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Manganese Dioxide Catalyzed *N*-Alkylation of Sulfonamides and Amines with Alcohols under Air

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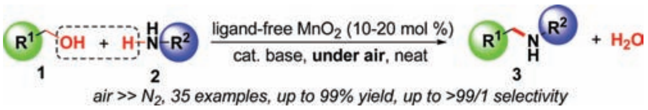
ABSTRACT



By simply running the reactions under air and solvent-free conditions using catalytic amounts of manganese dioxide, a practical and efficient *N*-alkylation method for a variety of sulfonamides and amines using alcohols as green alkylating reagents was developed.

Organonitrogen compounds such as amine and amide derivatives are not only important nitrogen sources in synthesis but also important chemicals abounding in natural products as well as biochemically and pharmaceutically active molecules.[1] In addition to other methodologies such as transition-metal-catalyzed amination of organohalides, reductive amination of carbonyl compounds, etc.,[2] in recent years, *N*-alkylation of amines and amides with alcohols catalyzed by transition metal complexes, namely, the borrowing hydrogen or hydrogen autotransfer methodology, has been considered as a greener and more environmentally benign alternative for amine derivatives using alcohols as the alkylating reagents in a one-pot manner and high atom efficiency achievable by producing water as the only byproduct.[3] However, there still remains much room for improvement of the method, because the reactions usually employ air-sensitive, preformed noble metal complexes derived from ruthenium and iridium or addition of capricious ligands for catalyst activation and require inert atmosphere protection and sometimes even special apparatuses such as the glovebox to manipulate the catalysts and reactions. Therefore, developing greener and more efficient reactions that can be performed under less demanding conditions and/or using non-noble metal catalysts are highly desirable.

Recently, we accidentally found that air can promote a Rh-catalyzed *N*-alkylation reaction of sulfonamides with alcohols,[4a] which later led to a general and advantageous air-promoted metal-catalyzed aerobic *N*-alkylation

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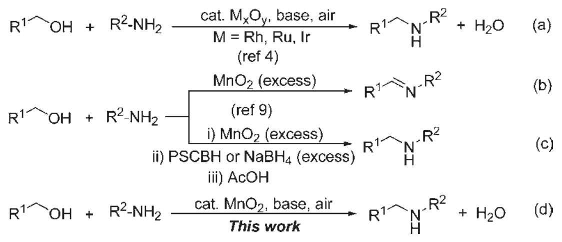
method and discovery of a new mechanism[4b] that has never been proposed in metal-catalyzed *N*-alkylation reactions.[3,4] We also noticed that the more easily disposable metal oxides were also effective catalysts (Scheme 1a).[4b] With an intension to further explore the scope of the aerobic *N*-alkylation method and develop more preferable catalysts, we envisioned that simple metal oxides, especially those derived from the cheaper, more available, and less toxic non-noble metals, may also be suitable catalysts for the reaction.

Scheme 1. Metal Oxide Mediated C−N Bond Formations



However, to our knowledge, an efficient reaction catalyzed by a simple metal oxide was not yet known. In the past, these reactions were carried out under rather harsh conditions such as high temperature (> 200 °C), high pressure, and/or with long reaction times.[3f,5] Recently, a number of heterogeneous noble metal catalysts (Ru, Ir, Pd, Pt, Au, Ag) supported by metal oxides (CeO_2, ZrO_2, Al_2O_3, SiO_2, MgO, ZnO, TiO_2, Fe_2O_3, Fe_3O_4, etc.) or hydroxides were developed,[6] but severe drawbacks still remain. For example, these reactions usually suffer from the requirement of inert atmosphere protection, high temperatures (> 150 °C), long reaction times, or the use of solvents, large excess amounts of alcohols, amines, or bases. Among the usual metal oxides, we found manganese dioxide (MnO_2) had not been used in the reactions yet.[3−6]

