Chemistry & Biology Interface, 2022, 12, 2, 33-36

REVIEW PAPER ISSN: 2249 –4820

CHEMISTRY & BIOLOGY INTERFACE

An official Journal of ISCB, Journal homepage; www.cbijournal.com

Chemo-, Regio- and Stereoselectivity of Acyl Transfer Agents: A Brief Review

R.M.Yasanga Kaumadi Suraweera[a], S. Porwal [a]

[a] *Department of Chemistry, Lovely Professional University, Phagwara, Punjab, India-144411*

Received; 14 March 2022, Accepted; 30 April 2022

Abstract: Acyl transfer agents are recently widely utilized for chemo-, regio- and stereoselective acylation. This review gives information about the combination of acyl transfer agent and substrate which could provide desired selectivity especially enantioselectivity in transfer acylation reaction with some emphasis on S-nucleophilic acyl transfer agents. The brief review covers information of acyl transfer agents published till year 2019.

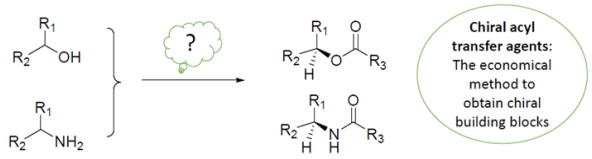
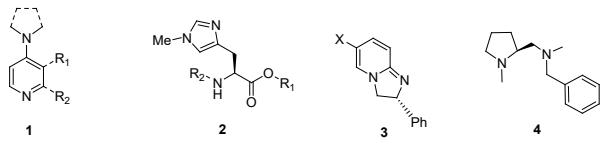


Figure 1.N-nucleophilic acyl transfer agents.

Most of the reported chiral acyl transfer agents could be grouped as N-nucleophilic, P-nucleophilic, C-nucleophilic and O-nucleophilic. N-nucleophilic acyl transfer agents comprises the largest family of chiral acyl transfer agents which could be further subdivided in DMAP and its derivatives, N-alkyl imidazole, amidines, and vicinal diamines.(Fig. 1)



First chiral DMAP derivative was introduced by Vedejs and Chen[2,3] (5, Fig. 2), and these were further developed by Fu, Spivey, Johansen, Gotor, Levacher and Yamada.[8] Fu and co-workers introduced ferrocene based chiral DMAP derivatives (6, Fig. 2).[4,5]Fuji and Kawabata catalysts were based on chiral modification of 4-pyrrolidine core of 4-pyrrolidino substituted DMAP (PPY)[6] which were used in resolution of cycloalkane-1, 2-diol and their derivatives(7).[7]

Spivey group created axially chiral DMAP derivatives,[8] while, Yamada group developed DMAP catalyst which switched the conformation on formation of acylium cation.[9] In general, substrate scope of DMAP based catalyst is limited to resolution of alcohol containing aromatic or unsaturated moieties.

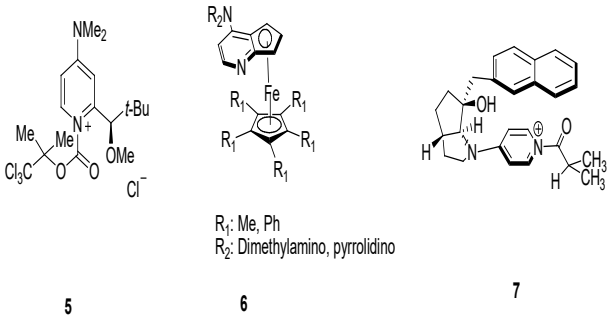


Figure 2. Chiral DMAP derivatives.

Miller and co-workers introduced peptide-based catalysts which were found effective in resolving saturated alkyl alcohols having basic Bronsted site at α-position. These peptide-based catalysts possess N-methylimidazole instead of DMAP as catalytic site.[10] Millers group incorporated catalytic N-methylimidazole in β-hairpin peptide structures (8, Fig. 3), while Schreiner et al. used γ-aminoadamantane carboxylic acid to introduce β-turn in their peptide catalysts (9, Fig. 3).[11]Shinisha[12] and recently Liao and Homo group[13] explained computationally the stereoselection of N-alkyl imidazole incorporating peptide catalyst. Ishihara[14] and Quo[15] studied catalyst where N-alkylimidazole moiety was incorporated on non-peptidic scaffold (10, Fig. 3).

