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Heart Cut

March 7, 2005

- Optically pure 3-amino-1,2-diols from asymmetric epoxides
- Control catalytic bond breaking on nickel surfaces
- Remove arylallyl protecting groups with *tert*-butyllithium
- Minimize gas emissions during deprotection reactions
- Large, stable channels in a mesoporous isopolymolybdate
- Confining polymers in nanoscale pores changes their shape
- Minimize byproducts during tertiary amine formation
- Templated bioactive hydrogels for tissue engineering

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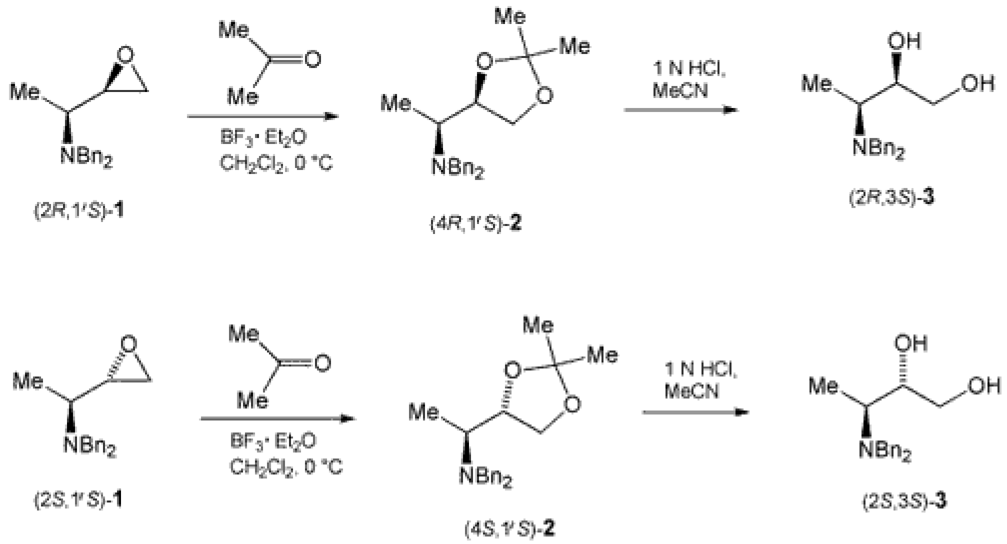
Prepare optically pure 3-amino-1,2-diols from the corresponding epoxides. J. M. Concellón and coworkers at the University of Oviedo, Spain, previously reported the efficient synthesis of enantiopure 1-aminoalkyloxirane isomers (**1**) by the total stereoselective reduction of a-amino-a´-chloroketones with LiAlH$_4$. Now they have found that the isomers of **1** can be treated with ketones in the presence of BF$_3$•Et$_2$O to form 1,3-dioxolanes (**2**) as the sole products with >98% de.



Intermediates **2** can be deprotected easily with acid to give the enantiopure isomers (**3**) in very high yield. The conformation of each epoxide isomer is retained in the products.

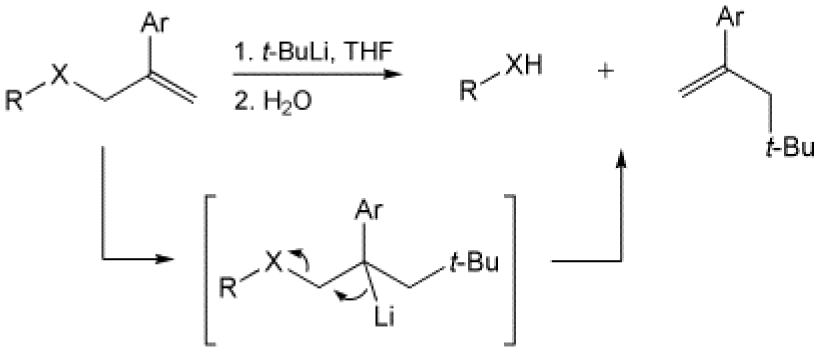
The procedure works best with symmetrical ketones. Using unsymmetrical ketones resulted in a ~1:1 mixture of diastereoisomers, although these isomers could be separated by conventional column chromatography. (*Org. Lett*. **2005**, *7*, 247 − 250; W. Jerry Patterson) Go to top

Control the catalytic bond-breaking selectivity of nickel surfaces. F. Besenbacher and coauthors at the University of Aarhus, the Technical University of Denmark, Lyngby, and Haldor Topsøe, Lyngby (all in Denmark) studied the influence of step sites on the catalytic selectivity of nickel in the bond-breaking reactions of ethylene. They demonstrated the control of the catalytic selectivity by blocking the nickel steps with silver to decrease the number of step sites.

