

Alcohol Oxidation

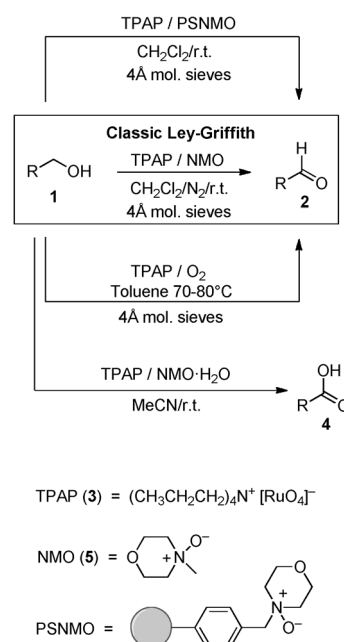
NMO·TPB: A Selectivity Variation on the Ley–Griffith TPAP Oxidation

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Dedicated to Professor Steven V. Ley on the occasion of his 70th birthday

Abstract: A non-hygroscopic tetraphenylborate salt of *N*-methylmorpholine-*N*-oxide (NMO) is reported (NMO·TPB), which modulates the standard Ley–Griffith oxidation such that benzylic and allylic alcohols are oxidised selectively. An attractive feature of this new protocol is that anhydrous conditions are not required for this selective tetra-*n*-propylammonium perruthenate (TPAP) oxidation, superseding the requirement of molecular sieves.

Oxidation of alcohols to carbonyl compounds (i.e., aldehydes, ketones and carboxylic acids) is part of everyday life for the practicing synthetic chemist, whether in industry or academia. Of the extensive range of reagents and catalysts that are available to perform alcohol oxidation,^[1] practitioners tend to prefer controlled oxidations, for example, the one-step oxidation of a primary alcohol (**1**) to an aldehyde (**2**; Scheme 1).^[2] This transformation, however, requires a specially designed oxidation protocol, or reagent system, to access the synthetically important aldehyde functional group. Historically, alcohol to aldehyde oxidation methods were dominated by the use of chromium reagents (e.g., pyridinium chlorochromate (PCC),^[3] pyridinium dichromate (PDC)^[4]), sulfur activation protocols (e.g., Swern,^[5] Corey–Kim,^[6a] Parikh–Doering^[6b]) and manganese oxides (e.g., MnO₂^[7]). This was followed by the introduction of the hypervalent iodides^[8] (for example, Dess–Martin periodinane (DMP)^[9]), the nitroxyl radicals (e.g., (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO))^[10] and later combinations thereof.^[11] In more recent times, advances in this general area include revived hypervalent iodides (e.g., 2-iodoxybenzoic acid (IBX) and derivatives^[12]), nitroxyl radicals^[13] (e.g., 2-azaadamantane *N*-Oxyl (AZADO)^[14] and F-AZADO^[15]), Oppenauer conditions,^[16] in addition to iridium,^[17] bismuth^[18] and photochemical-mediated oxidations.^[19] Although, in this recent timeframe, substantial effort by the community in developing molecular oxygen based protocols has witnessed a deluge of new meth-



Scheme 1. The Ley–Griffith oxidation and selected variants.

ods for aldehyde synthesis,^[20] using transition metals (e.g., Cu,^[21] Pd,^[22] Au,^[23] V,^[24] Ru,^[25] Co^[26]) and metal-free systems.^[27]

Beyond the legacy reagents, and recent elegant innovations, however, the trident systems that continue to hold a high position within this landscape are the Swern oxidation, DMP/IBX and the Ley–Griffith reagent^[28] tetra-*n*-propylammonium perruthenate (TPAP, **3**; (*n*Pr₄N)[RuO₄]). The popularity of these systems is clearly justified by the mild conditions required to promote oxidation, proven wide functional-group tolerance,^[29] and limited toxicity. However, they are not totally without complications, for example, the Swern oxidation generates a pungent odour on workup (Me₂S),^[30] whereas IBX can drive unwanted acid-mediated side reactions,^[31] and has been known to explode,^[32] although a stabilised version (SIBX) is available.^[33] Both DMP and TPAP are sensitive to the atmosphere, and require the oxidations to be performed under anhydrous conditions. In the case of TPAP, if water is not removed from the system, over oxidation to a carboxylic acid can occur (**4**), and this has been capitalised upon as a synthetic method.^[34] Traditionally, *N*-methyl morpholine-*N*-oxide (NMO, **5**),^[35] which is considerably hygroscopic, is used as the co-oxidant in TPAP oxidations in the form of polymer-bound PSNMO.^[35b] However,

