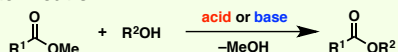


高活性第四級アンモニウム塩触媒を用いるエステル交換反応

(名大院工) 波多野学、吉田有梨花、多畑勇志、小倉義浩、山下賢二、石原一彰*



Transesterification



Conventional catalysts: $Bu_2SnO/Bu_2Sn(NCS)_2$, Sb_2O_3 , $Ti(Oi-Pr)_4$, $ZnCl_2 \cdot 2THF$

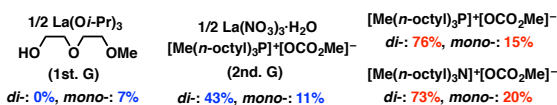
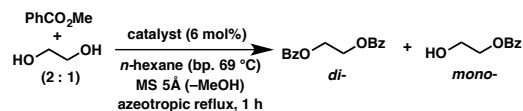
For a review: Otera, J. *Chem. Rev.* 1993, 93, 1449.

For an account: Hatano, M.; Ishihara, K. *Chem. Commun.* 2013, 49, 1983.

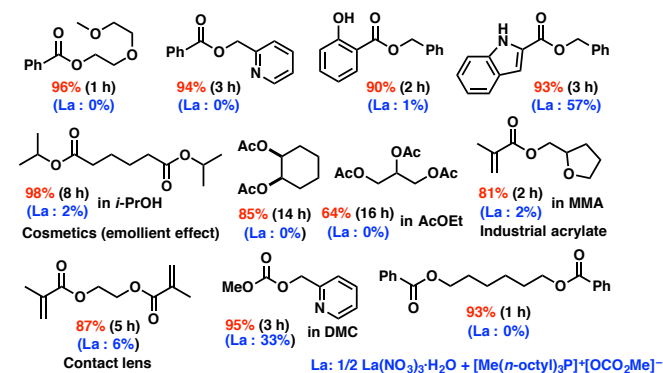
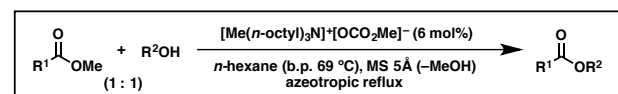
「エステル化合物の製造方法」石原一彰、古家吉朗、特許第5167483号(平成25年3月21日)

「エステル製造方法」石原一彰、波多野学、特許第5804472号(平成28年11月4日)

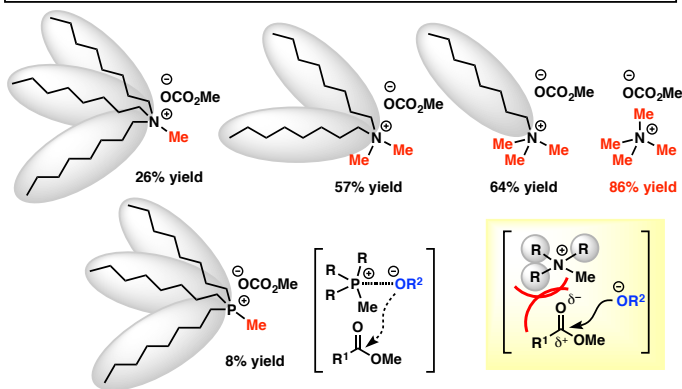
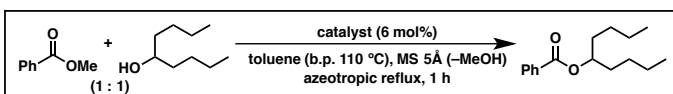
1. Preliminary results for chelatable substrates



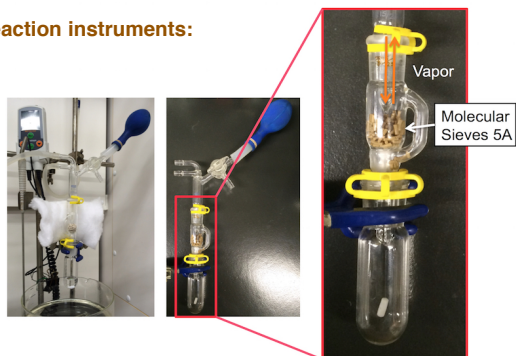
2. Ammonium catalyst for chelatable substrates