The authors exposed Ni(111) surfaces to 10^{-8} torr ethylene at room temperature and used scanning tunneling microscopy to observe that the decomposition of ethylene induced the formation of a “ brim ” structure at the upper steps. Density functional theory calculations showed that the energy barriers to ethylene − nickel binding, ethylene dissociation, and ethylene dehydrogenation at the step sites are all lower than those on the flat surfaces. Furthermore, the activation barrier for dissociation decreases more than that for dehydrogenation, and the barriers for the two reactions become comparable at the step sites. The selectivity of nickel toward ethylene dissociation or dehydrogenation is largely controlled by the ratio of step sites to “terrace” atoms.

To test the blocking effect on another catalytic reaction, the authors deposited silver on the nickel catalyst at room temperature and post-annealed it at 800 K. The step sites were again covered by silver, which lowered the rate constant for ethane hydrogenolysis. The authors concluded that this approach to controlling the selectivity of catalytic reactions might lead to nanoscale catalyst design. (*Nat. Mater*. **2005**, *4*, 160 – 162; George Xiu Song Zhao) Go to top

Arylallyl protecting groups for amines, amides, and alcohols can be readily removed with *tert*-butyllithium. J. Barluenga and coauthors at the Universities of Oviedo and Burgos, both in Spain, report that the 2-arylallyl group can be used to protect amines, amides, and alcohols during organic synthesis. This protecting group is readily removed with *t*-BuLi at −78 to 0 °C for amines and amides and −78 °C for alcohols. a-Bromomethylstyrene is a typical protecting reagent.



X is O or NR′; R and NR′ are alkyl or aryl. The authors believe that removing the arylallyl group with *t*-BuLi involves anionic attack at the allylic double bond and eliminates the starting amine, amide, or alcohol. They obtained yields of 75 – 95% of the deprotected compounds over a wide range of aryl and alkyl substituents. (*Chem. Commun*. **2005**, 933 – 935; David A. Schiraldi) Go to top

Minimize isobutylene emissions during large-scale *tert*-butoxycarbonyl deprotection reactions. Gas emission measurements during *tert*-butoxycarbonyl (Boc) deprotections in various solvents revealed that 1 equiv of gas was released when THF was used as the solvent, but emissions were reduced by 65 – 95% in solvents such as alcohols, CH_2Cl_2, and toluene.

E. L. Dias*, K. W. Hettenbach, and D. J. am Ende of Pfizer showed that in alcohols the isobutylene reacts to form alkyl *tert*-butyl ethers as byproducts, whereas in CH_2Cl_2 and toluene isobutylene oligomers are formed. They used this observation to develop a scrubbing system to minimize isobutylene emissions during Boc deprotections. The most suitable system was 4.6 – 6.6 g/L solutions of $MeSO_3H$ in toluene. (*Org. Process Res. Dev*. **2005**, *9*, 39 – 44; Will Watson) Go to top

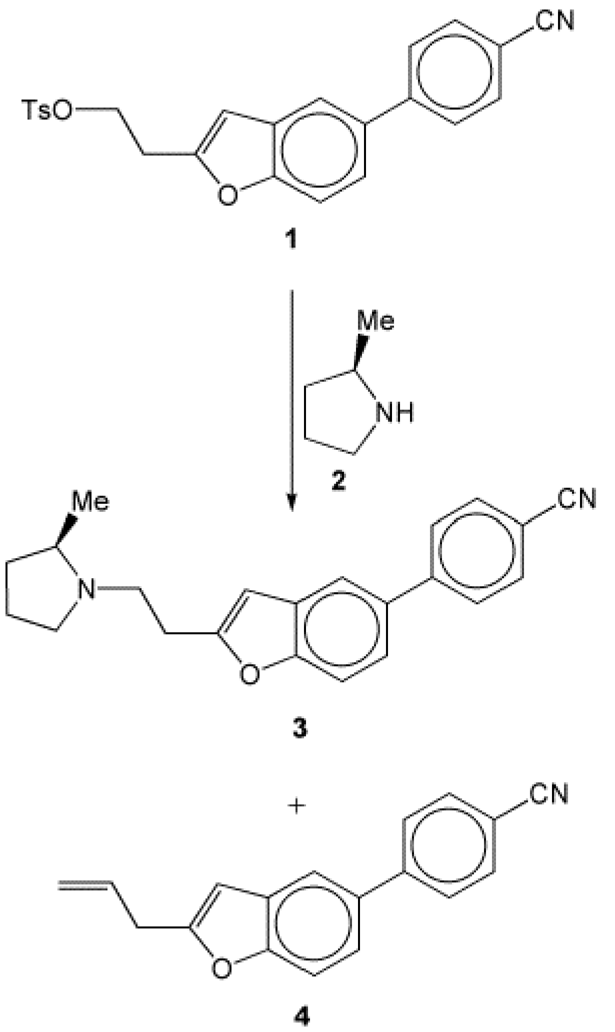
This mesoporous isopolymolybdate framework has large, stable channels. R. Atencio*, A. Briceño, and X. Galindo at the Venezuelan Institute of Scientific Investigation, Caracas, assembled a mesoporous organic – inorganic hybrid material by exploiting extensive hydrogen bonding between the isopolymolybdate $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$ and H_2bpy^{2+} (bpy is 4,4′-bipyridine). The resulting structure contained large mesoporous channels (~1.9 nm × 0.5 nm) that could accommodate 28 molecules of water of crystallization per unit cell.

