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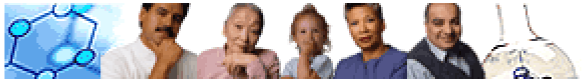

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Heart Cut

March 27, 2006

- Molybdenum catalysts for polymerizing cyclopropenes
- Zeolite-catalyzed dimethyl ether-to-methyl acetate reaction
- Use water to prevent the overalkylation of a sulfone
- Here is a new route to 3-D photonic band gap materials
- The alkaloid nostocarboline is a potent algaecide
- Casting solvent influences morphology of nanoparticle mixture
- Gold(I) catalyzes the oxidative cleavage of double bonds
- Nanoliter-scale method for optimizing reaction conditions

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Oxidized molybdenum compounds initiate the ring-opening metathesis polymerization of disubstituted cyclopropenes. Living ring-opening metathesis polymerization (ROMP) reactions have been reported for bicyclic olefins such as bicycloheptenes and bicyclooctenes. ROMPs of monocyclic olefins offer the potential for preparing block copolymers with elastomeric properties, but the limited number of monocyclic substrates suitable for living ROMPs has limited progress in this area.

R. Singh, C. Czekelius, and R. R. Schrock* at MIT report that the living ROMP of cyclopropenes can be readily initiated by a group

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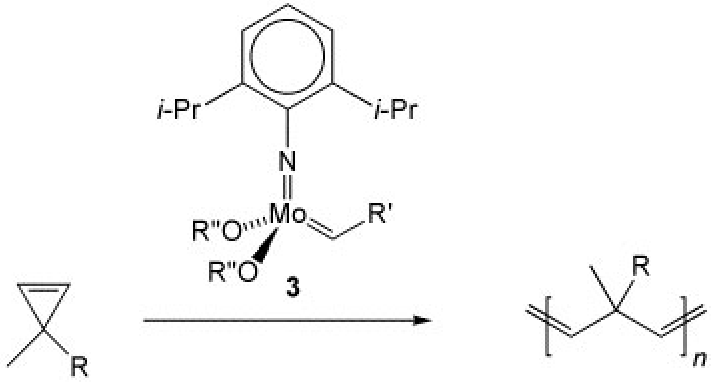
of molybdenum-based Schrock catalysts.



1 R = Ph

2 R = —CH_2CH_2OMe

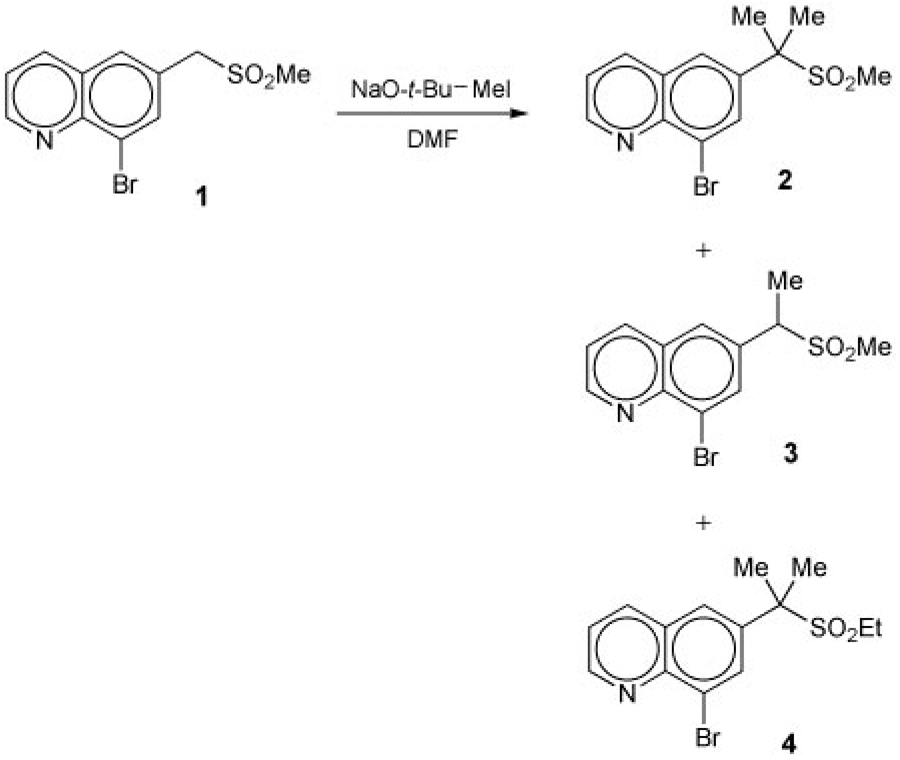
3-Methyl-3-phenylcyclopropene (**1**) and 3-(2-methoxyethyl)-3-methylcyclopropene (**2**) were the representative monomers for the homopolymerization. When **1** was polymerized using Schrock catalyst **3** with R′ = *t*-Bu and R" = –CMe_2Ph for 1 h at room temperature, the reaction proceeded characteristically for a living ROMP with a high polymer yield (95%). The polymer had a molecular weight (M_n) close to its theoretical value and a polydispersity index as low as 1.05, typical for a living ROMP.

