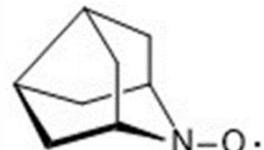


**Alcohol  
Oxidation**

# nor-AZADO

## Features

- ◆ Ultra-high activity alcohol oxidation catalyst
- ◆ Applicable to various substrates
- ◆ Possible to oxidize secondary alcohols with large steric hindrance
- ◆ Air oxidation of alcohol is possible
- ◆ Bulk supply available



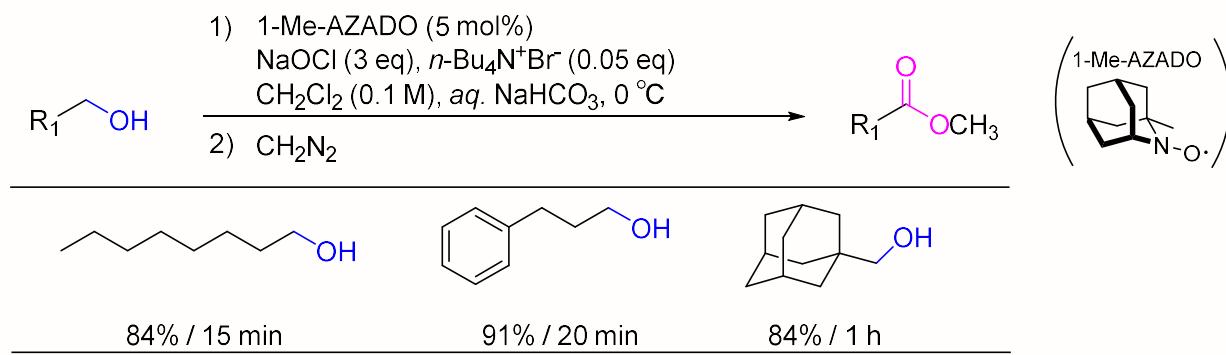
## Reaction Example

■ Oxidation of primary and secondary alcohols under very small amount of catalyst

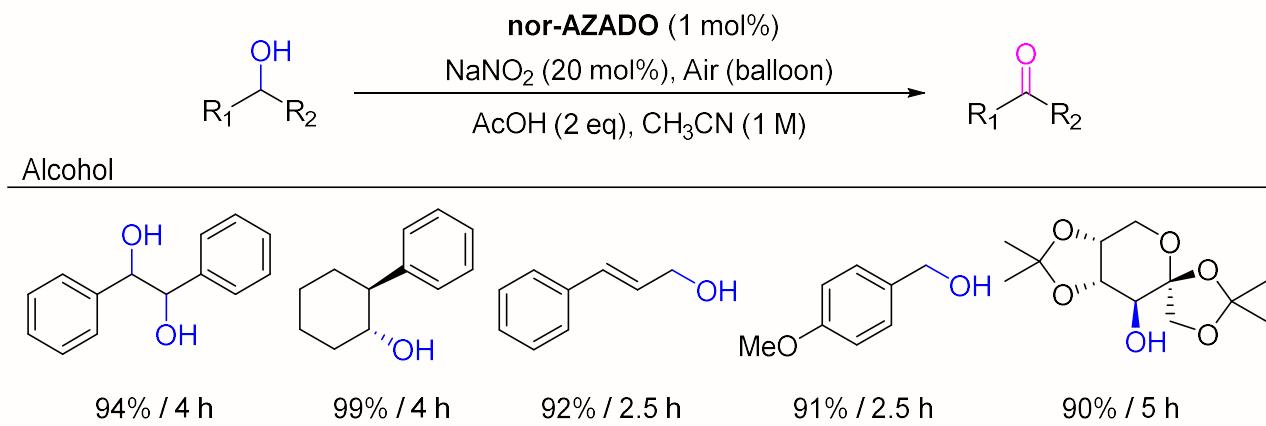
Substrate	cat (X mol%)	NaOCl (1.5 eq)	KBr, <i>n</i> -Bu <sub>4</sub> N <sup>+</sup> Br <sup>-</sup>	aq. NaHCO <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 0 °C	R <sub>1</sub> —C(=O)—R <sub>2</sub>
	1				
	0.01				
	0.003				
	1				
	0.01				
	0.005				
	0.003				
	1				
	0.01				
	0.005				
	0.003				

The table shows the results of the oxidation of three different substrates using two different catalysts. The substrates are 1-phenylpropan-1-ol, 1-phenylpropan-2-ol, and 2-methyl-2-phenylcyclohexan-1-ol. The reaction conditions are aq. NaHCO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, with NaOCl (1.5 eq) and KBr, *n*-Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>. The loading amount of the catalyst (X mol%) is varied. The yield of the product is indicated in the last column. The catalyst TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is shown in the first column, and nor-AZADO (2-norbornyl-N-oxyl) is shown in the second column, both enclosed in a red box.