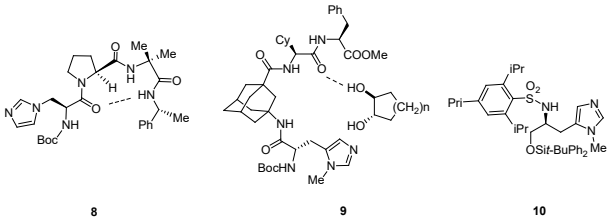


Figure 3. Peptide based catalysts.

Birman et al. developed much used amidine based chiral acyl transfer agents. He started by creating at etramisol based catalyst, which were later evolved to benzotetraamisol (BTM, 11, Fig. 4) and found very efficient in kinetic resolution of aryl alkyl, allyl alkyl alcohol.[16]

Oriyama and co-workers reported vicinal diamine-based catalyst (12, Fig. 4). These are good in resolution of cyclic diols and cyclic β-hydroxy sulfides.[17] Cinchona based alkaloid was used in kinetic resolution of racemic aryl alkyl thiol.[18]

Vedejs et al. introduced P-nucleophilic acyl transfer catalyst. The bicyclic chiral phosphines were found highly effective in resolution of aryl alkyl alcohol (13, Fig. 4).[19] Suzuki[20] and Maruoka et al.[21] are credited with development of C-nucleophilic N-heterocyclic carbene based chiral acyl transfer catalyst (14, Fig. 4). Tarek Samakia's group introduced serene protease inspired O-nucleophilic acyl transfer catalyst (15, Fig. 4).[22]

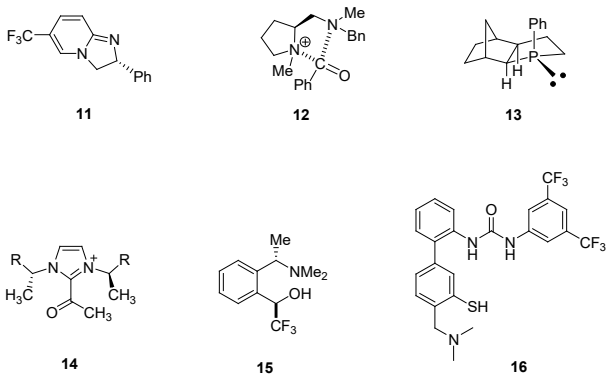


Figure 4: Acyl transfer agents based on different nucleophilic sites.

A through literature search about S-nucleophilic catalyst revealed that activated thioester (S-aroylate dcystein) were used in site specific N-acylation of glucosamine[23] and peptide cyclization,[24] respectively. Diacyldisulfide activated by DMAP was used in chemoselective acylation of phenol,[25] and thioacids activated by photocatalysis[26] and Cu-salt[27] was used in chemosective acylation of amines. Activated thioester or thioester (used as acyl donor)

activated by catalyst were used in regio- and chemoselective acylation, but these cannot be regarded as acyl transfer agent or catalyst which transfer acyl group from acyl donor to nucleophilic site. The catalyst which could be classified as S-nucleophilic acyl transfer agent is recently reported by Arora[28] et al. (16, Fig. 4), but no example of thioester based chiral acyl transfer agent (or S-nucleophilic acyl transfer agents working through thioester mode) was reported in literature to the best of our knowledge.Interestingly, the catalyst reported by Arora et al. is similar to small molecule model of cysteine protease developed by R. S. Brown group.[29]

In summary, the N-, P-nucleophilic acyl transfer agents work through cationic acylium ion intermediate having an electron deficient carbonyl group. However, O-, S-nucleophilic acyl transfer (mimicking enzymes like cysteine protease, histone acyl transferase, serine protease etc.) agents involves neutral and activated ester intermediate. Though we are aware something about substrate scope of O-nucleophilic chiral acyl transfer agents, but no study is done on S-nucleophilic chiral acyl transfer agents. Development of sulfur atom-based chiral acyl transfer agents may provide a very different substrate scope and there is a need of exploration in this area.