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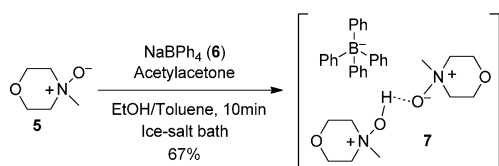
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more recent developments have demonstrated that molecular oxygen can be utilised in conjunction with heating,^[36] although this seems not to have been widely adopted (Scheme 1).

Herein, we report a novel, easy-to-prepare, non-hygroscopic, bis-NMO salt, and demonstrate its utility in the selective TPAP-mediated oxidation of benzylic and allylic alcohols, without the requirement for anhydrous solvents, and/or an inert atmosphere.

When attempting to extend our previous study involving the double deprotonation of NMO (5),^[37] we discovered that reaction of 5 with benzoic anhydride and sodium tetraphenylborate (NaTPB, 6), afforded crystals of a monoprotonated 2:1 NMO-TPB salt (abbreviated name NMO-TPB) in low yield (7; Scheme 2),^[38] as confirmed by X-ray crystallographic analysis



Scheme 2. Synthesis of the NMO-TPB (7) salt.

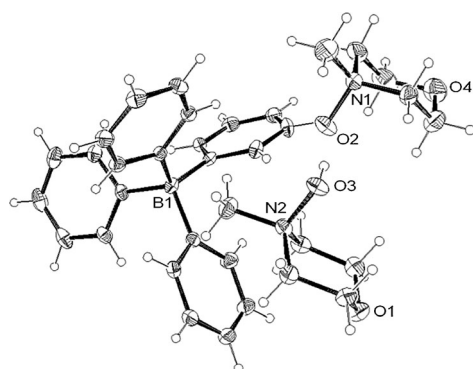


Figure 1. X-Ray crystal structure of the NMO-TPB (7) salt at 30% ellipsoid probability.

(Figure 1). During these investigations it was surmised that benzoic anhydride was acting as a ligand to drive salt formation, thus, substitution of the anhydride for acetylacetonate, pleasingly afforded salt 7 in 67% yield (Scheme 2). NMO-TPB (7) was found to be a non-hygroscopic, bench-stable white crystalline solid, containing no waters of hydration.^[39]

Having devised a reproducible protocol, with easy access to scalable quantities of NMO-TPB (7), we investigated the potential for 7 to promote TPAP oxidations with the intended advantage being a more easily handled co-oxidant compared to hygroscopic NMO (5). The initial results with aliphatic alcohols were disappointing, with yields of aldehyde ranging from trace amounts to a maximum of ~20% (gentle heating gave no improvement). However, select benzylic alcohols performed well, but a solvent switch from dichloromethane to acetonitrile was required for increased solubility of 7, which led us to investigate HPLC grade acetonitrile in the absence of molecular

Table 1. Aryl and allylic aldehydes, and ketones, obtained from NMO-TPB (7)/TPAP (3) oxidation. [BRMS = yield based on recovered starting material].

Entry	Aldehyde	Yield [%] (BRSM)	Entry	Aldehyde	Yield [%] (BRSM)
1		75 ^[a,b]	11		88
2		> 95 ^[a]	12		70
3		> 95	13		< 5
4		64 (71)	14		60 (77)
5		89 ^[c]	15		72 (85)
6		87	16		80 ^[f]
7		95 ^[d]	17		94
8		77 ^[d,e]	18		95
9		68	19		69 (79)
10		67	20		74

[a] Yield based on ¹H NMR; [b] Literature TPAP yield 80%;^[28b] [c] Literature TPAP yield 68%;^[28b] [d] Workup modified to 1:1 pentane/diethyl ether extraction; [e] Literature TPAP yield 91%;^[28b] [f] Literature TPAP yield 98%.^[28b]

sieves. With much delight, it was observed that this did not alter the reaction outcome. Application of the optimised conditions to a range of aryl benzylic and allylic substrates (Table 1) gave the corresponding benzaldehydes **8a–k** (Table 1, entries 1–11), arylketones **8n–o** (Table 1, entries 14, 15) and allylic aldehydes **8p–t** (Table 1, entries 16–20) in good to excellent yields. Unfortunately, the 2-pyridyl system, **8m**, reacted poorly (Table 1, entry 13), most likely due to chelation effects.

