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Amines *vs.* *N*-Oxides as Organocatalysts for Acylation, Sulfonylation and Silylation of Alcohols: 1-Methylimidazole *N*-Oxide as an Efficient Catalyst for Silylation of Tertiary Alcohols

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Abstract: A comparison of the relative catalytic efficiencies of Lewis-basic amines *vs.* *N*-oxides for the acylation, sulfonylation and silylation of primary, secondary and tertiary alcohols is reported. Whilst the amines are generally superior to the *N*-oxides for acylation, the *N*-oxides are superior for sulfonylation and silylation. In particular, 1-methylimidazole *N*-oxide (NMI-O) is found to be a highly efficient catalyst for sulfonylation and silylation reactions. To the best of our knowledge, NMI-O is the first amine or *N*-oxide Lewis basic organocatalyst capable of promoting the efficient silylation of *tert*-alcohols in high yield with low catalyst loading under mild reaction conditions.

Keywords: acylation; Lewis base catalysis; 1-methylimidazole *N*-oxide; organocatalysis; silylation; sulfonylation

The development of Lewis basic organocatalysts for the acylation, sulfonylation and silylation of alcohols has received much attention from the synthetic organic community over the past decade.[1] A particular focus has been the development of chiral catalysts based on N-heterocycles, phosphines, N-heterocyclic carbenes and alcohols.[2–9] Whilst these catalysts have been primarily evaluated on their ability to impart enantioselectivity, the intrinsic Lewis basicity of their cores strongly impacts on their catalytic efficiency. Data relating to the efficiency of these catalophores[10] is generally inferred from the performance of the appropriate small molecule unsubstituted achiral Lewis bases.[11–13] Although some comparative studies have been reported for specific reaction types, e.g., for acylation[14–17] and for silylation,[18] to the best of our knowledge a comparative study of the relative abilities of the most commonly used N-heterocycles to catalyse acylation, sulfonylation and silylation of alcohols has not been reported. We considered that comparative data of this type would be valuable to allow selection of the optimal Lewis base for a given transformation and might also provide insight into preferred structural features for particular types of transformations.

We have recently reported the use of pyridine *N*-oxide[19] and particularly 2-aryl-4-dimethylaminopyridine *N*-oxide derivatives[20] as highly efficient Lewis base catalysts for the phosphorylation of alcohols by phosphoryl chlorides to give the corresponding phosphates. We expected that pyridine *N*-oxide and other *N*-oxides would also act as efficient catalysts for the formation of carboxylic esters, sulfonic esters and silyl ethers from alcohols and the appropriate acyl, sulfonyl and silyl chlorides,[21] and sought to benchmark their activity against the most commonly used Lewis-basic amine catalysts (Figure 1).

Herein, we report the results of a systematic comparison of the performance of five amines (**1**–**5**) and

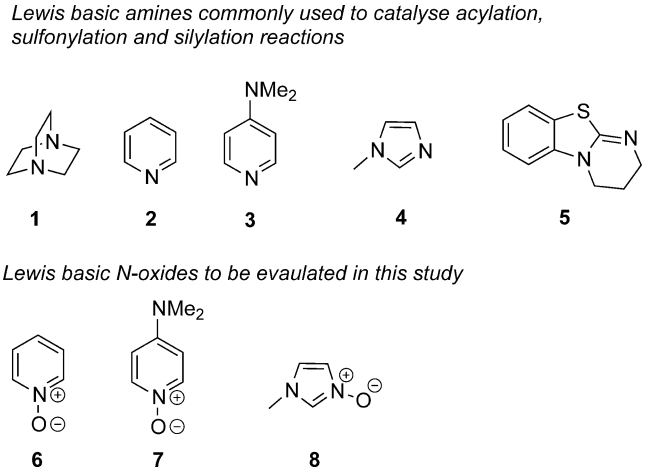
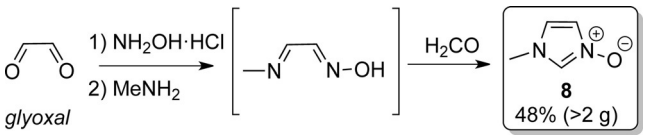


Figure 1. Amines and *N*-oxides evaluated as catalysts in this study.

three *N*-oxides (**6**–**8**) as catalysts for the acylation, sulfonylation and silylation of primary alcohol **9a**, *sec*-alcohol **9b** and *tert*-alcohol **9c** using acyl chloride **10** (Table 1), sulfonyl chloride **12** (Table 2) and silyl chloride **14** (Table 3), respectively.

