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1 Organocatalytic Methods

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Abstract

Reactions carried out with substoichiometric quantities of organic molecules as catalysts have received much attention over the past decade. This review highlights progress in 2008 towards highly enantioselective organocatalytic systems and the natural product/biologically active compounds that can be prepared using these types of processes.

1.0 Introduction

Once again the number of reports for organocatalysed reactions has grown significantly during 2008, with over 700 articles using the word organocatalysis, or one of its derivatives.ⁱ As Macmillan reported in a personal account of the area organocatalysis has become an intensive area of research with over 1,500 manuscripts describing the use of organocatalysis from 1998-2008, a remarkable statistic given that there were no reports containing the word “organocatalysis” in 1995 (there was of course organocatalysis research being published but the phrase had not yet been coined).ⁱⁱ Several excellent reviews have again been reported in this highly topical area,ⁱⁱⁱ and in fact these reviews highlight still further the tremendous amount of work being carried out as these review articles are split into discrete areas of organocatalysis. The present review covers achievements from 2008, but regrettably, with the considerable number of publications in this area, it is not possible to report every contribution to this field. In contrast to previous years this review is divided into sections according to the mode of action, followed by sections on oxidation, domino reactions, theoretical considerations and a summary of some of the elegant natural product architectures prepared by organocatalysis in 2008 (section 9.0).

2.0 Enamine Catalysis

Although the first use of this generic mode of action was reported in 2000 there continues to be a large number of reports in this area. Below are a selected set of examples. In the majority of cases this mode is catalysed by proline or proline derivatives, however, some recent reports have now applied other catalysts in this area. For example, List has reported the primary-amine-catalysed enantioselective intramolecular aldolization of a range of diones using the epiquinine derived catalyst **1** (Scheme 1).^{iv} Excellent yields and ees of the α,β -unsaturated cyclic ketones were observed, and the highly enantioselective synthesis of either enantiomer of celery ketone was reported (See section 9.0).

Scheme 1 List's asymmetric cyclic ketone synthesis.

There are still a range of useful procedures reported in 2008 using proline derivatives. For example, the direct Mannich reaction using acetaldehyde has been reported by Hayashi.^v Treatment of a range of protected imines (Bz, Boc or Ts) with acetaldehyde and the proline-derived catalyst **2** followed by reduction with lithium aluminium hydride affords a range of amino alcohols with excellent levels of enantiomeric excess and moderate to good yields (Scheme 2).

Scheme 2 Hayashi's Mannich mediated amino alcohol synthesis.

A highly enantioselective *anti*-Mannich reaction has been reported by Melchiorre and co-workers, in which the Boc or CBZ protected imine is generated *in situ*, thus obviating the need to prepare unstable intermediates and allowing the synthesis of previously unobtainable Boc and CBZ protected amino aldehydes (Scheme 3).^{vi} The synthetic utility of this methodology was then exemplified through the highly enantioselective synthesis of a β -lactam from **3** (Scheme 4). In a related study Melchiorre and co-workers have shown that the proline-catalysed asymmetric formal α -amination of aldehydes is possible by the *in situ* preparation of vinylogous iminium ion intermediates generated from arylsulfonyl indoles (Scheme 5).^{vii}

Scheme 3 Melchiorre's highly enantioselective *anti*-Mannich reaction.

Scheme 4 Melchiorre's β -lactam synthesis from **3**.

Scheme 5 Melchiorre's α -amination of aldehydes.

Massi and Dondoni have reported the synthesis of a range of C-glycosyl amino acids.^{viii} Direct α -amination of C-glycosylalkyl aldehydes with DBAD using proline as the catalyst affords a range of enantiomerically enriched hydrazines with d.e.s of greater than 95% (Scheme 6). This methodology was then extended to a variety of C-glycosylalkyl aldehydes with varying chain lengths (Figure 1).

