as *N*-methylpyrrolidine to proceed and results in aldehyde with approximately 50% conversion to product and most of the rest of the starting acid chloride remaining intact. The reaction pathway possibly goes through a silyl ether intermediate which converts to the aldehyde in time but can also be cleaved by TBAF, running through a silica plug, or an aqueous workup. Despite the moderate yield, this method provides an efficient option for circumstances when either

1) prioritizing step-efficiency in a synthesis or 2) dealing with sensitive functional groups.

4. Experimental

4.1. General information

All chemicals were obtained from commercial sources and used without further purification. 1-Hydrosilatane was prepared using a published method [22]. ¹H, ¹³C, and ²⁹Si NMR were recorded using a 400 MHz Bruker multi-probe NMR instrument. Chemical shifts were reported in ppm referenced to the chloroform-*d* signal at 7.26 ppm or to the *p*-anisaldehyde at 9.89 ppm or to benzaldehyde at 10.04 ppm in mixtures where the chloroform-*d* signal could not be resolved. The internal standard used for calculating ¹H NMR yields were either *p*-tolualdehyde or ethyl acetate.

4.2. Typical anhydrous reduction procedure in dichloromethane

To a flame-dried round bottom flask under nitrogen equipped with a stir bar was added the acid chloride (68 mg, 0.4 mmol). Dichloromethane (1.0 mL) was added via a syringe flushed with nitrogen, and then the silatrane (105 mg, 0.6 mmol) was added in one portion. Lastly, NMPi (62 μL, 0.6 mmol) was added via a microsyringe flushed with nitrogen. The reaction was stirred at room temperature for 1 h, after which the mixture was passed through a short silica plug with dichloromethane as the eluent. The fractions were concentrated followed by addition of an internal standard and chloroform-*d* for characterization by ¹H NMR. The chemical shifts of the aldehyde product were compared to those in the literature [23].

4.3. Typical open-air reduction procedure in chloroform-*d*

To a round bottom flask equipped with a stir bar was added the acid chloride (68 mg, 0.4 mmol). Chloroform-*d* was added via syringe, and then the silatrane (105 mg, 0.6 mmol) was added in one portion. Lastly, NMPi (62 μL, 0.6 mmol) was added via a microsyringe. The reaction was stirred at room temperature for 1 h, followed by addition of an internal standard for characterization by ¹H NMR. The chemical shifts of the aldehyde product were compared to those in the literature [23].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.122130.

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