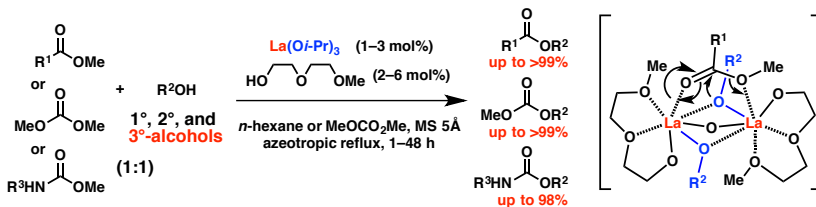
3. Ammonium catalyst vs. phosphonium catalyst



Reaction instruments:

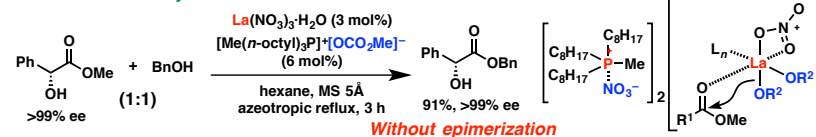


1st Generation: Basic



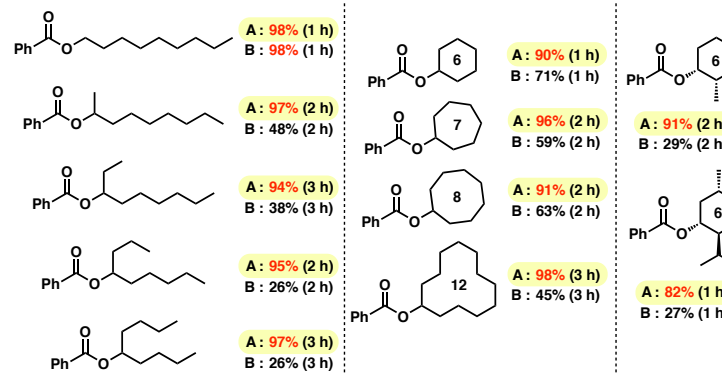
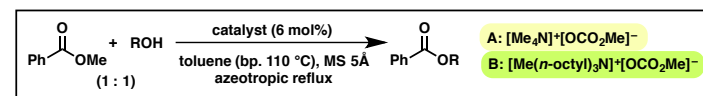
Hatano, M.; Furuya, Y.; Shimmura, T.; Moriyama, K.; Kamiya, S.; Maki, T.; Ishihara, K. *Org. Lett.* 2011, 13, 426.
Hatano, M.; Kamiya, S.; Moriyama, K.; Ishihara, K. *Org. Lett.*, 2011, 13, 430.

2nd Generation: Nearly neutral

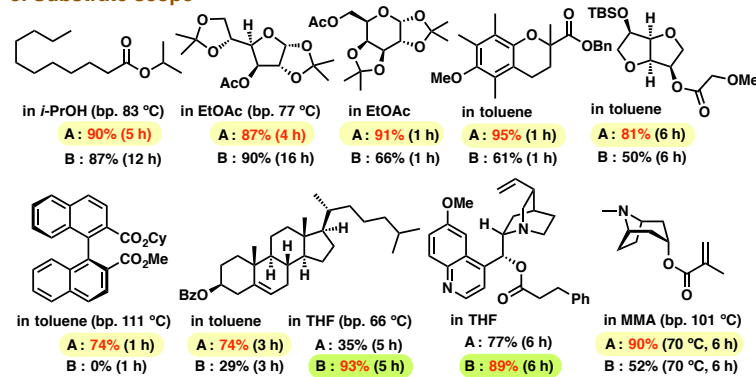


Hatano, M.; Kamiya, S.; Ishihara, K. *Chem. Commun.* 2012, 48, 9465.