Scheme 6 Massi and Dondoni's α -amination of C-glycosylalkyl aldehydes

Figure 1 C-glycosylalkyl aldehydes with varying chain lengths prepared by Massi and Dondoni's methodology

Jørgensen has reported an alternative to enzymatic, metal- or cinchonidine-catalysed kinetic resolution for the synthesis of 5-(trialkylsilyl)cyclohex-2-enones (Scheme 6).^{ix} These substituted cyclohexanones have been used in the synthesis of a wide variety of natural and biologically active substances, for example, rugulosin and sarcodictyenone. Treatment of a β -ketoester and a silylated α,β -unsaturated aldehyde with the proline-

derived catalyst **2** affords the corresponding substituted cyclohexanones upon decarboxylation of the ester moiety in excellent ee and moderate to good yield.

Scheme 6 Jørgensen's highly enantioselective synthesis of 5-(trialkylsilyl)cyclohex-2-enones.

Hajra and Giri have developed a one-pot approach to enantiomerically enriched butyrolactones using proline as the catalyst.^x Treatment of methyl-4-oxobutyrates with an aldehyde and proline affords an initial addition product which is reduced *in situ* to afford the corresponding lactone in moderate yield and excellent enantiomeric excess (Scheme 7).

Scheme 7 Hajra and Giri's synthesis of butyrolactones

Gaunt has recently reported a highly enantioselective dearomatization approach to compounds such as **4** using the proline-derived catalyst **5** (Scheme 8).^{xi} Oxidation of the phenol ring in **6** followed by enamine catalysed Michael addition affords the corresponding product in excellent yield, diastereo- and enantiomeric excess. A range of ring sizes and heteroatoms are tolerated.

Scheme 8 Gaunt's enantioselective dearomatisation approach

3.0 Iminium Catalysis

As with enamine catalysis, iminium ion catalysis has been extremely well studied over the past decade, and interesting novel reports continue to be published in this area. For

example, Carter has reported the intramolecular heteroatom Michael addition, which gives rise to homoproline, pelletierine and homopipicolinic acid (Scheme 9).^{xii} A mechanistic model for the observed stereochemical outcome of the reactions was also postulated (Scheme 10).

Scheme 9 Carter's intramolecular heteroatom Michael addition

Scheme 10 Carter's postulated mechanistic model.

Lu and Deng have shown that bifunctional catalysts such as **1** are useful mediators for the aza-Michael reaction of α,β -unsaturated ketones.^{xiii} Excellent ees were obtained upon the addition of protected hydroxyl amines; removal of the O-benzyl group was effectively achieved by treatment with Raney nickel, with only minimal loss of optical purity (93% vs 90%, Scheme 11).

Scheme 11 Lu and Deng's aza-Michael reaction.

The asymmetric transfer hydrogenation of a range of α,β -unsaturated aldehydes has been achieved in a water/THF mix using a resin-supported *N*-terminal prolyl peptide **7** and a Hantzsch ester (Scheme 12).^{xiv} The origin of selectivity for the catalyst is believed to be attributed to the presence of a β -turn and a polyleucine chain that provides a hydrophobic cavity in aqueous media.

Scheme 12 Resin-supported *N*-terminal prolyl peptide-catalysed transfer hydrogenation

4.0 SOMO Catalysis

As reported in volume 104, MacMillan expanded the scope of aminocatalysis (iminium or enamine catalysis) by introducing a new mode of action.^{i,xv} The intermediate enamine formed from the condensation of an aldehyde and a secondary amine can be intercepted by an oxidizing reagent (CAN) to generate a singularly occupied molecular orbital (SOMO) at nitrogen. Subsequent reaction with, for example, allylsilane affords α -allylated aldehydes with good yields and excellent levels of enantioselectivity.

The scope of SOMO-activated reactions was expanded using a range of allylsilanes and gave rise to products of α -arylation, α -cyclization, and α -enolation.^{xvi} MacMillan has since reported the α -vinylation of aldehydes (Scheme 13) and the carbo-oxidation of styrenes (Scheme 14) using catalyst **8**.^{xvii,xviii} More importantly, the MacMillan group have demonstrated that direct asymmetric alkylation of aldehydes is possible by merging photoredox catalysis with organocatalysis.^{xix} Excellent yields and ees have been observed for the alkylation of a variety of aldehydes and a plausible mechanism has been devised (Scheme 15).