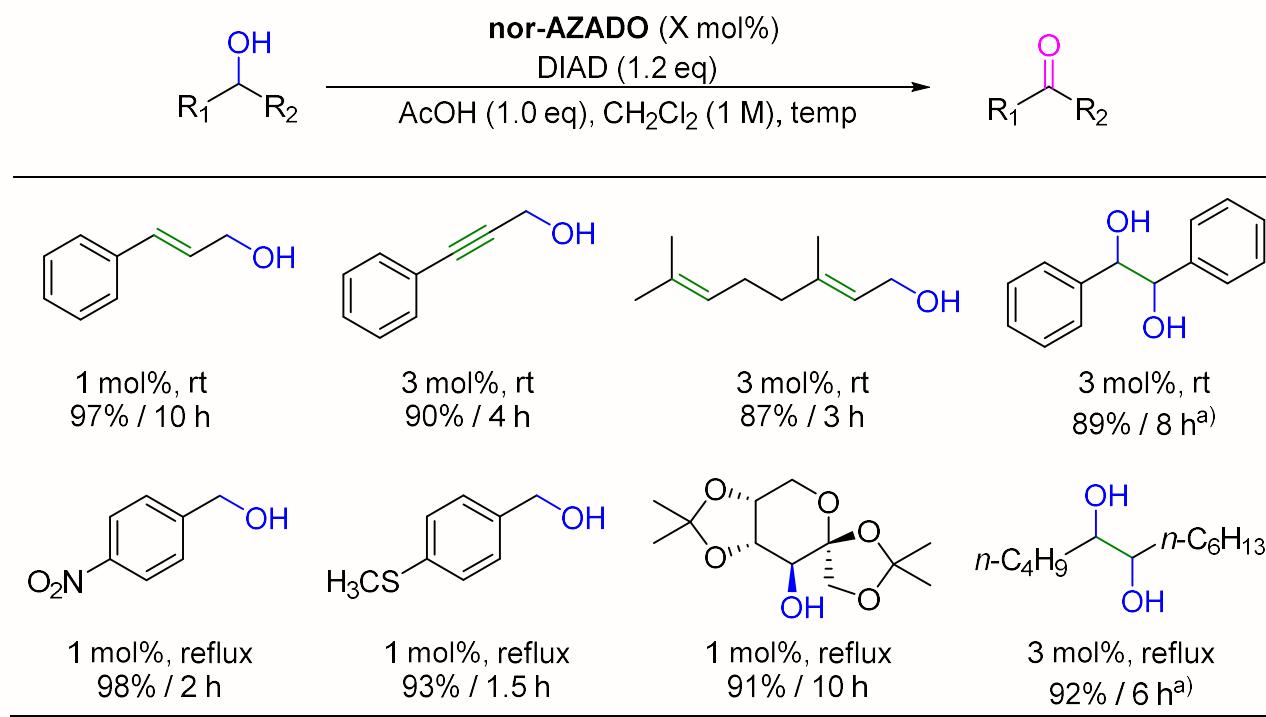
■ Oxidation of primary alcohols to carboxylic acids



■ Air oxidation of alcohols with  $\text{NO}_x$  as co-oxidant



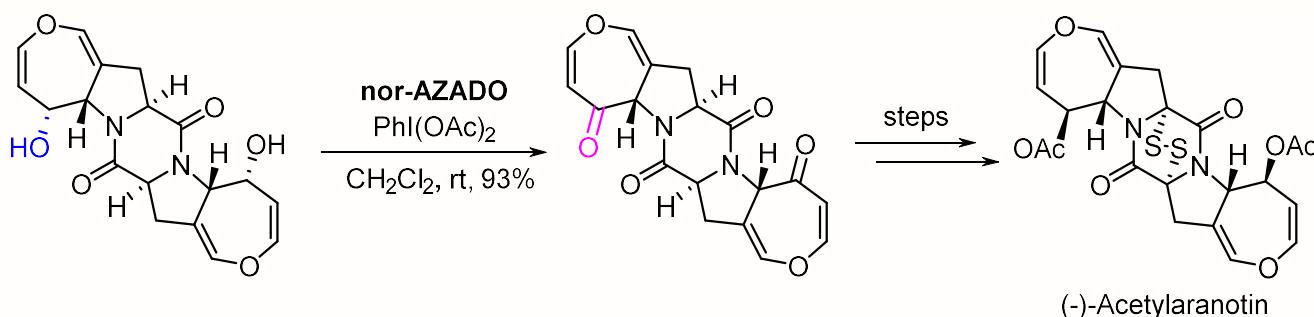
■ Oxidation of alcohols with Mitsunobu reagent DIAD as co-oxidant