The study reveals, for the first time, that 1-methylimidazole *N*-oxide (NMI-O, **8**) is a highly efficient catalyst for the sulfonylation and silylation of alcohols, including *tert*-alcohols. NMI-O has been prepared previously during an investigation into the use of its salts as components of ionic liquids, but in that work it was prepared *via* an 8-step synthesis from glyoxal.[22] By contrast, we prepared NMI-O (**8**) directly from glyoxal in 48% overall yield (Scheme 1).[22–25]



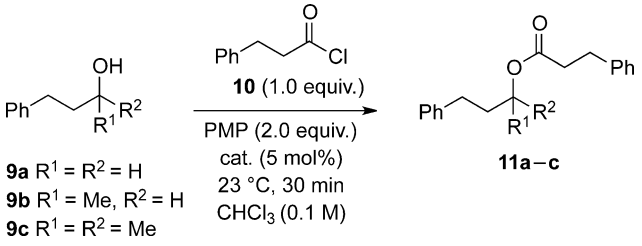
Scheme 1. Synthesis of 1-methylimidazole *N*-oxide (NMI-O, **8**) from glyoxal.

Our initial studies focused on evaluating the efficiency of catalysts **1**–**8** (5 mol%) in the acylation of alcohols **9a–9c** using hydrocinnamyl chloride (**10**) as the electrophile and pentamethylpiperidine (PMP) as a non-nucleophilic stoichiometric base in chloroform (0.1 M) at room temperature for 30 min (Table 1).

General base catalysis by the stoichiometric PMP accounted for 10% conversion for the acylation of *sec*-alcohol **9b**, and this along with some uncatalysed reaction accounted for 51% conversion of primary alcohol **9a** under the conditions used (entry 1). 1,4-Diazabicyclo[2.2.2]octane (DABCO, **1**), pyridine (**2**), 4-dimethylaminopyridine (4-DMAP, **3**), NMI (**4**) and 4-DMAP *N*-oxide (**7**) were all catalytically active for both substrates (entries 2–5 and 8). Interestingly, whilst 4-dimethylaminopyridine (4-DMAP, **3**) proved the most efficient catalyst in the acylation of primary alcohol **9a** (92% conversion, entry 4), *N*-methylimidazole (NMI, **4**) was the most effective catalyst in the acylation of *sec*-alcohol **9b** (55% conversion, entry 5). Pyridine *N*-oxide (**6**) was catalytically active only for primary alcohol **9a** (entry 8), and NMI-O (**8**) and Okamoto's isothiourea **5** were essentially catalytically inactive (entries 9 and 6). Acylation of *tert*-alcohol **9c** was not achieved by any catalyst under the conditions described; no conversion was observed after 24 h in all cases and starting alcohol **9c** was recovered quantitatively.

Sulfonyl chloride **12** was then utilised as the electrophile for evaluation of the same eight catalysts in the sulfonylation of alcohol **9a** under conditions otherwise identical to those used for acylation. However,

Table 1. Acylation of alcohols **9a–c** with acyl chloride **10**.



9a $R^1 = R^2 = H$
9b $R^1 = Me$, $R^2 = H$
9c $R^1 = R^2 = Me$

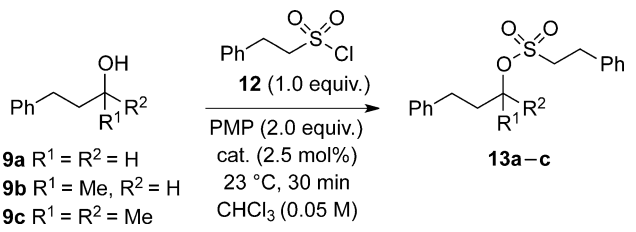
Entry	Catalyst[a]	Yield [%][b]		
		11a[c]	**11b**[d]	**11c**[c,e]
1	none (no base)	51 (15)	10 (0)	0 (0)
2	**1**	83	30	0
3	**2**	83	20	0
4	**3**	92	27	0
5	**4**	84	55	0
6	**5**	54	13	0
7	**6**	73	13	0
8	**7**	67	29	0
9	**8**	49	14	0