Scheme 13 MacMillan's α -vinylation of aldehydes

Scheme 14 MacMillan's carbo-oxidation of styrenes

Scheme 15 Macmillan's photoredox/organocatalysis proposed mechanism

5.0 Hydrogen Bonding Catalysis

Over the last few years interest in hydrogen bonding catalysis has grown significantly, and several reviews on this subject have appeared.^{xx} During 2008 several new systems have been developed. For example, Zhou's glycosyl thiourea catalyst **9** was shown to be highly enantioselective for the aza-Henry reaction (Scheme 16).^{xxi} Dixon and co-workers have used the thiourea catalyst **10** in the highly enantioselective synthesis of both the antidepressant (*R*)-rolipram **11** and the selective serotonin reuptake inhibitor (3*S*,4*R*)-paroxetine **12**. The key transformation steps are shown in scheme 17.^{xxii} Using the same catalyst the highly enantioselective synthesis of a multicyclic piperidinone was achieved (Scheme 18).^{xxiii}

Scheme16 Zhou's highly enantioselective glycosyl thiourea catalyst.

Scheme17 Dixon's Michael adducts of malonate and nitro olefins.

Scheme18 Dixon's synthesis of piperidinone derivatives.

Connon has recently reported the use of urea or thiourea catalysts for the dynamic kinetic resolution (DKR) of azalactones (Table 1) and the desymmetrization of meso-anhydrides (Scheme 19).^{xxiv} Connon also demonstrated that the DKR reaction could be carried out in one-pot from *N*-benzoyl aminoacids and DCC (Scheme 20).

Table 1 Connon's dynamic kinetic resolution of azalactones

Entry	Substrate	Product	Time (h)	Yield (%)	ee (%)
1			28	98	88
2			30	97	79
3			28	98	78

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Scheme 19 Connon's desymmetrization of meso-anhydrides

Scheme 20 One-pot DKR from protected amino acids

Rawal has developed a novel series of H-bonding catalysts containing a squaramide core.^{xxv} In comparison to the related thiourea catalysts, the squaramide H-bonding distances are approximately 0.6 Å further apart; the authors believe that this could provide an interesting activation unit as squaramides are known to be bioisosteres of ureas. Preparation of the catalysts from dimethyl squarate is relatively straightforward; for example catalyst **14** was prepared in 61% yield over two steps. The catalyst provided excellent ees and yields in the asymmetric addition of 1,3-dicarbonyl compounds to nitro olefins with catalyst loadings as low as 0.5 mol% (Scheme 21).

Scheme 21 Rawal's squaramide H-bonding catalysis

List has reported a short approach to enantiomerically enriched β^2 -amino acids through hydrogen bonding asymmetric transfer-hydrogenation.^{xxvi} Reaction of a nitro alkene with Jacobsen's catalyst **15** and a Hantzsch ester affords the reduced products in up to 95% ee. Further hydrogenolysis of the nitro group with H₂, palladium on charcoal affords the corresponding β^2 -amino acids (Scheme 22).

Scheme 22 List's hydrogen bonding asymmetric transferhydrogenation

6.0 Counterion Catalysis

Jacobsen first reported the use of asymmetric counterion catalysis in 2007. Jacobsen has extended his group's work in this area through the asymmetric addition of nucleophiles to oxocarbenium ions.^{xxvii} Using the catalyst **16**, boron trichloride and a silyl ketene acetal, several isocroman derivatives were synthesized in excellent ees.

Scheme 23 Jacobsen's asymmetric counterion catalysis.