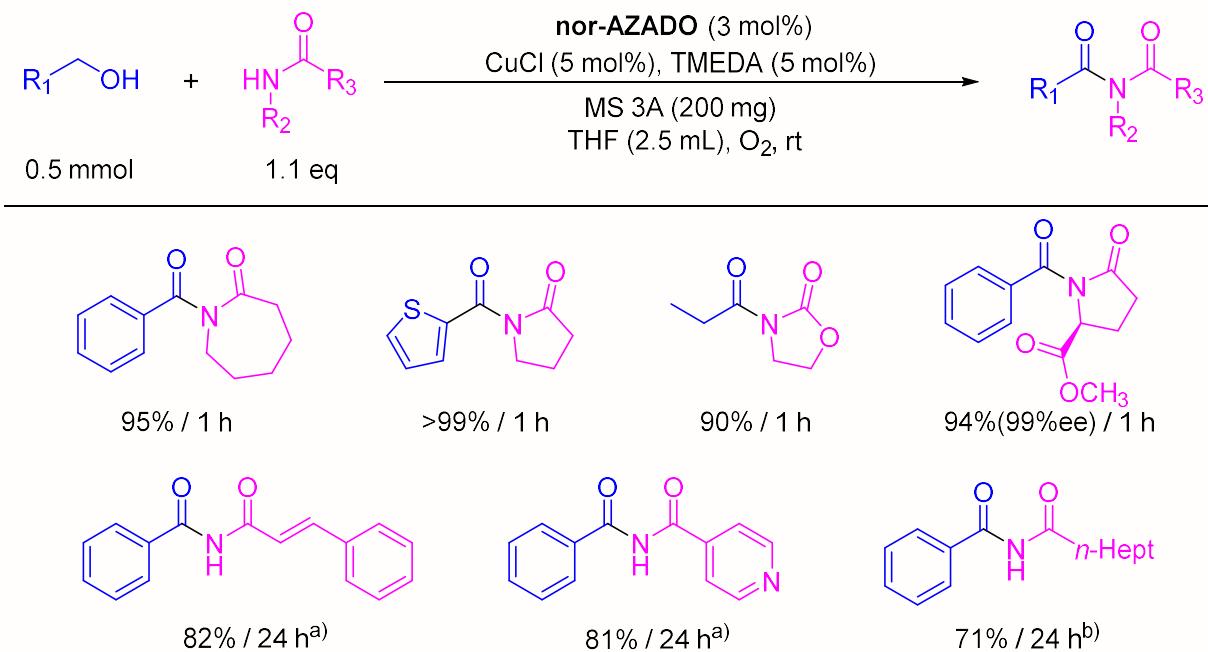
a) 2 eq of DIAD

DIAD =

■ Application to natural product synthesis



■ Acylation of amide compounds with alcohols



a) tBuOK (1 eq) was used. b) tBuOK (0.5 eq) was used.

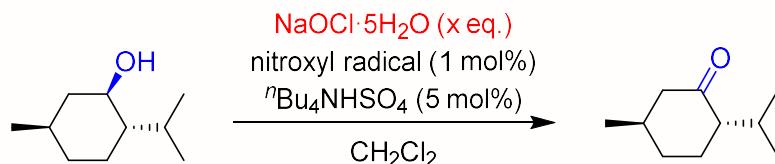
⟨References⟩

- Iwabuchi, Y. et al. : *Chem. Pharm. Bull.*, **59**, 1570 (2011).
- Iwabuchi, Y. et al. : *Chem. Pharm. Bull.*, **61**, 1197 (2013).
- Iwabuchi, Y. et al. : *Organic Square*, **45**, 2 (2013).
- Iwabuchi, Y. et al. : *Chem. Asian J.*, **10**, 1004 (2015).
- Iwabuchi, Y. et al. : *Chem. Sci.*, **9**, 4756 (2018).

Code No.	Product Name	Package Size
012-24981	nor-AZADO <span style="float: right;">Ref</span>	100mg
016-24984		1g
012-24986		5g
010-24982		100g
197-02206	Sodium Hypochlorite Solution [NaOCl]	500ml
040-27682	Diisopropyl Azodicarboxylate [DIAD] <span style="float: right;">Ref</span>	25ml
042-27681		100ml
049-32961	(Diacetoxyiodo)benzene [PhI(OAc) <sub>2</sub> ]	5g
047-32962		25g

## NaOCl·5H<sub>2</sub>O

- Stable compared to solutions
- Can be used at high concentration  
(effective chlorine 39.0% or more)



nitroxyl radicals	$\text{NaOCl}\cdot\text{5H}_2\text{O}$ (x eq.)	Temp. (°C)	Time (h)	Yield (%)
TEMPO	1.6	15	2	96
1-Me-AZADO	1.4	rt	0.5	98

<Reference>

• Okada, T., Asawa, T., Sugiyama, Y., Kirihsara, M., Iwai, T. and Kimura, Y.: *Synlett.*, **25**, 596 (2014).

Code No.	Product Name	Package Size
195-17212	Sodium Hypochlorite Pentahydrate	25g
199-17215		500g

## TEMPO

- The most common nitroxyl radical
- Our TEMPO is not a lump but a fine crystal



Code No.	Product Name	Package Size
209-19501	2,2,6,6-Tetramethyl-1-piperidinyloxy, Radical [TEMPO]	5g
207-19502		25g
205-19503		100g

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