[a] These remained unaltered at the end of the reactions as evidenced by ^{1}H NMR of the crude reaction mixtures after quenching into MeOD-d_4.
[b] Determined by ^{1}H NMR of crude reaction mixtures after quenching.
[c] Using 1,3,5-trimethoxybenzene as internal standard.
[d] Using 1,3,5-mesitylene as internal standard.
[e] No reaction occurred even after 24 h, alcohol **9c** was recovered quantitatively. PMP = 1,2,2,6,6-pentamethylpiperidine.

complete conversion to sulfonate ester **13a** (>99%) was observed for all catalysts, demonstrating that sulfonylation is significantly faster than acylation under these conditions. To allow evaluation of catalyst activity, subsequent sulfonylation reactions with alcohols **9a–c** were therefore conducted at lower concentration (0.05 M) and lower catalyst loading (2.5 mol%, Table 2).

Under these sulfonylation conditions, general base catalysis by the stoichiometric PMP accounted for 56% and 61% conversion for the reactions of *sec*-alcohol **9b** and primary alcohol **9a**, respectively (entry 1). Broadly speaking, *N*-oxides **6–8** provided slightly superior rate enhancements relative to amines **1–5**. NMI-O (**8**, entry 9) proved the most efficient catalyst for the sulfonylation of primary alcohol **9a** and highly effective for the sulfonylation of *sec*-alcohol **9b** (although it was outperformed by 4-DMAP, entry 4). Interestingly, both general base promoted (i.e., in the absence of catalysts, entry 1), and Lewis base promoted (i.e., in the presence of the catalysts, entries 2–9) sulfonylations of *sec*-alcohol **9b** were found to occur at comparable rates to those of primary alcohol **9a**. This is in contrast to the analogous acylation process, for which the primary alcohol was significantly more

Table 2. Sulfonylation of alcohols **9a–c** using sulfonyl chloride **12**.

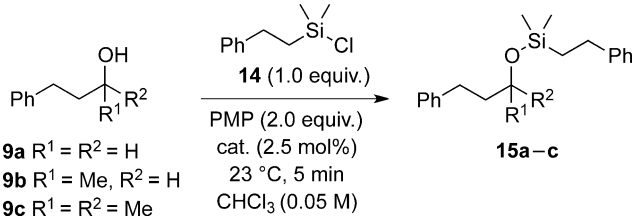


9a $R^1 = R^2 = H$
9b $R^1 = Me$, $R^2 = H$
9c $R^1 = R^2 = Me$

Entry	Catalyst[a]	Yield [%][b]		
		13a	**13b**	**13c**
1	none (no base)	61 (0)	56 (0)	0[c] (0[d])
2	**1**	73	80	0[c]
3	**2**	68	63	0[c]
4	**3**	89	>99	0[c]
5	**4**	75	65	0[c]
6	**5**	90	77	0[c]
7	**6**	75	62	0[c]
8	**7**	84	87	0[c]
9	**8**	97	93	0[c]

[a] These remained unaltered at the end of the reactions as evidenced by ^{1}H NMR of the crude reaction mixtures after quenching into MeOD-d_4.
[b] Determined by ^{1}H NMR of crude reaction mixture after quenching and using 1,3,5-trimethoxybenzene as internal standard.
[c] <10% alcohol **9c** was recovered in these reactions; a complex mixture of the derived chloride, indane and alkenes was formed, see the Supporting Information for details.
[d] No reaction occurred, alcohol **9c** was recovered quantitatively. PMP = 1,2,2,6,6-pentamethylpiperidine.

Table 3. Silylation of alcohols **9a–c** using silyl chloride **14**.



9a $R^1 = R^2 = H$
9b $R^1 = Me$, $R^2 = H$
9c $R^1 = R^2 = Me$

Entry	Catalyst[a]	Yield [%][b]		
		15a[c]	**15b**[d]	**15c**[c,e]
1	none (no base)	53 (0)	32 (0)	0 (0)
2	**1**	53	51	29
3	**2**	60	42	35
4	**3**	>99	75	34
5	**4**	66	53	30
6	**5**	>99	74	32
7	**6**	83	56	40
8	**7**	75	73	38
9	**8**	>99	>99	72

