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Noteworthy Chemistry

April 27, 2009

- Chain mobility dictates as-cast thin-film morphology
- Use carbon nanotube catalysts to convert synthesis gas to diesel fuel
- Make tricyclic isoindolinones in four steps in one pot
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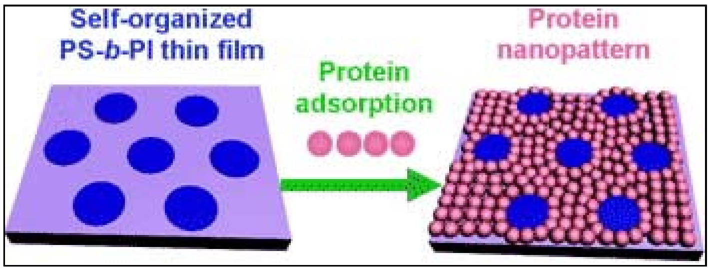
Chain mobility dictates as-cast thin-film morphology. D. Liu, T. Wang, and J. L. Keddie* at the University of Surrey (Guildford, UK) explored the role of molecular mobility of polymer blocks in protein patterning on the template surface of self-organized hydrophobic polystyrene-*b*-polyisoprene (PS-*b*-PI) thin films. When the authors investigated the as-processed (nonequilibrium) symmetric films (spin-cast from toluene on silicon, 12–60 nm thick), they found that morphology shifts cause film thickness to increase from a perpendicular lamellar organization (12 nm thick) to dotted patterns (16 or 19 nm) to a “patchwork quilt” arrangement (60 nm).



The authors expected that the lower surface energy PI would create a wetting layer in equilibrated films. Atomic force microscopy (AFM), however, showed that PS and PI are present at the nonequilibrium thin-film surface. In asymmetric PS-*b*-PI, the nonequilibrium structures shift from cubic (PI spheres in a PS matrix) at 12 nm thick to a striped pattern of cylinders parallel to the substrate (19 nm, with decreasing cylinder length up to 25 nm) to a mixture of spheres and short ribbons at 39 nm.

Using PS-*b*-PI thin films with dot morphology and striped patterns, the authors determined that bovine serum albumin (BSA) adsorbs only on the PS regions and that the patterned morphologies are stable at BSA concentrations up to 1 mg/mL and incubation up to 2 h. These findings are consistent with observations that BSA adsorbs on the surface of PS homopolymer thin films, but resists adsorption on PI homopolymer.

Surface analyses indicated that the symmetric PS-*b*-PI thin films have a higher fraction of PI blocks at the film surface compared with the asymmetric PS-*b*-PI copolymers and that the amount of PI at the surface correlates with lower BSA adsorption. As the film thickness exceeds that of the equilibrium domain spacing, the equilibrium morphology prevails and favors a PI-rich surface layer. These findings suggest that chain mobility may play a role in protein resistance, which is usually explained in terms of hydrophilicity. (*Langmuir* **2009,** *25,* 4526–4534; LaShanda Korley)

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Use carbon nanotube catalysts to convert synthesis gas to diesel fuel. The Fischer–Tropsch (FT) synthesis is a key step in using synthesis gas (syngas) to transform nonpetroleum feedstocks to hydrocarbon fuels. Ruthenium-based FT catalysts are the basis of recent studies of syngas conversion. Building on this research, Q. Zhang, Y. Wang, and co-workers at Xiamen University (China) report that ruthenium nanoparticles supported on carbon nanotubes (CNTs) provide excellent selectivity for producing the C_{10}–C_{20} hydrocarbon fraction used routinely for diesel fuels.

The scope of this study spanned optimizing the ruthenium-based catalyst system, including CNT pretreatment, and determining the most useful ruthenium nanoparticle sizes. CNT pretreatment plays a key role in determining hydrocarbon selectivities. The ruthenium species are reduced almost completely to metallic ruthenium (H_2 at 300 °C for 2 h) during the pretreatment phase. The authors found that pretreating the CNTs with 68% HNO_3 results in FT products with significantly higher hydrocarbon selectivities compared with untreated controls. They also determined that Ru/CNT catalysts with a mean ruthenium particle size of ~7 nm provide the highest selectivities to C_{10}–C_{20} hydrocarbon fractions.