MnO_2 is a less toxic, easily handled, readily available, and recyclable reagent. It has long been known as a mild oxidant frequently used in alcohol oxidations (usually in large excess amounts, 5−50 equiv).[7,8] In 2001, Taylor et al. reported an imine preparation method from alcohols and amines by using large excess amounts (10 equiv) of MnO_2 as the oxidant (Scheme 1b), for which, if followed by a reduction reaction using polymer-supported cyanoborohydride (PSCBH) or $NaBH_4$ as the reductant, a one-pot, *in situ* oxidation-condensation-reduction process could be achieved for *N*-alkylated amines (Scheme 1c).[9,10] Since large excess amounts of oxidants and reductants were required, which may be toxic and hazardous, the reactions not only were costly and tedious in operation and work-up but also may result in waste disposal and environmental problems. In contrast with the above-mentioned methods,[3,5,6,9,10] herein we report, using catalytic amounts of MnO_2, a practical and efficient dehydrative *N*-alkylation method for sulfonamides and amines with alcohols that can be readily achieved under air and solvent-free conditions (Scheme 1d).

Initially, various simple metal oxides (10 mol %) were tested in the model reaction of benzyl alcohol **1a** and benzenesulfonamide **2a** (Table 1). Sc_2O_3, TiO_2, V_2O_4, MnO, Fe_2O_3, Co_3O_4, NiO, and Ni_2O_3 gave no, trace, or low yields of the target product, while MnO_2 afforded the product, *N*-benzyl-benzenesulfonamide **3aa**, in 73% yield and high selectivity under the same conditions (run 1).[11] Examination of MnO_2 and base loadings showed that 20 and 50 mol % were the best at 120 °C (run 2). Higher loadings gave no higher yields of the product, but lower loadings could result in slightly lower yields. No reaction occurred without MnO_2 (run 3), indicating it is essential for the reaction. Besides, by solvent and base screening, the reaction was found to be better carried out under solvent-free conditions using K_2CO_3 as the base. By running the reaction at a higher temperature of 135 °C, base loadings were further reduced to 20 mol % and the product yield was enhanced to 96% (89% isolated) (run 4). More conditions revealed that 10−20 mol % MnO_2 and 10−20 mol % K_2CO_3 were all satisfactory choices (runs 4−6), but less loadings only led to inefficient reactions. In contrast, the reaction under nitrogen was ineffective, affording only a low yield of the product (run 7). The reason for this difference is unclear at present but may be explained by the fact that like other metal oxides that are good alcohol oxidation[7] and effective *N*-alkylation[4b] catalysts under aerobic

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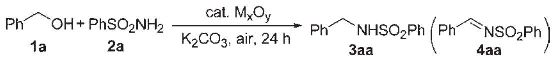
(10) More recently, Cossy and coworkers also reported a similar process using TEMPO-PhI(OAc)$_2$ as the stoichiometric oxidant and $NaBH_4$ or NaBH(OAc)$_3$ as the reductant. See: Guérin, G.; Bellosta, V.; Guillamot, G.; Cossy, J. *Org. Lett.* **2011**, *13*, 3534.

(11) An in situ prepared activated MnO_2 (according to refs 7 and 8) and commercial MnO_2 were both examined, showing similar activities.

conditions, MnO_2 behaved similarly in activities in both reactions[12] (vide infra).

Table 1. Condition Screening[a]



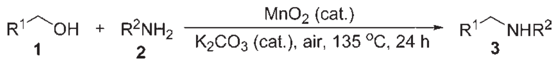
run	MnO_2 (mol %)	K_2CO_3 (mol %)	temp (°C)	**3aa**%[b]	**3aa**/**4aa**[b]
1	10	50	120	73	99/1
2	20	50	120	87	99/1
3	0	50	120	ND[c]	–
4	20	20	135	96 (89)	99/1
5	20	10	135	96	99/1
6	10	10	135	96	99/1
7[d]	20	10	135	45	99/1

[a] Unless otherwise noted, the mixture of **1a** (4 mmol), **2a** (3 mmol), and the metal oxides was heated in a 20 mL sealed Schlenk tube under air and then heated and monitored by TLC and/or GC-MS. [b] Yields and **3**/**4** ratios determined by GC-MS (isolated yield in parentheses) based on **2a**. [c] No product detected by TLC. [d] Under nitrogen.