[a] These remained unaltered at the end of the reactions as evidenced by ^{1}H NMR of the crude reaction mixtures after quenching into MeOD-d_4.
[b] Determined by ^{1}H NMR of crude reaction mixtures after quenching.
[c] Using 1,3,5-trimethoxybenzene as internal standard.
[d] Using 1,3,5-mesitylene as internal standard.
[e] Reaction time increased to 4 h. PMP = 1,2,2,6,6-pentamethylpiperidine.

reactive than the secondary alcohol (*cf.* Table 1) indicating that the steric environment of the alcohol nucleophile plays a lesser role in these sulfonylation reactions as compared to the acylation reactions. Consistent with this trend, although the product of sulfonylation of *tert*-alcohol **9c** (i.e., compound **13c**) could not be isolated using any of the conditions evaluated, its transient formation in all the reactions was manifested by the poor recovery of alcohol **9c** (<10%) and the formation of a complex mixture of secondary products including: (3-chloro-3-methylbutyl)benzene, 1,1-dimethyl-2,3-dihydro-1*H*-indene, (3-methylbut-3-en-1-yl)benzene and (3-methylbut-2-en-1-yl)benzene (see the Supporting Information for details). Sulfonyl esters of *tert*-alcohols are known to be highly labile and prone to elimination,[26] but the notably low levels of alcohol recovery under our conditions suggest that probably one or more of the secondary products in these reactions reacts further to consume additional starting alcohol **9c**.

Silyl chloride **14** was then utilised as the electrophile for evaluation of the array of catalysts in the silylation of alcohols **9a–c**. These reactions proved to be the most rapid of those studied and so although the conditions employed were identical to those used for sulfonylation, these reactions were quenched after just 5 min for the primary and secondary alcohols (*cf.* 30 min for sulfonylation) and after 4 h for the tertiary alcohol substrate (Table 3).

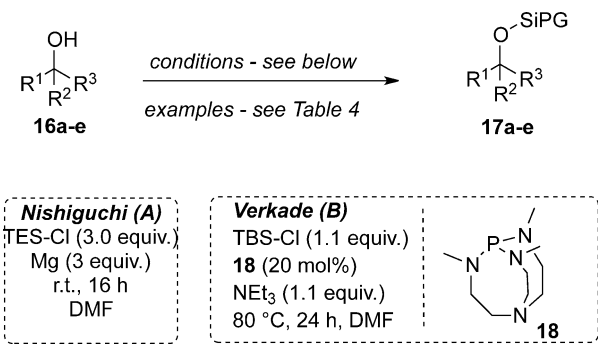
Silylation of all three alcohol substrates, including *tert*-alcohol **9c**, was achieved. Whilst primary alcohol **9a** could be silylated quantitatively using 4-DMAP, Okamoto's isothiourea **5** and NMI-O (**8**) (entries 4, 6 and 9), clearly the most efficient catalyst for both the *sec*-alcohol **9b** and the *tert*-alcohol **9c** was NMI-O (**8**, entry 9). Indeed, although 4-DMAP (**3**) was generally more efficient than 4-DMAP-*N*-oxide (**7**), both pyridine *N*-oxide (**6**) and NMI-O (**8**) were more effective than their parent heterocycles **2** and **4** in these processes (*cf.* entries 3–5 *vs.* 7–9). The performance of NMI-O (**8**), particularly as an efficient catalyst for the silylation of *tert*-alcohol **9c** is striking and noteworthy, giving 72% conversion after 4 h.

The preparation of silyl ethers of *tert*-alcohols has attracted significant levels of attention since the synthetic potential of silyl protecting groups (PGs) was first recognised in the 1970s.[27] The introduction of even the minimally bulky trimethylsilyl (TMS) group onto *tert*-alcohols is non-trivial and often inefficient using TMS-Cl under standard Lewis base promoted

conditions, e.g., TMS-Cl (1.2 equiv.), imidazole (2.5 equiv.) in DMF.[28] Consequently, alternative reagents and conditions have been developed for preparation of TMS ethers of *tert*-alcohols,[29–34] of which the use of $(TMS)_2NH$ (0.8 equiv.), iodine (1 mol%) in DMF[35] is amongst the most mild and economic.