Reference:

1. Mueller, C. E.; Schreiner, P. R. Organocatalytic enantioselective acyl transfer onto racemic as well as meso alcohols, amines, and thiols. AngewandteChemie International Edition 2011, 50, 6012-6042.
2. Wurz, R. P. Chiral dialkylaminopyridine catalysts in asymmetric synthesis. Chemical reviews2007, 107, 5570-5595.
3. Vedejs, E.; Chen, X. Kinetic resolution of secondary alcohols. Enantioselective acylation mediated by a chiral (dimethylamino) pyridine derivative. Journal of the American Chemical Society 1996,118, 1809-1810.
4. Fu, G. C. Asymmetric catalysis with "planar-chiral" derivatives of 4-(dimethylamino) pyridine. Accounts of Chemical Research2004, 37(8), 542-547.
5. Arai, S.; Bellemin-Laponnaz, S.; Fu, G. C. Kinetic resolution of amines by a nonenzymatic acylation catalyst. AngewandteChemie International Edition2001, 40, 234-236.
6. Kawabata, T.; Yamamoto, K.; Momose, Y.; Yoshida, H.; Nagaoka, Y.; Fuji, K. Kinetic resolution of amino alcohol derivatives with a chiral nucleophilic catalyst: access to enantiopure cyclic cis-amino alcohols. Chemical Communications2001, 24, 2700-2701.
7. Kawabata, T.; Nagato, M.; Takasu, K.; Fuji, K.Nonenzymatic Kinetic Resolution of Racemic Alcohols through an "Induced Fit" Process. Journal of the American Chemical Society1997, 119, 3169 -3170.
8. Spivey, A. C.; Zhu, F.; Mitchell, M. B.; Davey, S. G.; Jarvest, R. L. Concise synthesis, preparative resolution, absolute configuration determination, and applications of an atropisomericbiaryl catalyst for asymmetric acylation. The Journal of Organic Chemistry2003, 68, 7379-7385.
9. Yamada, S.; Misono, T.; Iwai, Y.; Masumizu, A.; Akiyama, Y. New Class of Pyridine Catalyst Having a Conformation Switch System: Asymmetric Acylation of Various sec-Alcohols. The Journal of Organic Chemistry2006, 71, 6872-6880.
10. Davie, E. A. C.; Mennen, S. M.; Xu, Y.; Miller, S. J. Asymmetric catalysis mediated by synthetic peptides. Chemical reviews 2007,107, 5759-5812.
11. Hrdina, R.; Müller, C. E.; Schreiner, P. R. Kinetic resolution of trans-cycloalkane-1, 2-diols via Steglich esterification. Chemical Communications2010, 46, 2689-2690.
12. Shinisha, C. B.; Sunoj, R. B. On the Origins of Kinetic Resolution of Cyclohexane-1, 2-diols Through Stereoselective Acylation by Chiral Tetrapeptides. Organic Letters 2009, 11, 3242-3245.
13. Liao, R. Z.; Santoro, S.; Gotsev, M.; Marcelli, T.; Himo, F. Origins of Stereoselectivity in Peptide-Catalyzed Kinetic Resolution of Alcohols. ACS Catalysis 2016, 6, 1165-1171.
14. (a) Ishihara, K.; Kosugi, Y.; Umemura, S.; Sakakura, A. Kinetic resolution of racemic carboxylic acids by an L-histidine-derived sulfonamide-induced enantioselective esterification reaction. Organic Letters2008, 10, 3191-3194. (b) Zhang, H.; Xie, M.; Qu, G.; Chang, J. Dynamic Kinetic Resolution of α-Purine Substituted Alkanoic Acids: Access to Chiral Acyclic Purine Nucleosides. Organic Letters 201921, 120-123.
15. Geng, X. L.; Wang, J.; Li, G. X.; Chen, P.; Tian, S. F.; Qu, J. Kinetic Resolution of Racemic Alcohols Using Thioamide Modified 1-Methyl-histidine Methyl Ester. The Journal of Organic Chemistry2008 73, 8558-8562.
16. Li, X.; Liu, P.; Houk, K. N.; Birman, V. B. Origin of enantioselectivity in CF3− PIP-catalyzed kinetic resolution