Similar results were obtained for ROMPs of cyclopropene **2** catalyzed by **3** with various R′ and R″ groups. The living nature of the ROMPs was confirmed by the copolymerization of **1** and **2** with other known ROMP-active cycloolefins such as norbornadiene and cyclododecene derivatives, which yielded diblock and triblock copolymers with high M_n (up to 34,300) and polydispersities as low as 1.04. (*Macromolecules* **2006,** *39,* 1316 – 1317; Ben Zhong Tang and Sally Peng Li) Go to top

Convert dimethyl ether to methyl acetate via zeolite catalysis. E. Iglesia and coauthors at the University of California, Berkeley, and BP Chemicals (Hull, UK) report that halide-free zeolite catalysts promote dimethyl ether (DME) carbonylation to methyl acetate at low temperatures (150 – 190 ° C) with >99% selectivity. The rate of methyl acetate synthesis is highest using an H-MOR zeolite with a Si/Al ratio of 10:1.

The authors propose that DME reacts with acidic zeolite protons to generate methyl-saturated surface species. These methyl groups would then react with CO to produce acetyl species, which will react with DME to produce methyl acetate and regenerate the surface methyl species. Such a pathway potentially avoids the expensive rhodium and corrosive halide ions currently used in MeOH carbonylation processes. The authors point out that current productivities are below expected commercial targets but increase linearly with CO pressure. This initial report shows significant promise for practical use of the zeolite system. (*Angew. Chem., Int. Ed.* **2006,** *45,* 1617 – 1620; David A. Schiraldi and W. Jerry Patterson) Go to top

Use water to prevent the overalkylation of a sulfone. The methylation of sulfone **1** with MeI and NaO-*t*-Bu can generate two unwanted impurities—the underalkylated compound **3** and the overalkylated compound **4**—in addition to the desired product (**2**). D. A. Conlon and co-workers at Merck (Rahway, NJ, and Pointe Claire-Dorval, QU) explored the effect of water on this reaction and found that that at higher water concentrations (4 – 6 g/L, 0.9 – 1.3 equiv), the formation of overalkylation product **4** was reduced, and the conversion of intermediate **3** to compound **2** was improved.