Table 2. Yield verification, and extended scope, facilitated by phenyl Grignard trapping of crude aldehyde.

Entry	Diaryl Carbinol	Yield ^[a] [%]	Entry	Diaryl Carbinol	Yield ^[a] [%]
1		82 (75) ^[b]	4		82 (81) ^[b]
2		> 95 (> 95) ^[b]	5		60 (59) ^[b]
3		71	6		50

[a] Overall yield based on a two-step reaction sequence (i.e., oxidation and phenyl Grignard addition); [b] Isolated yield of intermediate aldehyde.

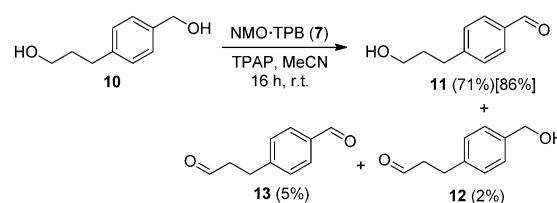
Only in the cases of benzyl- and 4-fluorobenzyl alcohol did we observe trace amounts of carboxylic acid formation, **8a** and **9d** (Table 1, entry 1 and Table 2, entry 4), in addition to the aldehyde. However, these two arylaldehydes are well known to undergo auto-oxidation to the corresponding carboxylic acid.^[40] Furthermore, in some cases involving non-polar/volatile arylaldehydes, trace amounts of biphenyl were detected as a minor by-product in this oxidation protocol, which in these cases was difficult to remove by chromatography or distillation. To verify the reported yields in these specific cases **8a, b** (Table 1, entries 1, 2), the reactions were repeated, and crude aldehyde then trapped with phenyl magnesium bromide, providing **9a, b** (Table 2). Considering this analysis equates to a two-step reaction process, it demonstrates that the yields of aryl aldehydes obtained above, **8a–b** (Table 1, entries 1, 2) are on the conservative side. This evaluation was extended to other difficult-to-handle aldehydes, affording the corresponding diaryl carbinols **9c–f** (Table 2, entries 3–6) in acceptable overall yields ranging from 50–82% yield for this two-step process.

The fact that the NMO-TPB (**7**)/TPAP (**3**) reagent combination was much less reactive towards aliphatic saturated primary and secondary alcohol oxidation, but totally consumed aryl and allylic alcohols, a competition experiment was undertaken with bi-functional diol **10**. Pleasingly, oxidation was highly selective for the benzylic position (i.e., **11**), with only slight oxidation at the primary position (i.e., **12** and **13**; Scheme 3). In comparison, applying standard Ley–Griffith conditions to **10** yielded less of **11** (i.e., 60% yield BRSM), and more of **13** (25% yield BRSM). The yield of compound **12** remained unchanged.

In terms of understanding the selectivity created by NMO-TPB (**7**), as opposed to NMO (**5**), it is possible that NMO-TPB (**7**) offers a substantial hydrophobic environment due to the large TPB anion, and/or provides electronic stabil-

ization of the active ruthenium species. Evaluation of both **5** and **7** by using cyclic voltammetry provided a clear distinction between the two; where **5** was inert, but **7** had an observable oxidation potential of 3.1 eV. More extensive studies involving cyclic voltammetry, in combination with TPAP, are required for further mechanistic understanding, and will be reported in due course.

In conclusion, a novel NMO complex (NMO-TPB, **7**) has been discovered, and applied to the Ley–Griffith oxidation reaction. Utilising newly developed conditions for **7**, it was found that benzylic and allylic alcohols react with considerable selectivity over primary and secondary alcohols, making this method amenable to protecting group free oxidations in the case of bi-functional diols (e.g., **10**). A key feature of this method is that the NMO-TPB (**7**) complex is non-hygroscopic and the oxidations can be run in non-anhydrous solvents open to the atmosphere. The scope of NMO-TPB (**7**) is currently under investigation in other NMO-based reactions to probe its wider applicability.