4. Comparison of ammonium catalysts



5. Substrate scope



6. Summary of our catalysts

Catalyst	Less coordinating alcohols 1°	2°	3°	Coordinating substrates	Chiral esters	Selective O-acylation
1st Generation $1/2 La(Oi-Pr)_3$ $HO(CH_2)_6OMe$	+	++	+++	-	-	+
2nd Generation $1/2 La(NO_3)_3 \cdot H_2O$ $[Me(n-octyl)_3P]^+[OCO_2Me]^-$	+	+	+	-	+++	-
3rd Generation (This work) $[Me(n-octyl)_3N]^+[OCO_2Me]^-$ $[Me_4N]^+[OCO_2Me]^-$	++	++	-	+	-	+
	+++	+++	-	++	-	+

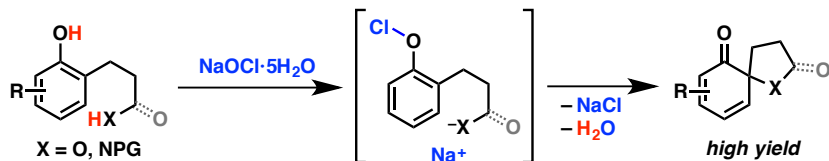
次亜塩素酸ナトリウム・5水和物を用いる効率的酸化及び塩素化反応



(名大院工¹・(株)カネカ化成事業部²) UYANIK Muhammet,¹ 中嶋史雄,¹ 石原一彰,¹ 桑畑光良,² 江島靖和²

フェノールの実践的酸化的脱芳香族化反応

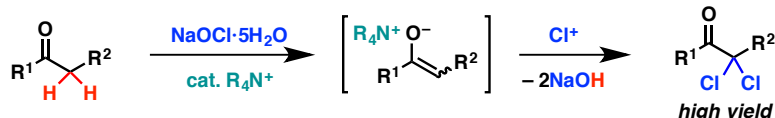
Uyanik, Sasakura, Kuwahata, Ejima, Ishihara, *Chem. Lett.* 2015, 44, 381.



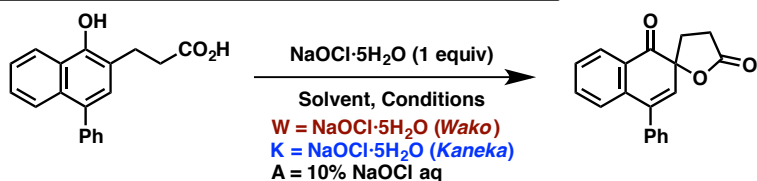
NaOCl·5H₂O

- ▶ 固体針状結晶 (正確に秤量可能)
- ▶ 高い有効塩素濃度~42% (従来の水溶液の3~4倍)
- ▶ pH ~11 (NaOH, NaClの含有量が少ない)
- ▶ 長期保存可 (冷蔵)
- ▶ NaOCl·5H₂Oを用いた様々な酸化反応:
Kiriara, Kimura et al. *Synlett* 2014, 596.
Kiriara, Kimura et al. *Chem. Lett.* 2015, 44, 185.
Kiriara, Kimura et al. *Synlett* 2015, 2547.