The catalytic asymmetric aziridination of diazoacetamides and *N*-boc imines has been

reported by Maruoka and co-workers.^{xxviii} The catalysts are based on axially chiral dicarboxylic acids, with catalyst **17** affording up to 99% ee and up to 70% yield. A slight drawback to the methodology is the competing formation of the unwanted side product **18** which at best can only be reduced to 10% of the final mass balance of the reaction (Scheme 24). A novel tetraaminophosphonium carboxylate catalyst **19** has been reported by Ooi to catalyse a direct Mannich-type reaction (Scheme 25).^{xxix} Recently List has introduced counteranion-directed catalysis (see section 7.0).

Scheme 24 Maruoka's asymmetric aziridination of diazoacetamides and *N*-boc imines

Scheme 25 Ooi's direct Mannich-type reaction

7.0 Epoxidation

Deng and co-workers have reported the highly enantioselective peroxidation of α,β -unsaturated ketones.^{xxx} The nature of the stoichiometric oxidant and the temperature of the reaction played a significant role in determining which product was formed. When using *tert*-butyl hydroperoxide at room temperature, the hydroperoxide addition product was the major constituent, but when using dimethylphenyl hydroperoxide as the stoichiometric oxidant and carrying the reaction out at 0 °C, the epoxide was the major product.

List and co-workers have also reported on asymmetric epoxidation, however, their first report was restricted to cyclic α,β -unsaturated ketones.^{xxxi} Excellent levels of enantiomeric excess were observed over a range of substrates and catalysts. In a later publication List also described independent work on the highly enantioselective peroxidation of α,β -unsaturated ketones using catalyst **20** (Scheme 26).^{xxxii} Interestingly the stoichiometric oxidant employed, hydrogen peroxide, affords the peroxyhemiketal

product, which can either be reduced to form the hydroxyl group or treated with base to give the epoxide. Excellent ees for the peroxyhemiketal, epoxide or hydroxyl products were observed over a range of substrate types. In a separate publication List also reports the highly enantioselective epoxidation of enals using chiral phosphoric acid salts using counteranion-directed catalysis.^{xxxiii}

Lattanzi has reported an extension to his group's original findings on epoxidation of chalcones using the β -amino alcohol **21** as catalyst (Scheme 27).^{xxxiv} High ees for a range of chalcones were observed when using this amino alcohol catalyst. Subsequent modification of the amino alcohol structure proved fruitless, with ees in some cases being dramatically decreased. Page and co-workers have reported several new oxidation systems for oxaziridinium salt mediated epoxidation. Conditions employing hydrogen peroxide as the stoichiometric oxidant and sodium carbonate to generate percarbonate were reported to give ees of up to 56%.^{xxxv} In a subsequent report the group also describe an electrochemical batch system for the generation of percarbonate and persulfate; addition of an iminium salt and alkene affords the corresponding epoxides in up to 64% ee.^{xxxvi} The latter system is particularly attractive as the stoichiometric oxidant can be prepared directly without transport or storage issues. A range of simple binaphthalene amino alcohol iminium salts has been developed by Page to give ees of up to 81%, and Lacour has also suggested further factors that are required for high ee in the epoxidation of alkenes when using biaryl azepinium salts.^{xxxvii,xxxviii} Shi has recently reviewed dioxirane and iminium ion epoxidation methods.^{xxxix}

Scheme 26 List's asymmetric epoxidation

Scheme 27 Lattanzi asymmetric epoxidation using a prolinol derived catalyst

8.0 Organocatalytic Domino Reactions

Melchiorre has recently reported the highly enantioselective iminium-enamine sequential approach to aziridines.^{xi} Initially a domino Michael-addition-intramolecular aldol sequence using hydroxyl amines and catalyst **22** afforded 5-hydroxyisoxazolidines (Scheme 28). Modification of the hydroxylamine by tosylation of the free hydroxyl group provided access to enantiomerically enriched aziridines when using catalyst **23** (Scheme 29).

Scheme 28 Melchiorre's highly enantioselective 5-hydroxyisoxazolidine synthesis.

Scheme 29 Melchiorre's highly enantioselective 5-hydroxyisoxazolidine synthesis.