Scheme 3. Competition experiment using diol **10**; (isolated yield); [BRMS = yield based on recovered starting material].

Experimental Section

Synthesis of NMO-TPB (7): NMO (5.00 g, 42.7 mmol) was dissolved in a 1:1 mixture of ethanol (50 mL) and toluene (50 mL). Sodium tetraphenylborate (7.30 mg, 21.3 mmol) was added, and the reaction cooled in an ice/sodium chloride bath for 5 min before the addition of acetylacetone (7.85 mL, 76.4 mmol) drop-wise over 5 min. The reaction was stirred for an additional 10 min, then filtered cold, and the solid washed with toluene (20 mL). The resulting white solid was air dried for 20 min, providing NMO-TPB (**7**) (8.95 g, 76%). The crude salt was dissolved in acetone/water (250 mL, 3:2) then the solution was concentrated under reduced pressure below 30°C (~160 Torr, ~100 mL removed) until crystallisation was initiated. The solution was then cooled in an ice bath for 1 h. The resulting white solid was filtered, washed with water (40 mL), air dried for 10 min then dried under high vacuum for 1 h providing a white crystalline product (7.85 g, 67%).

Representative NMO-TPB (7)/TPAP (3) oxidation protocol: Alcohol (1 mmol) was dissolved in HPLC grade acetonitrile (2.0 mL), followed by addition of NMO-TPB (**7**; 416 mg, 0.75 mmol). After stirring for 10 min at room temperature, TPAP (**3**; 17.6 mg, 5 mol%) was added. The reaction was stirred at room temperature for 12–16 h before quenching with water (8.0 mL). The solution was then extracted with a mixture of pentane and diethyl ether (3:1, 3 × 10 mL). The organic phases were combined, dried (Na₂SO₄), and the solvent removed by atmospheric distillation affording crude al-

dehyde, which was purified by silica gel column chromatography (9:1 to 1:1 petroleum ether/ethyl acetate) as required.

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Keywords: alcohol oxidation · aldehydes · Ley–Griffith oxidation