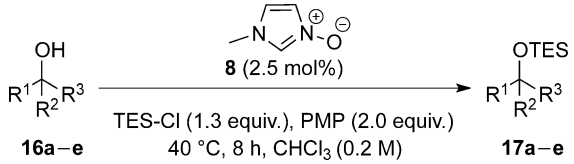
For the formation of silyl ethers of *tert*-alcohols with more bulky silyl PGs such as triethylsilyl (TES)[36] and *tert*-butyldimethylsilyl (TBS)[28] ethers, which are synthetically more useful than TMS ethers due to their improved stability towards acids and bases,[37–39] silyl triflate and silyl perchlorate reagents are generally relied upon [e.g., TBS-OTf (1.5 equiv.), 2,6-lutidine (2 equiv.) in CH_2Cl_2[40] or TBS-$OClO_3$ (1.5 equiv.), pyridine (2 equiv.) in CH_3CN[41]]. However, these silylating reagents are significantly more hydrolytically unstable and expensive than the corresponding silyl chlorides. Interestingly, the reactions of both TBS-OTf and TBS-$OClO_3$ have recently been shown to be insensitive to Lewis base catalysis.[42] The only efficient processes for preparing silyl ethers of *tert*-alcohols with bulky silyl PGs using silyl chlorides that we are aware of are one developed by Nishiguchi using Mg as a promoter [TES-Cl (3 equiv.), Mg (3 equiv.) in DMF at room temperature][43] and one developed by Verkade using proazaphosphatrane **18** as a Lewis base catalyst [TBS-Cl (1.1 equiv.), **18** (20 mol%) in DMF at 80 °C].[44] Although the Verkade catalyst **18** is commercially available, it is expensive and reacts with oxygen and with water to give the oxide and hydroxide, respectively.[45] As far as we are aware, no amine or *N*-oxide Lewis base has previously been reported to efficiently catalyse the formation of bulky silyl ethers from *tert*-alcohols (Scheme 2).[18]

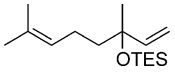
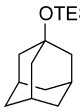
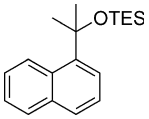
To highlight the utility of NMI-O (**8**) as an unusually efficient organocatalyst for this type of transformation, we therefore decided to examine its use as a catalyst for the preparation of sterically hindered silyl ethers of various *tert*-alcohols. Unfortunately, no synthetically useful yields could be obtained with TBDMS-Cl or triisopropylsilyl chloride (TIPS-Cl), however, TES-Cl provided the desired tertiary TES-ethers in excellent yields whilst maintaining a low catalyst loading (2.5 mol%) at 40 °C in $CHCl_3$ (Table 4).



Scheme 2. Previous methods for silylation of *tert*-alcohols with TES-Cl or TBS-Cl.

Table 4. Silylation of *tert*-alcohols **16a–e** with TES-Cl catalysed by NMI-O (**8**) and comparison with the above reported previous methods.



Entry	Product		Yield [%][a]	Previous Conditions (Yield [%])
1		**17a**	92	**A** (85)[43] **B** (86, TBS)[44]
2		**17b**	95	**B** (80, TBS)[44]
3		**17c**	97	NA
4		**17d**	87	**B** (12, TBS)[44]
5		**17e**	98	NA

In conclusion, we have directly compared a series of five commonly used Lewis-basic amines (**1**–**5**) and three *N*-oxides (**6**–**8**) as catalysts for the acylation, sulfonylation and silylation of primary, secondary and tertiary alcohol derivatives **9a–c**. Whilst the amine catalysts are generally more efficient in the acylation processes, the *N*-oxides are generally more effective catalysts in the analogous sulfonylation and silylation reactions. In particular, 1-methylimidazole *N*-oxide (NMI-O) has been shown to be a highly efficient catalyst for the sulfonylation and silylation of alcohols and, importantly, the first effective non-phosphorus based Lewis-basic catalyst for the silylation of *tert*-alcohols with TES-Cl. Further investigations into the catalytic capabilities of NMI-O and its derivatives are ongoing in our laboratory.

Experimental Section

General Procedure for Synthesis of TES Ethers of *tert*-Alcohols

To a solution of the alcohol component (1.75 mmol), 1-methylimidazole *N*-oxide (**8**, 4.3 mg, 2.5 mol%) in $CHCl_3$ (8.75 mL, 0.2 M) was added PMP (0.63 mL, 3.50 mmol) followed by TES-Cl (0.367 mL, 2.19 mmol). The reaction mixture was then heated to 40 °C for 8 h before the addition of MeOH (1 mL) to quench the reaction. The resulting solution was concentrated under vacuum and the residue purified by flash chromatography to afford the product; yield: 87–98%.

Acknowledgements

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