The optimized conditions were then applied to various sulfonamides, amines, and alcohols to extend the scope of the method (Table 2). As investigated, all the electron-rich and -deficient sulfonamdies (runs 1–9), including heteroaromatic and aliphatic ones, and benzylic alcohols (runs 10–14) gave good to high yields of the products.[13] Like *para*- and *meta*-substituted substrates, the sterically more bulky *ortho*-substituted ones also gave good results (runs 3, 6, 12). Beside the sulfonamides, a variety of electron-rich and -deficient, aromatic or heteroaromatic amines also reacted efficiently under similar conditions to give good to high yields of the products (runs 15–35). In these cases, like the literature reports,[3–6] alkali metal hydroxides were more effective bases. Although the scope of the method remains to be fully investigated, these results revealed its potential utility and the advantages of using MnO_2 instead of other metal catalysts[3–6] and the oxidation-condensation-reduction methods.[9,10]

As an ongoing study in the aerobic *N*-alkylation methods,[4] mechanistic aspects of the reaction are therefore our interest and next concern. As demonstrated below based on the studies of the individual reactions, this reaction most probably proceeds via a process similar to the mechanism we recently proposed[4b] (Scheme 2). The first step is the Mn-mediated alcohol oxidation (step i), a known process in the literature.[12] In our hands, trace benzaldehyde **5a** was observed when absolute benzyl alcohol **1a** was heated with 15% MnO_2 under N_2 (Table 3, run 1). The same reaction under air was more efficient (run 2), showing that air can promote the oxidation to some extent even without optimizing the conditions, consistent with the literature reports.[12] These contrastive results may also account for the observed different efficiencies of the aerobic and anaerobic reactions (Table 1), revealing again that the aerobic condition is a more effective alcohol activation alternative. In addition, no deactivation of MnO_2 by the ligating amides/amines was observed, for similar amounts of **5a** could be observed when **2a** was added (run 3). In contrast, MnO, found unable to oxidize the alcohol under N_2 (run 4) but able

Table 2. MnO_2-Catalyzed *N*-Alkylation of Sulfonamides and Amines with Alcohols under Air



run	**1, 2**	**3**%[a]
1[b,c]	$PhCH_2OH$ (**1a**), $PhSO_2NH_2$ (**2a**)	96 (89)
2[c,d]	**1a**, *p*-$CH_3C_6H_4SO_2NH_2$ (**2b**)	98
3[c,d]	**1a**, *o*-$CH_3C_6H_4SO_2NH_2$ (**2c**)	94
4[c,d]	**1a**, *p*-$CH_3OC_6H_4SO_2NH_2$ (**2d**)	61
5[c,d]	**1a**, *p*-$ClC_6H_4SO_2NH_2$ (**2e**)	76
6[c,d]	**1a**, *o*-$ClC_6H_4SO_2NH_2$ (**2f**)	93
7[c,d]	**1a**, 2-naphthalenesulfonamide (**2g**)	99
8[c,d]	**1a**, 2-(5-chlorothiophene)sulfonamide (**2h**)	78
9[c,d]	**1a**, $CH_3SO_2NH_2$ (**2i**)	98
10[c,d]	*p*-$CH_3C_6H_4CH_2OH$ (**1b**), **2a**	76
11[c,d]	*p*-$CH_3OC_6H_4CH_2OH$ (**1c**), **2a**	87
12[c,d]	*o*-$CH_3OC_6H_4CH_2OH$ (**1d**), **2a**	82
13[c,d]	*p*-$ClC_6H_4CH_2OH$ (**1e**), **2a**	99
14[c,d]	*m*-$ClC_6H_4CH_2OH$ (**1f**), **2a**	83
15[d,e]	**1a**, 2-aminopyrimidine (**2j**)	88
16[d,e]	**1c**, **2j**	93
17[d,e]	**1d**, **2j**	95 (82)
18[d,e]	**1e**, **2j**	95
19[d,e]	*o*-$ClC_6H_4CH_2OH$ (**1g**), **2j**	88 (74)
20[d,f]	**1a**, 2-aminopyridine (**2k**)	90
21[d,f]	**1c**, **2k**	85
22[d,f]	**1d**, **2k**	76 (63)
23[d,f]	**1e**, **2k**	66
24[d,f]	**1g**, **2k**	68 (55)
25[d,f]	**1a**, 3-aminopyridine (**2l**)	83
26[d,f]	**1a**, 5-chloro-2-aminopyridine (**2m**)	89 (79)
27[d,f]	**1a**, $PhNH_2$ (**2n**)	90
28[b,e]	**1b**, **2n**	77
29[d,f]	**1c**, **2n**	76
30[b,f]	**1a**, *p*-$CH_3C_6H_4NH_2$ (**2o**)	84
31[b,f]	**1a**, *m*-$CH_3C_6H_4NH_2$ (**2p**)	97
32[d,f]	**1a**, *p*-$EtOC_6H_4NH_2$ (**2q**)	92 (85)
33[b,f]	**1a**, *p*-$ClC_6H_4NH_2$ (**2r**)	97
34[b,g]	**1a**, *m*-$ClC_6H_4NH_2$ (**2s**)	98
35[b,f]	**1a**, *o*-$ClC_6H_4NH_2$ (**2t**)	91