of secondary benzylic alcohols. Journal of the American Chemical Society 2008, 130, 13836-13837.
17. Oriyama, T.; Imai, K.; Sano, T.; Hosoya, T. Highly efficient catalytic asymmetric acylation of meso-1, 2-diols with benzoyl chloride in the presence of a chirai diamine combined with Et_3N. Tetrahedron letters1998, 39, 3529-3532.
18. Peschiulli, A.; Procuranti, B.; O'Connor, C. J.; &Connon, S. J. Synergistic organocatalysis in the kinetic resolution of secondary thiols with concomitant desymmetrization of an anhydride. Nature Chemistry 2010, 2, 380-384.
19. (a) MacKay, J.A. and Vedejs, E. Synthesis and reactivity of new chiral bicyclic phospholanes as acyl-transfer catalysts. The Journal of Organic Chemistry, 2006, 71, 498-503. (b) Vedejs, E.; Daugulis, O. A highly enantioselective phosphabicyclooctane catalyst for the kinetic resolution of benzylic alcohols. Journal of the American Chemical Society2003, 125, 4166-4173.
20. Suzuki, Y.; Yamauchi, K.; Muramatsu, K.; Sato, M. First example of chiral N-heterocyclic carbenes as catalysts for kinetic resolution. Chemical Communications2004, 23, 2770-2771.
21. Kano, T.; Sasaki, K.; Maruoka, K. Enantioselective acylation of secondary alcohols catalyzed by chiral N-heterocyclic carbenes. Organic Letters2005, 7, 1347-1349.
22. (a) Notte, G. T.; Sammakia, T.; Steel, P. J. Kinetic resolution of α-acetoxy N-acyl oxazolidinethiones by a chiral O-nucleophilic acyl transfer catalyst. Journal of the American Chemical Society2005, 127, 13502-13503. (b) Nothling, M. D.; Xiao, Z.; Bhaskaran, A.; Blyth, M. T.; Bennett, C. W.; Coote, M. L.; Connal, L. A. Synthetic Catalysts Inspired by Hydrolytic Enzymes. ACS Catalysis2018, 9, 168-187.
23. Du, J. J.; Gao, X. F.; Xin, L. M.; Lei, Z.; Liu, Z.; Guo, J. Convergent synthesis of N-linked glycopeptides via aminolysis of ω-Asp p-nitrophenyl thioesters in solution. Organic Letters2016, 18, 4828-4831.
24. Agrigento, P.; Albericio, F.; Chamoin, S.; Dacquignies, I.; Koc, H.; Eberle, M. Facile and mild synthesis of linear and cyclic peptides via thioesters. Organic Letters2014, 16, 3922-3925.
25. Liu, H. X.; Dang, Y. Q.; Yuan, Y. F.; Xu, Z. F.; Qiu, S. X.; Tan, H. B. Diacyl Disulfide: A Reagent for Chemoselective Acylation of Phenols Enabled by 4-(N, N-Dimethylamino) pyridine Catalysis. Organic Letters2016, 18, 5584-5587.
26. Liu, H.; Zhao, L.; Yuan, Y.; Xu, Z.; Chen, K.; Qiu, S.; Tan, H. Potassium thioacids mediated selective amide and peptide constructions enabled by visible light photoredox catalysis. ACS Catalysis2016, 6(3), 1732-1736.
27. Mali, S. M. Bhaisare; R. D.; Gopi, H. N. Thioacids mediated selective and mild N-acylation of amines. The Journal of Organic Chemistry2013, 78, 5550-5555.
28. Wu, H.; Raj, M.; Arora, P. S. Iterative Design of a Biomimetic Catalyst for Amino Acid Thioester Condensation. Organic Letters2017, 19, 5122-5125.
29. Brown, R. S.; Aman, A. Intramolecular catalysis of thiol ester hydrolysis by a tertiary amine and a carboxylate. The Journal of Organic Chemistry1997, 62, 4816-4820.