The results demonstrate that Ru/CNT catalyst systems can produce the diesel hydrocarbon fraction with a selectivity as high as 60%—the highest value reported for the diesel fraction from FT synthesis. (*Angew. Chem., Int. Ed.* **2009,** *48,* 2565–2568; W. Jerry Patterson)

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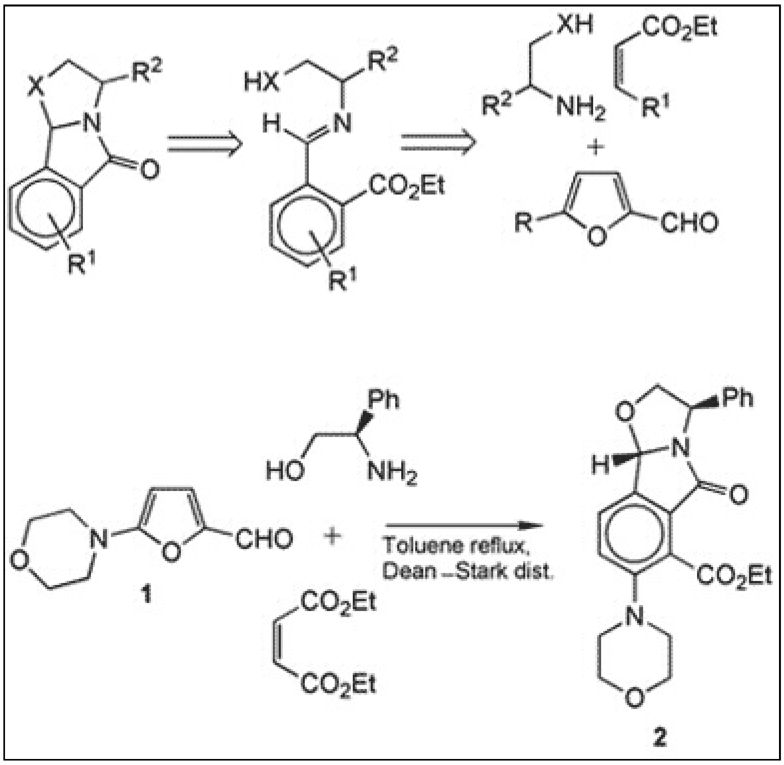
Make tricyclic isoindolinones in four steps in one pot. Cascade multicomponent reactions (CMCRs) are a powerful tool for organic synthesis; they make it possible to prepare complex molecules in a single operation. A retrosynthetic analysis of the target molecules consists of a Diels–Alder reaction followed by cyclization and formation of an imine, as shown in the first line in the figure.



S. Marque, D. Prim, and coauthors at the University of Versailles-Saint-Quentin-en-Yvelines (France) and the National Institute of Physicochemical Research and Analysis (Thabet, Tunisia) solved a problem in the Diels–Alder step of the multicomponent reaction by using a more reactive diene (**1**) in place of the traditional furaldehyde. They envisaged that the initial formation of an imine would promote the cycloaddition. They detected a furylimine by an NMR analysis of the crude reaction mixtures and then optimized the conditions for the multicomponent reaction (toluene reflux and Dean–Stark distillation).

The authors found only one diastereomer (**2**) and assigned its configuration by nuclear Overhauser effect and single-crystal X-ray analysis. They expanded the CMCR synthesis to several amino alcohols and 5-aminofuraldehydes in good yields. An amino alcohol with an additional chiral center did not improve the selectivity.

This method was successfully run in solvent-free conditions in a sealed tube at 115 °C with a 41% yield. This technique decreased reaction time without loss of yield or stereoselectivity. (*Org. Lett.* **2009,** *11,* 1817–1820; **José C. Barros**)

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Should you choose an enol triflate or an enol tosylate as the substrate for a palladium catalyzed amidation? The final coupling of an amide with an enol trifluoromethanesulfonate (triflate) generates a substrate for asymmetric hydrogenation in the later stages of the synthesis of taranabant, a CB1R inverse antagonist for the treatment of obesity.

D. E. Wallace, K. R. Campos, C. S. Shultz, and coauthors at Merck Research Laboratories (Rahway, NJ) and Solvias AG (Basel, Switzerland) prepared the enol triflate with the expensive triflating agent $NPhTf_2$ as a 90:10 mixture of geometric isomers. The product was noncrystalline and had to be purified chromatographically. However, using toluenesulfonic anhydride instead of $NPhTf_2$ gave the same mixture of geometric isomers as a crystalline solid, from which the authors isolated the desired major isomer as a single product in 85% yield without needing chromatography. (*Org. Process Res. Dev.* **2009,** *13,* **84–90**; **Will Watson**)