The authors found that conventional arrangements based on giant polyoxomolybdates are usually very unstable and tend to lose water easily. However, the mesoporous organic – inorganic network reported here showed reversible water sorption behavior and maintained its remarkable crystal integrity. (*Chem. Commun*. **2005**, 637 – 639; George Xiu Song Zhao) Go to top

Confinement of diblock copolymers in nanoscale pores can lead to changes in morphology. Micro- and nanoscale confinement effects are being exploited to alter materials’ structures and properties in systems ranging from nanocomposites to block copolymers. Molecular-scale confinement can create regions within a material that differ markedly from its normal bulk structure.

T. P. Russell and co-workers at the University of Massachusetts, Amherst, report that when diblock polymers that normally form cylinders are confined within nanoscale pores in alumina membranes, a novel helical morphology is generated. Polystyrene-*block*-polybutadiene was cast into a film, heated, and then drawn into the pores by capillary force. Once the copolymer was constrained within the pores, the alumina was removed with alkali to leave the polymer in its new morphology. The helical structure had a pitch of 18° and a period of 30 nm, and it closely reflected the dimensions of the pores. This work, combined with similar recent discoveries, provides a new tool for controlling molecular structure. (*Macromolecules* **2005**, *38*, 1055－1056; David A. Schiraldi) Go to top

The correct choice of base and solvent can minimize elimination byproducts during tertiary amine formation. The final step in the synthesis of ABT-239, a benzofuranoid H_3 antagonist, is the coupling of *p*-toluenesulfonate (tosylate) **1** with chiral pyrrolidine **2**. Y-M. Pu and co-workers at Abbott Laboratories screened several bases, solvents, and leaving groups to optimize the formation of tertiary amine **3** in preference to the elimination byproduct **4**.



The authors found that trifluoromethanesulfonate gave similar selectivity to tosylate but also reacted with many of the tertiary amines screened as base catalysts for the reaction. Nonpolar solvents such as toluene resulted in slow reactions and low yields, whereas polar solvents such as DMF and *N*-methylpyrrolidone or protic solvents such as EtOH gave the olefin as the major product. Lower polarity MeCN was the solvent of choice.

The authors found K_2CO_3 to be the optimal base; it was superior to weak organic bases such as Et_3N and *i*-Pr_2EtN. But even under the best set of conditions, ~15% of the elimination byproduct was formed. Further work showed that only a trace of the olefin is formed in the absence of the chiral amine, suggesting that an E2 elimination pathway caused by the pyrrolidine reactant itself forms the byproduct. Because all of the byproducts of the reaction are neutral, the product could be readily purified by extraction into aqueous acid. (*Org. Process Res. Dev*. **2005**, *9*, 45－50; Will Watson) Go to top

Colloidal-crystal-templated bioactive hydrogels can be used for tissue engineering. D. J. Irvine and co-workers at MIT describe the formation of bioactive hydrogels with self-assembled colloidal crystals as the templates. The hydrogels have interconnected 3-D porosity at moderate void fractions and maintain a compressive stiffness that is comparable to native tissues. The authors took advantages of the versatile properties of hydrogels and the interconnected pores of colloidally templated structures to construct improved artificial tissues.

A reciprocating shaking method produced self-assembled monodisperse poly(methyl methacrylate) (PMMA) microspheres (20－60 mm), which formed a close-packed colloidal crystal. Infiltration of poly (ethylene glycol) (PEG) into the voids of the crystal template by a centrifugation method, followed by UV polymerization, yielded a PMMA–PEG composite. Removing the PMMA spheres with HOAc resulted in a PEG scaffold with an ordered cellular structure, interconnected macroporosity, and robust mechanical properties.

The authors studied the properties of cell attachment and migration by functionalizing the PEG networks with peptides. Their experiments showed that mouse cells could be attached inside the scaffolds over several days. In addition, the highly motile cells can migrate through the scaffolds in three dimensions. (*Adv. Mater*. **2005**, *17*, 399–403; George Xiu Song Zhao) Go to to

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