カルボニル化合物の触媒的α-塩素化反応

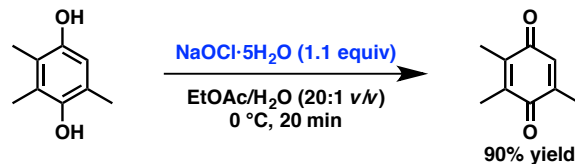
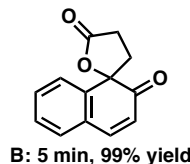
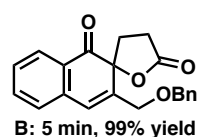
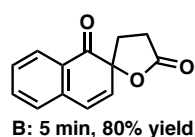
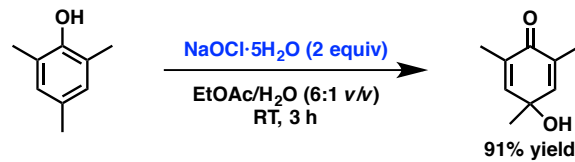
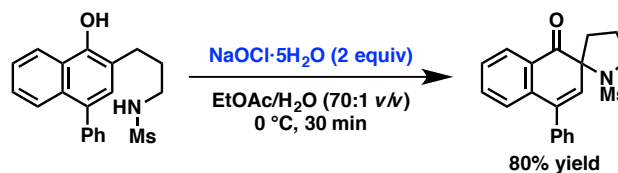
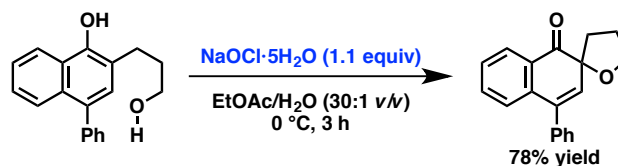
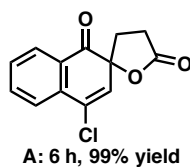
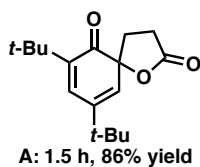
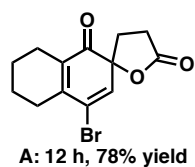


フェノールの酸化的脱芳香族化反応の開発

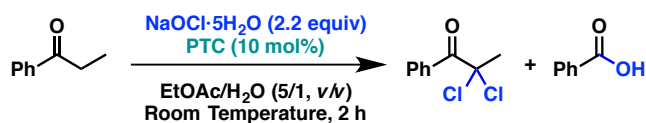


Entry	NaOCl	Solvent	Conditions	Yield (%)
1	W	EtOAc	-20 °C, 9 h	98
2	K	EtOAc	-20 °C, 4 h	99 ← Method A
3	A	EtOAc/H ₂ O (79:1 v/v)	0 °C, 2 h	74
4	W	EtOAc/H ₂ O (79:1 v/v)	0 °C, 2 h	92
5*	W or K	EtOAc/H ₂ O (20:1 v/v)	0 °C, 5 min	96 ← Method B

* NaOCl·5H₂O (1.1 equiv)

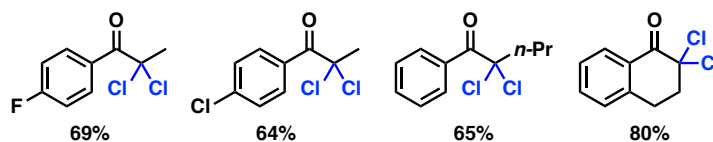


カルボニル化合物の触媒的α-塩素化反応の開発

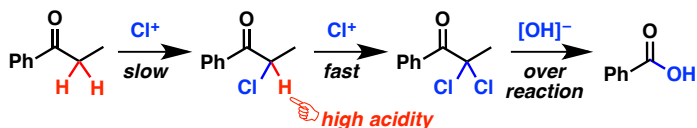
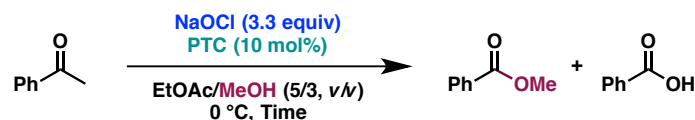


Entry	PTC	A, Yield (%)	B, Yield (%)
1	—	<1	0
2	[<i>n</i> -Bu ₄ N] ⁺ Cl ⁻	59	3
3	[(C ₁₈ H ₃₇) ₂ NMe ₂] ⁺ Cl ⁻	68	2
4*	[(C ₁₈ H ₃₇) ₂ NMe ₂] ⁺ Cl ⁻	60	5
5†	[(C ₁₈ H ₃₇) ₂ NMe ₂] ⁺ Cl ⁻	59	19

* 10% NaOCl aq. † EtOAc



Haloform Reaction & Esterification



NaOCl	Time (h)	C, Yield (%)	B, Yield (%)
NaOCl·5H ₂ O	1	91	8
10% NaOCl aq	6	46	14