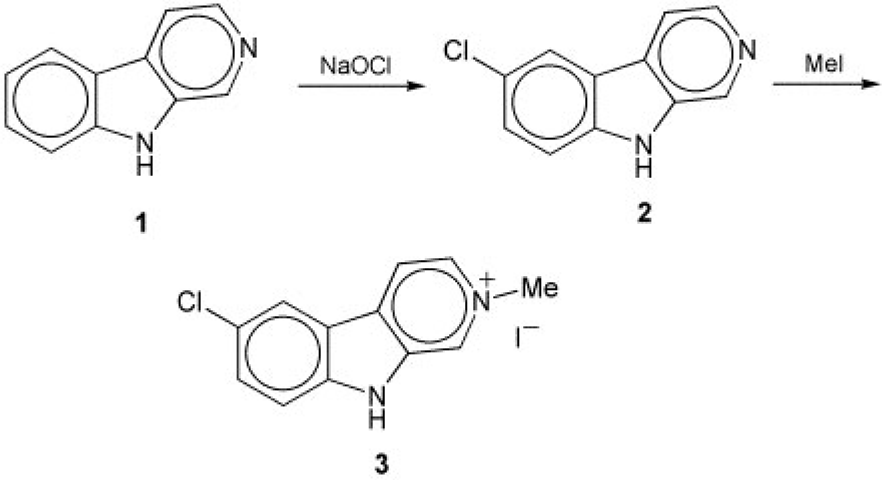
The authors rationalized their findings by noting that the active base in the water-rich system is NaOH, which is not strong enough to deprotonate the sulfone methyl group under these conditions, and that the reaction remains as a solution or very thin slurry throughout. Compound **2** is an important intermediate in the synthesis of a type-4 phosphodiesterase inhibitor for treating diseases such as asthma and chronic obstructive pulmonary disease. (*Org. Process Res. Dev.* **2006,** *10,* 36 – 45; Will Watson) Go to top

Here is a new route to 3-D photonic band gap materials. G. A. Ozin and coauthors at the University of Toronto, the University of Karlsruhe (Germany), and the Helmholtz-Gemeinschaft Karlsruhe Research Center report a novel, versatile, scalable, and cost-effective silicon double-inversion method to synthesize the first silicon replica of a polymeric photonic crystal. This method can be applied to any photoresist template produced by direct-laser writing, holographic laser lithography, or a combination of the two. It also incorporates a template-independent step to fine-tune the filling fraction of the high-index material, thereby allowing larger photonic band gaps to be obtained than with the template alone.

The procedure consists of straightforward, inexpensive processes that are compatible with the semiconductor industry. It is suitable for mass-producing complex and functionalized photonic-crystal-based devices and permits the inclusion and replication of functional elements such as point and line defects. (*Adv. Mater.* **2006,** *18,* 457 – 460; George Xiu Song Zhao) Go to top

The alkaloid nostocarboline is a potent algaecide. The adsorption of bacteria and algae onto submerged surfaces is a significant biofouling problem for ships, oil platforms, and nuclear power plants. The current solution—organotin-based antifouling coatings—is coming under increasing environmental scrutiny and more and more countries are banning their use.

K. Gademann and coauthors at ETH Zürich, the University of Zürich (Kilchberg, Switzerland), and Actelion Percurex AG (Basel) previously reported that nostocarboline (**3**) is a cholinesterase inhibitor that quickly inhibits the growth of cyanobacteria and green algae. They now report a simple synthesis of **3** and several of its derivatives from the commercially available starting material norharmane (**1**).



The phenyl ring in compound **1** was chlorinated at the 6-position using NaOCl. The chlorinated intermediate (**2**) was methylated using MeI to give the desired product **3** as the iodide salt in high yield.

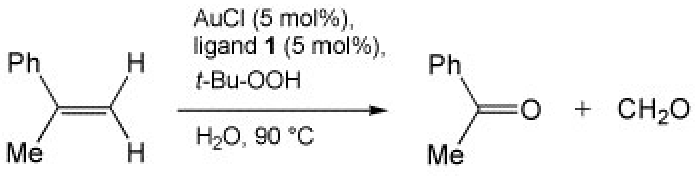
The evaluation of compound **3** showed that it is a potent growth inhibitor for cyanobacteria and green algae, with an MIC of 1 μM (MIC is the minimum inhibitory concentration for growth reduction). At 10 μM, the compound killed cyanobacterial cells rapidly within 24 h. The authors found that the quaternary nitrogen group was essential for biological activity; demethylated derivatives were inactive.