- [1] a) R. C. Larock, *Comprehensive Organic Transformations, A Guide to Functional Group Preparations*, Vol. 1 and 2, 2nd ed., Wiley, Hoboken, **2010**; b) M. B. Smith, J. March, *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, Wiley, Hoboken, **2007**; c) L. Kurti, B. Czako, *Strategic Applications of Named Reactions in Organic Synthesis*, Elsevier, Amsterdam **2005**.
- [2] G. Tojo, M. I. Fernandez, *Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice (Basic Reactions in Organic Synthesis)*, Springer, Berlin **2006**.
- [3] E. J. Corey, W. Suggs, *Tetrahedron Lett.* **1975**, *16*, 2647–2650.
- [4] J. C. Collins, W. W. Hess, F. J. Frank, *Tetrahedron Lett.* **1968**, *9*, 3363–3366.
- [5] a) K. Omura, D. Swern, *Tetrahedron* **1978**, *34*, 1651–1660; b) A. J. Mancuso, D. S. Brownfain, D. Swern, *J. Org. Chem.* **1979**, *44*, 4148–4150; c) W. W. Epstein, F. W. Sweat, *Chem. Rev.* **1967**, *67*, 247–260.
- [6] a) E. J. Corey, C. U. Kim, *J. Am. Chem. Soc.* **1972**, *94*, 7586–7587; b) J. R. Parikh, W. v. E. Doering, *J. Am. Chem. Soc.* **1967**, *89*, 5505–5507.
- [7] a) R. J. Gritter, T. J. Wallace, *J. Org. Chem.* **1959**, *24*, 1051–1056, and references therein; For a recent development in this area, see; b) A. Shaabani, P. Mirzaei, S. Naderia, D. G. Lee, *Tetrahedron* **2004**, *60*, 11415–11420, and c) R. J. K. Taylor, M. Reid, J. Foot, S. A. Raw, *Acc. Chem. Res.* **2005**, *38*, 851–869.
- [8] a) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, *108*, 5299–5358; b) T. Wirth, *Angew. Chem. Int. Ed.* **2005**, *44*, 3656–3665; *Angew. Chem.* **2005**, *117*, 3722–3731.
- [9] a) D. B. Dess, J. C. Martin, *J. Org. Chem.* **1983**, *48*, 4155–4156; b) D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287.
- [10] a) P. Lucio Anelli, C. Biffi, F. Montanari, S. Quici, *J. Org. Chem.* **1987**, *52*, 2559–2562; b) J. Einhorn, C. Einhorn, F. Ratajczak, J.-L. Pierre, *J. Org. Chem.* **1996**, *61*, 7452–7454; c) A. Gheorghie, T. Chinnusamy, E. Cuevas-Yañez, P. Hilgers, O. Reiser, *Org. Lett.* **2008**, *10*, 4171–4174.
- [11] See, for example, a) A. De Mico, R. Margarita, L. Parlanti, A. Vescovi, G. Piancatelli, *J. Org. Chem.* **1997**, *62*, 6974–6977; b) S. Zhang, L. Xu, M. L. Trudell, *Synthesis* **2005**, 1757–1760.
- [12] a) M. Uyanik, M. Akakura, K. Ishihara, *J. Am. Chem. Soc.* **2009**, *131*, 251–262; b) A. Duschek, S. F. Kirsch, *Angew. Chem. Int. Ed.* **2011**, *50*, 1524–1552; *Angew. Chem.* **2011**, *123*, 1562–1590.
- [13] L. Tebben, A. Studer, *Angew. Chem. Int. Ed.* **2011**, *50*, 5034–5068; *Angew. Chem.* **2011**, *123*, 5138–5174.
- [14] a) S. Hamada, T. Furuta, Y. Wada, T. Kawabata, *Angew. Chem. Int. Ed.* **2013**, *52*, 8093–8097; *Angew. Chem.* **2013**, *125*, 8251–8255; b) For related systems, see also; M. Hayashi, M. Shibuya, Y. Iwabuchi, *J. Org. Chem.* **2012**, *77*, 3005–3009.
- [15] M. Shibuya, Y. Osada, Y. Sasano, M. Tomizawa, Y. Iwabuchi, *J. Am. Chem. Soc.* **2011**, *133*, 6497–6500.
- [16] C. R. Graves, B.-S. Zeng, S. T. Nguyen, *J. Am. Chem. Soc.* **2006**, *128*, 12596–12597.
- [17] a) R. Kawahara, K.-i. Fujita, R. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 3643–3646; b) M. Königsman, N. Donati, D. Stein, H. Schönberg, J. Harmer, A. Sreekanth, H. Grützmacher, *Angew. Chem. Int. Ed.* **2007**, *46*, 3567–3570; *Angew. Chem.* **2007**, *119*, 3637–3640.
- [18] Y. Matano, H. Nomura, *Angew. Chem. Int. Ed.* **2002**, *41*, 3028–3031; *Angew. Chem.* **2002**, *114*, 3154–3157; b) Y. Matano, T. Hisanaga, H. Yamada, S. Kusakabe, H. Nomura, H. Imahori, *J. Org. Chem.* **2004**, *69*, 8676–8680.
- [19] See, for example; a) A. Tanaka, K. Hashimoto, H. Kominami, *J. Am. Chem. Soc.* **2012**, *134*, 14526–14533; b) W. Chen, F. N. Rein, R. C. Rocha, *Angew. Chem. Int. Ed.* **2009**, *48*, 9672–9675; *Angew. Chem.* **2009**, *121*, 9852–9855.
- [20] a) T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037–3058; b) M. J. Schultz, M. S. Sigman, *Tetrahedron* **2006**, *62*, 8227–8241; c) J. Piera, J.-E. Bäckvall, *Angew. Chem. Int. Ed.* **2008**, *47*, 3506–3523; *Angew. Chem.* **2008**, *120*, 3558–3576; d) C. Parmeggiani, F. Cardona, *Green Chem.* **2012**, *14*, 547–564.