[a] See Table 1 for operation. K_2CO_3 was used as the base unless otherwise noted. GC yield (isolated yield in parentheses) based on **2**. Byproduct **4** was usually formed in low selectivity (< 1%). [b] 10 mol % MnO_2. [c] 10 mol % K_2CO_3. [d] 20 mol % MnO_2. [e] 40 mol % NaOH used. [f] 40 mol % CsOH used. [g] 40 mol % KOH used.

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(12) Unlike other metal oxides (ref 7), Mn-catalyzed aerobic alcohol oxidations are still rare and less effective. See: (a) Kimura, T.; Fujita, M.; Sohmiya, H.; Ando, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1149. (b) Fu, X.; Feng, J.; Wang, H.; Ng, K. M. *Nanotechnology* **2009**, *20*, 37601. (c) Son, Y. C.; Makwana, V. D.; Howell, A. R.; Suib, S. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4280. (e) Makwana, V. D.; Son, Y. C.; Howell, A. R.; Suib, S. L. *J. Catal.* **2002**, *210*, 46. (e) Makwana, V. D.; Garces, L. J.; Liu, J.; Cai, J.; Son, Y. C.; Suib, S. L. *Catal. Today* **2003**, *85*, 225.

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to under air (run 5), was deactivated by the addition of **2a**, giving only trace **5a** under air. These results (runs 3 and 6) may account for the reason why MnO_2 is much more active than MnO in the reaction (vide supra). Since MnO cannot oxidize the alcohol under nitrogen (run 4), Mn(II) may be generated from Mn(IV) under nitrogen (Scheme 2, step i), but clearly it is not complete and not an effective alcohol activation protocol (Table 3, run 1) as it only led to an ineffective anaerobic reaction (Table 1, run 7).

Scheme 2. Proposed Reaction Path

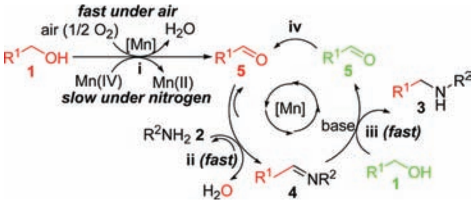
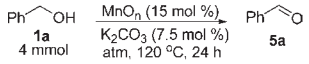


Table 3. Mn-Mediated Alcohol Oxidations

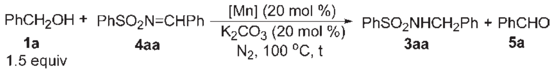


run	MnO_n	atm	additive (mol %)	**5a**%[a]
1	MnO_2	N_2	–	0.6
2	MnO_2	air	–	3.6
3	MnO_2	air	**2a** (30)	5.4
4	MnO	N_2	–	0
5	MnO	air	–	2.9
6	MnO	air	**2a** (30)	0.7

[a] Yields were determined by ^{1}H NMR analysis based on **1a**.