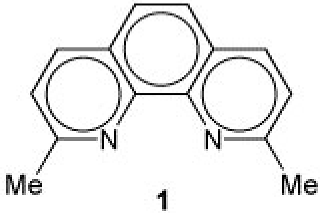
To determine the mechanism of growth inhibition, experiments were carried out with an initial growth phase in the dark. Almost no inhibitory action was observed for concentrations of **3** up to 50 μM, which suggests that its activity is correlated to photosynthesis of the organisms. This algaecide features rapid and potent growth reduction of aquatic organisms, simple and inexpensive preparation, selectivity for photosynthetic organisms, and ease of structural modification for additional derivatives. (*Org. Lett.* **2006,** *8,* 737 – 740; W. Jerry Patterson) Go to top

The morphology of nanoparticle mixtures of poly(styrene-*b*-isoprene) and magnetic γ-iron(III) oxide is influenced by the casting solvent. K. Char* and co-workers at Seoul National University (Korea) investigated the effect of the casting solvent on the phase behavior of a mixture of a cylindrical poly(styrene-*b*-isoprene) (PS-*b*-PI) diblock copolymer and magnetic γ-Fe_2O_3 nanoparticles. The authors chose toluene as the “neutral” solvent for the PS and PI blocks and hexane as the selective solvent for the PI block.

The nanoparticles were more likely to aggregate than to incorporate into the PI microphase during the evaporation of toluene, which destroyed the long-range ordering of PS-*b*-PI. The original cylindrical morphology was significantly suppressed with increasing nanoparticle load, and a new ordered spherical phase was obtained with as much as 15% nanoparticle content when the mixture was cast from toluene. When hexane was used as the casting solvent, the γ-Fe_2O_3 nanoparticles were selectively incorporated into the miscible PI microphase, resulting in a completely disordered morphology. (*Langmuir* **2006,** *22,* 1375-1378; Sally Peng Li) Go to top

Gold(I) chloride catalyzes the oxidative cleavage of double bonds. Z. Shi and coauthors at Peking University (Beijing), the Chinese Academy of Sciences (Shanghai), and East China Normal University (Shanghai) report an unusual gold-mediated cleavage of olefins in water with *t*-BuOOH as the oxidant. This oxidative cleavage leads to ketones or aldehydes, depending on the structure of the olefinic substrate.





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A key to the success of this reaction was using the bidentate nitrogen ligand neocuprione (**1**). When 1,1-diphenylethylene was oxidized in the absence of **1**, the product yield was <5%; adding 5 mol% **1** gave a 92% yield. Most of the other olefinic substrates in this study led to significantly lower ketone or aldehyde yields. In the example shown, the yield of acetophenone was 66%.

The authors used methyl *p*-vinylbenzoate as a substrate to examine the reaction products. In addition to the expected benzaldehyde derivative, the authors also detected CH_2O during the reaction. They used $PhNHNH_2$ to trap the CH_2O, and isolated a 30% yield of $PhNHN{=}CH_2$. This strongly indicated that the C=C bond was split into two carbonyl products. (*Org. Lett.* **2006,** *8,* 693－696; W. Jerry Patterson) Go to top

This nanoliter-scale microfluidic method for optimizing reaction conditions uses the MALDI technique. T. Hatakeyama, D. L. Chen, and R. F. Ismagilov* of the University of Chicago report a microfluidic system for screening organic-chemical reactions on a nanoliter scale. Discrete droplets (~15 nL) of test reagents were loaded into a tubing “cartridge” with a fluorinated solvent. A pair of syringes was used to combine the reagent droplets with a solution of the substrate of interest, and the reaction was allowed to proceed at controlled temperatures and times. The droplets were then deposited on a matrix-assisted laser desorption–ionization (MALDI) detection plate and dried. The reaction results were analyzed by MALDI–mass spectrometry.

The authors used this method to determine the optimum reagent–reaction conditions for the deacetylation of a complex biological molecule, ouabain hexaacetate. (*J. Am. Chem. Soc.* **2006,** *128,* 2518–2519; David Schiraldi) Go to top

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