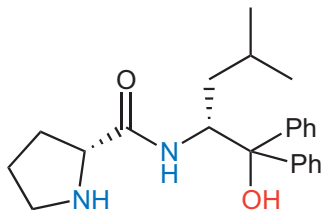


than both the corresponding zeolite and a conventional MMS. Quantitatively measuring the acidity of the new material showed many accessible strong acid sites, which are responsible for the high catalytic activity. NW

ORGANOCATALYSIS

Higher or lower?

Angew. Chem. Int. Ed. <http://dx.doi.org/10.1002/anie.201008042> (2011)



Enantioselective organocatalysis is now a well established synthetic tool. A potential criticism is that many organocatalytic processes require large catalyst loadings (in comparison with metal-catalysed processes) for reactions to proceed at a useful rate. Now, Albrecht Berkessel, Harald Gröger and co-workers from the Universities of Cologne, Erlangen-Nuremberg and Düsseldorf have reported that in some cases a smaller catalyst loading could actually lead to a much improved enantioselectivity.

Gröger, Berkessel and co-workers were investigating an enantio- and diastereoselective route to chiral diols. They planned to combine an organocatalysed aldol reaction with an enzymatic reduction. The first step was to investigate the organocatalytic reaction in a medium that would be enzyme-compatible: aqueous sodium chloride. The first attempt, however, did not seem promising. The organocatalytic aldol reaction using 5 mol% catalyst gave the aldol product with only 47% e.e. compared with 70% e.e. in an organic solvent. On doubling the catalyst loading, the team were surprised to observe no enantioselectivity. Cutting the catalyst loading to just 0.5 mol% gave a dramatic improvement, with aldol product in 93% e.e.

The team attribute this initially surprising negative influence of increased catalyst loading to a change from kinetic to thermodynamic control. With a high catalyst loading, the reaction reached equilibrium quickly, and the reversibility of the reaction means that the enantioselectivity is eroded to produce a racemic product. At low catalyst loading, the reaction does not reach equilibrium

and remains under kinetic control with high enantioselectivity. Gröger, Berkessel and co-workers were ultimately able to combine the reaction with the planned enzymatic reduction — which also neatly traps the kinetic product — to produce a chiral diol with high diastereo- and enantioselectivity. SD

DYNAMIC COVALENT CHEMISTRY

Simple sorting solution

Angew. Chem. Int. Ed. <http://dx.doi.org/10.1002/anie.201102813> (2011)

Complex mixtures of different chemical components can, under the correct conditions, undergo a self-sorting process to form a specific set of products — any living organism offers a practical and powerful example of this phenomenon. In synthetic systems, however, the highly evolved biological machinery that often mediates this sorting is typically absent, and so careful design of the components — and the reactions they can undergo — is required. In particular, reversible interactions between the components are critical so that undesired products can be recycled back into an equilibrating mixture.

Now, Karolina Osowska and Ognjen Miljanić from the University of Houston have combined the self-sorting of a dynamic covalent library of imines with the simultaneous act of physically separating the products. In their initial experiment, two aldehydes (**1** and **2**) were mixed with two amines (**A** and **B**) to produce an equilibrating mixture of four different imines. When this mixture was distilled, the most volatile imine **1A** — made up of the lowest-molecular-weight aldehyde and amine — was removed from the system. As **1A** is depleted, the equilibrium shifts, and **2A** and **1B** are recycled to form more of **1A**. Once **1A** has been completely removed from the system, all that remains is **2B** and so two different compounds are isolated in high purity from a mixture of four possible products.

The principle is also shown to work on larger libraries — the sequential distillation at increasing temperatures of a mixture comprising five aldehydes and five amines gives just five different imines as the major products from a potential pool of 25 compounds. This strategy could prove useful for other reactions (such as esterification) and may also be relevant for industrial processes. SC

Written by Gavin Armstrong, Stuart Cantrill, Stephen Davey, Anne Pichon and Neil Withers.

blogroll

ChemBark, PI

A worrying tale of misconduct, a consideration of 'chemical intuition' and a very useful reference finder.

How can we distil more than five thousand words, spread across a series of blogposts, that themselves distil 167 pages of information about the misconduct of Columbia graduate student Bengu Sezen? The series comes from ChemBark, which has doggedly (pun only slightly intended) pursued this case for some time. In obtaining the documents, under a Freedom of Information Act request, ChemBark has uncovered a fascinating story that deserves to be widely read, if only to act as a warning. Starting with 'finicky or sensitive' reactions, that only seemed to work with Sezen in the lab, and progressing through doctored spectra before ending with retracted JACS papers, the whole story is bewildering and depressing. The documents themselves can be downloaded, and the posts are still ongoing at the time of writing (<http://go.nature.com/yM13jt>) and include a discussion on the role and responsibility of Sezen's advisor Dalibor Sames. For a summary of the case, take a look at *Chemical & Engineering News* (<http://go.nature.com/ZNKmrE>).

What is chemical intuition? The question is posed — but maybe not fully answered — at the Curious Wavefunction (<http://go.nature.com/zmoK7o>). Is intuition, however we define it, more important in chemistry than in physics? Wavefunction thinks so, but Google doesn't agree: 'chemical intuition' gets only ~31,000 hits, compared with ~135,000 for its physical counterpart. In any case, the post goes on to suggest some tips that Wavefunction has noticed from great chemists down the years. Don't ignore the obvious (like colour and smell), get a feel for energetics, stay in touch with the basics, and learn from other fields.

And finally...the editorial team just love the reference resolver (<http://chemsearch.kovsky.net/>) developed by Alex Zhurakovskiy — just type/paste in the reference in almost any style you like, and bingo! You're directed straight to the article.