Zhong and co-workers have reported the highly enantio- and diastereoselective tandem aminooxylation/aza-Michael reaction for the synthesis of tetrahydro-1,2-oxazines.^{xli} Their synthetic strategy involved the asymmetric α -hydroxylation of an aldehyde using L-proline and a suitable nitrosoamine followed by intramolecular Michael addition of the amine moiety to an activated α,β -unsaturated ester (Scheme 30).

Scheme 30 Zhong and co-workers tandem aminooxylation/aza-Michael reaction

Hong *et. al.* have developed a highly enantio- and diastereoselective Michael-aldol condensation to afford functionalized cyclohexene derivatives (Scheme 31).^{xlii} Treatment of glutaraldehyde or its ketone derivatives with an arylpropionic aldehyde and catalyst **24** afforded functionalized cyclohexenes with high levels of enantio- and diastereocontrol. Application of this methodology has allowed the synthesis of the full carbon skeleton of the biologically active agent rosmadial.

Scheme 31 Hong's Michael-aldol condensation to afford functionalized cyclohexene derivatives

9.0 Theoretical Considerations

Due to the ever-increasing popularity of organocatalysis, several groups have reported theoretical studies in this area. Most notably, Houk and co-workers, who have in the past reported theoretical studies on a range of topics including dioxirane, oxaziridine, and oxaziridinium ion catalysis, have reported on the origin of enantioselection in heteroatom-Diels-Alder reactions (Scheme 32).^{xliii} Calculations have allowed identification of the origin of enantioselection and the predicted outcome closely mirrored experimental results. It was found that the naphthyl-TADDOL **25** activates the carbonyl group through a cooperative hydrogen bond and the orientation of the aldehyde

by a CH- π interaction.

Scheme 32 Heteroatom-Diels-Alder reaction studied by Houk and co-workers

Goodman has probed the mechanism of Hantzsch ester hydrogenation with BINOL-based phosphoric acids.^{xliiv} Using a range of DFT methods the group found that the catalyst not only acts as a Brønsted acid but also establishes an interaction with the Hantzsch ester, which allowed them to explain the origin of enantioselectivity in the reaction.

Hayashi and co-workers found that B3LYP calculations allowed the discovery that the formation of the enamine intermediate in their Mannich-mediated amino alcohol synthesis (Scheme 2) is the rate determining step, and that attack of the protonated imine occurs with no activation barrier.^v

10.0 Natural Products Synthesized by Organocatalytic Reactions

Given the developments outlined in this review, it is again perhaps not surprising that there is now the capacity for organocatalysts to be applied to the total synthesis of a wide variety of natural products (Figure 2). List has reported the synthesis of both enantiomers of celery ketone.^{iv} Carter has reported the intramolecular heteroatom Michael addition, which gives rise to homoproline, pelletierine and homopiperic acid.^{xiii} Song *et. al.* have reported the asymmetric synthesis of the antibiotic linezolid and a range of analogues utilising a aldol condensation with proline-derived catalysts.^{xlv} Takayama has reported the first asymmetric synthesis of the cernuine-type *lycopodium* alkaloids cernuine and cermizine D using an asymmetric α -amination approach.^{xlvi} Kumaraswamy has applied Gaunt's asymmetric cyclopropanation conditions in the total synthesis of eicosanoid and one of its diastereoisomers.^{xlvii}

Figure 2 Several natural products produced using organocatalysis

9.0 Conclusion

Again the development of organocatalytic methods has grown significantly during 2008. Over the past year the development of non-metal catalysed reactions has again increased significantly. The level of enantiomeric excess and product yield obtained are now in many cases at excellent levels, with ees of over 95% commonplace. Catalyst loadings are still somewhat high when compared to transition metal catalysts, but as reported previously this can be offset, in some cases, by the actual cost of the catalyst. As we can see from the examples presented in this review, iminium ion catalysis remains one of the most extensively studied areas within organocatalysis. However, with the use of hydrogen bonding catalysts, such as thioureas, and Brønsted acid/base catalysts, and now counterion catalysis, a wide range of new organocatalytic reactions has been discovered. Overall organocatalysis looks set to again move forward with significant vigour over the coming year.

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