- [21] See, for example, and references therein; a) I. E. Markó, P. R. Giles, M. Tsukazaki, S. M. Brown, C. J. Urch, *Science* **1996**, *274*, 2044–2046; b) I. E. Markó, A. Gautier, R. Dumeunier, K. Doda, F. Philippart, S. M. Brown, C. J. Urch, *Angew. Chem. Int. Ed.* **2004**, *43*, 1588–1591; *Angew. Chem.* **2004**, *116*, 1614–1617; c) B. L. Ryland, S. S. Stahl, *Angew. Chem. Int. Ed.* **2014**, *53*, 8824–8838.
- [22] See, for example, and references therein; a) Z. Hou, N. Theyssen, A. Brinkmann, W. Leitner, *Angew. Chem. Int. Ed.* **2005**, *44*, 1346–1349; *Angew. Chem.* **2005**, *117*, 1370–1373; b) B. Karimi, S. Abedi, J. H. Clark, V. Budarin, *Angew. Chem. Int. Ed.* **2006**, *45*, 4776–4779; *Angew. Chem.* **2006**, *118*, 4894–4897; c) D. R. Jensen, M. J. Schultz, J. A. Mueller, M. S. Sigman, *Angew. Chem. Int. Ed.* **2003**, *42*, 3810–3813; *Angew. Chem.* **2003**, *115*, 3940–3943; d) B. A. Steinhoff, S. R. Fix, S. S. Stahl, *J. Am. Chem. Soc.* **2002**, *124*, 766–767.
- [23] See, for example, and references therein; a) H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi, *Angew. Chem. Int. Ed.* **2007**, *46*, 4151–4154; *Angew. Chem.* **2007**, *119*, 4229–4232; b) B. Guan, D. Xing, G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang, Z. Shi, *J. Am. Chem. Soc.* **2005**, *127*, 18004–18005.
- [24] See, for example, and references therein; a) C. Li, P. Zheng, J. Li, H. Zhang, Y. Cui, Q. Shao, X. Ji, J. Zhang, P. Zhao, Y. Xu, *Angew. Chem. Int. Ed.* **2003**, *42*, 5063–5066; *Angew. Chem.* **2003**, *115*, 5217–5220; b) N. Jiang, A. J. Ragauskas, *J. Org. Chem.* **2007**, *72*, 7030–7033.
- [25] See, for example, and references therein; a) K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2002**, *41*, 4538–4542; *Angew. Chem.* **2002**, *114*, 4720–4724; b) B.-Z. Zhan, M. A. White, T.-K. Sham, J. A. Pincock, R. J. Doucet, K. V. R. Rao, K. N. Robertson, T. S. Cameron, *J. Am. Chem. Soc.* **2003**, *125*, 2195–2199.
- [26] S. Jain, O. Reiser, *ChemSusChem* **2008**, *1*, 534–541.
- [27] See, for example, and references therein; a) R. Liu, X. Liang, C. Dong, X. Hu, *J. Am. Chem. Soc.* **2004**, *126*, 4112–4113; b) A. Rahimi, A. Azarpira, H. Kim, J. Ralph, S. S. Stahl, *J. Am. Chem. Soc.* **2013**, *135*, 6415–6418.
- [28] a) W. P. Griffith, S. V. Ley, G. P. Whitcombe, A. D. White, *J. Chem. Soc. Chem. Commun.* **1987**, 1625–1627; b) W. P. Griffith, S. V. Ley, *Aldrichimica Acta* **1990**, *23*, 13–19; c) W. P. Griffith, *Chem. Soc. Rev.* **1992**, *21*, 179–185; d) S. V. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis* **1994**, 639–666; e) P. Langer, *J. Prakt. Chem.* **2000**, *342*, 728–730; f) M. Pagliaro, S. Campestrini, R. Ciriminna, *Chem. Soc. Rev.* **2005**, *34*, 837–845; g) W. P. Griffith, *Ruthenium Oxidation Complexes: Their Uses as Homogeneous Organic Catalysts*, Vol. 34, Springer, Berlin, **2011**.
- [29] For a comparison of the three systems, see; G. A. Molander, D. E. Petrillo, *J. Am. Chem. Soc.* **2006**, *128*, 9634–9635.
- [30] Alternate sulfides can remedy this situation. See, S.-i. Ohsugi, K. Nishide, K. Oono, K. Okuyama, M. Fudesaka, S. Kodama, M. Node, *Tetrahedron* **2003**, *59*, 8393–8398.
- [31] M. J. Gallen, R. Goumont, T. Clark, F. Terrier, C. M. Williams, *Angew. Chem. Int. Ed.* **2006**, *45*, 2929–2934; *Angew. Chem.* **2006**, *118*, 2995–3000.
- [32] J. B. Plumb, D. J. Harper, *Chem. Eng. News* **1990**, *68*, 3.
- [33] A. Ozanne, L. Pouységu, D. Depernet, B. François, S. Quideau, *Org. Lett.* **2003**, *5*, 2903–2906.
- [34] A.-K. C. Schmidt, C. B. W. Stark, *Org. Lett.* **2011**, *13*, 4164–4167.
- [35] a) NMO is a commodity chemical utilised for industrial fibre production (Lyocell process), see; T. Rosenau, A. Potthast, H. Sixta, P. Kosma, *Prog. Polym. Sci.* **2001**, *26*, 1763; b) A polymer support version has been reported, see; D. S. Brown, W. J. Kerr, D. M. Lindsay, K. G. Pike, P. D. Ratcliffe, *Synlett* **2001**, 1257–1259.
- [36] a) I. E. Markó, P. R. Giles, M. Tsukazaki, I. Chellé-Regnaut, C. J. Urch, S. M. Brown, *J. Am. Chem. Soc.* **1997**, *119*, 12661–12662; b) R. Lenz, S. V. Ley,