The condensation step (Scheme 2, step ii), also a well-known standard organic reaction, can proceed in the absence of any catalysts.[13] In present cases, the reaction of **2a** and **5a** was also found to proceed smoothly in the presence of either MnO_2 or MnO. Similarly, the transfer hydrogenation step (Scheme 2, step iii)[14,15] could also be confirmed easily. Thus, in the presence of MnO_2 or MnO, good yields of the product could be obtained in the transfer hydrogenative reduction of **4aa** by **1a** in 8 h at only 100 °C (Table 4). As indicated by the NMR studies (Table 4),[16] byproduct aldehyde **5a** was analyzed to be regenerated quantitatively in the transfer hydrogenation step (Scheme 2, step iii). The regenerated aldehydes should be recovered in the next condensation reaction to complete the catalytic cycle (step iv). Moreover, according the proposed mechanism (Scheme 2), the originally inefficient anaerobic reaction (Table 1, run 7) should also be able to be accelerated by adding intermediate aldehyde or imine instead of running the reactions under air.[17] Indeed, when only catalytic amounts of either **4aa** or **5a** (10 mol %) were added to a standard reaction of **1a** and **2a** followed by heating under nitrogen, high yields of the product could be obtained (80% and 97%, respectively), which should also support the proposed mechanism. Therefore, as proven above and supported by corresponding literatures,[4,9,10,12−15] Scheme 2 should be the most possible mechanism for the Mn-catalyzed aerobic *N*-alkylation reactions.

Table 4. Mn-Catalyzed Transfer Hydrogenation


$$\underset{\substack{\mathbf{1a}\\1.5\text{ equiv}}}{PhCH_2OH} + \underset{\mathbf{4aa}}{PhSO_2N{=}CHPh} \xrightarrow[\substack{K_2CO_3\ (20\text{ mol }\%)\\N_2,\ 100\ ^{\circ}C,\ t}]{[Mn]\ (20\text{ mol }\%)} \underset{\mathbf{3aa}}{PhSO_2NHCH_2Ph} + \underset{\mathbf{5a}}{PhCHO}$$

run	MnO_n	time	**3aa**%[a]	**5a**%[a]	**5a**/**3aa**[a]
1	MnO_2	8 h	68	74	1.09/1.00
2	MnO	6 h	72	72	1.00/1.00
		8 h	79	83	1.05/1.00

[a] Yields and ratios were determined by ^{1}H NMR analysis.[16]

In conclusion, a practical and efficient *N*-alkylation method for various sulfonamides and amines using alcohols as greener alkylating reagents was developed by simply carrying out the reactions under air and solvent-free conditions using only catalytic amounts of MnO_2. Since this method avoids the use of noble metal catalysts, activating ligands, and both stoichiometric oxidants and reductants, requires no inert atmosphere protection, and can greatly simplify the operation and workup procedures, it may be a good alternative for the existing methods.[3−6,9,10] Further extensions of the metal oxide mediated *N*-alkylation methods are underway.

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Supporting Information Available. Experimental procedures, product characterization, mechanistic studies, and ^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Transfer hydrogenation of intermediate imines by alcohols to give product amines was also frequently employed to confirm the *N*-alkylation path in borrowing hydrogen reactions, albeit indirectly in our opinion. See ref 3 and references therein.

(15) For selected reviews and mechanistic discussions on transfer hydrogenation: (a) Reference 3b. (b) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226.

(16) See Supporting Information for detail.

(17) We are thankful one of the reviewers for this kind and proper suggestion.