- J. Chem. Soc. Perkin Trans. 1* **1997**, 3291–3292; c) M. Hasan, M. Musawir, P. N. Davey, I. V. Kozhevnikov, *J. Mol. Catal. A* **2002**, 180, 77–84; d) Hydrogen peroxide has also been utilized, see; S. Campestrini, M. Carraro, R. Ciriminna, M. Pagliaro, U. Tonellato, *Tetrahedron Lett.* **2004**, 45, 7283–7286.
- [37] P. M. Mirzayans, E. H. Krenske, C. M. Williams, *Aust. J. Chem.* **2014**, 67, 1309–1317.
- [38] A similar reaction has been reported, but a different product was obtained, see; O. E. Ansong, S. Jansen, Y. Wei, G. Pomrinc, H. Lu, S. Lib, Y. Guo, *J. Mater. Chem.* **2007**, 17, 4499–4507.
- [39] Note: If left exposed to light, NMO-TPB (7) will become slightly pink in colour, but over an extended timeframe. NaTPB (6) is also light sensitive, so this aspect was not too surprising.
- [40] M. Sankar, E. Nowicka, E. Carter, D. M. Murphy, D. W. Knight, D. Bethell G. J. Hutchings, *Nat. Commun.* **2014**, 5, 3332–3337.

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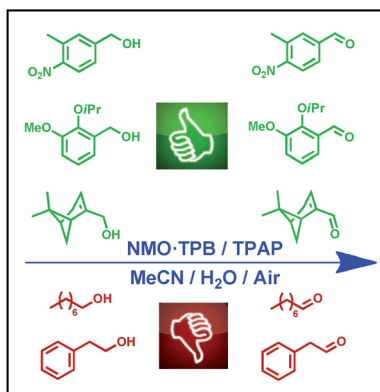
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Alcohol Oxidation

P. W. Moore, P. M. Mirzayans,
C. M. Williams*



NMO-TPB: A Selectivity Variation on the Ley–Griffith TPAP Oxidation



Ley–Griffith with salt please! The conversion of alcohols to aldehydes is synonymous with synthetic organic chemistry. The Ley–Griffith oxidation, utilising the tetra-*n*-propylammonium perruthenate (TPAP) reagent, is a very popular named reaction for performing this task. A variation on this reaction using a tetraphenylborate salt of *N*-methylmorpholine-*N*-oxide (NMO-TPB) is reported, which modulates the reactivity of TPAP such that anhydrous conditions are not required for benzylic and allylic oxidations.