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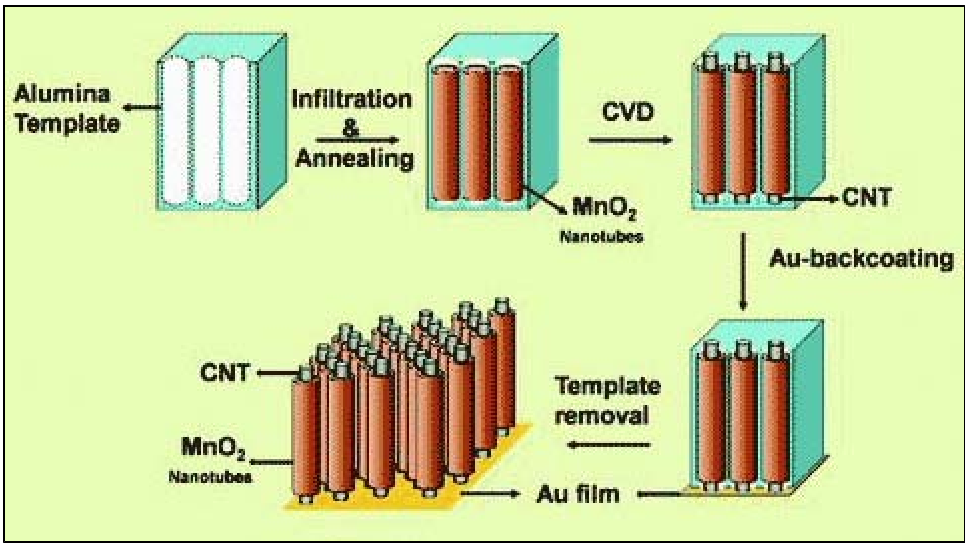
Coaxial composite electrodes have excellent cyclic stability and capacity. Transition-metal oxides with high theoretical capacity, low cost, and environmental acceptability are gaining increasing attention in energy devices such as lithium batteries and supercapacitors. However, the poor electronic conductivity and rapid capacity decay during continuous cycling limit their applications.

Manganese oxides are potential materials for lithium batteries and supercapacitors. Improving their electronic conductivity and solving volume-expansion problems are the key challenges. P. M. Ajayan and co-workers at Rice University (Houston) found that coaxial MnO_2–carbon nanotubes (CNTs) display high lithium storage ability, storage capacity, and electronic conductivity. The coaxial nanostructures were made by using vacuum infiltration and chemical vapor deposition (CVD) techniques with an anodic alumina template (see figure).



The reversible capacity of the composite electrodes is ~500 mA·h/g after 15 cycles, higher than pure MnO_2 nanotubes or CNTs alone. Several factors contribute to this improvement, including higher conductivity from the CNT cores, uniform coaxial alignment that provides well-directed conductive paths, and a dual lithium storage mechanism: insertion–deinsertion for the CNTs and formation–decomposition of Li_2O in the case of the MnO_2 nanotubes. (*Nano Lett.* **2009,** *9,* **1002–1006**; **George Xiu Song Zhao**)

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Use fatty-acid derivatives in renewable polyurethane networks. L. Hojabari, X. Kong, and S. S. Narine* at the University of Alberta (Edmonton) synthesized and characterized environmentally friendly polyurethanes (PUs) derived from fatty acid–based linear aliphatic diisocyanates. They obtained 1,7-heptamethylene diisocyanate (HPMDI) by a simple Curtius arrangement of 9-oxononanoic acid. They synthesized polyurethanes by treating the fatty acid–derived diisocyanate with two polyols: the commercial product Desmophen 900 (functionality ≥4) or a canola polyol based on triolein, a mixture of mono-ols, diols, and triols. For comparison, they also prepared PUs using a petroleum-based linear hexamethylene diisocyanate (HDI).

The authors report that the type of polyol affects hard domain ordering. For example, PUs with canola polyols feature hydrogen-bonding urethane carbonyls within crystalline hard domains along with free carbonyls; whereas PUs that contain commercial polyols yield amorphous domains with hydrogen-bonded carbonyl groups. Wide-angle X-ray scattering studies showed different crystal structures for the HDI-based canola PUs and the HPMDI-based canola PUs, possibly because of the number of methylene units in the polyols and diisocyanates (an odd–even effect).

The authors note that the network structure of the canola-based PUs is complicated by the variation in the reactivity of the hydroxyl groups in the mixture and the presence of dangling chains, and that the high degree of functionality of the commercial polyol generates PU networks with high cross-link densities. For example, a higher glass-transition temperature (T_g) and a higher storage modulus below the T_g are observed for commercial polyol-based PUs compared with canola polyol-based PUs made with the same diisocyanate. For PUs derived from the same polyol, the HPMDI-based PUs exhibit lower T_g and lower storage modulus below the T_g than HDI PUs.

The authors explored the mechanical behavior of the PUs in stress–strain experiments and confirmed key differences in tensile strength and strain-at-break as a function of the type of polyol and diisocyanate and the measurement temperature. One striking difference is an almost 5-fold increase in elongation accompanied by a modest increase in tensile strength for commercial polyol PUs derived from HPMDI when compared with those from HDI. Again, the complexity of the canola polyol affects network formation, which is reflected in lower tensile strength values but higher degrees of elongation for HPMDI and HDI. (*Biomacromolecules* **2009,** *10,* **884–891**; **LaShanda Korley**)

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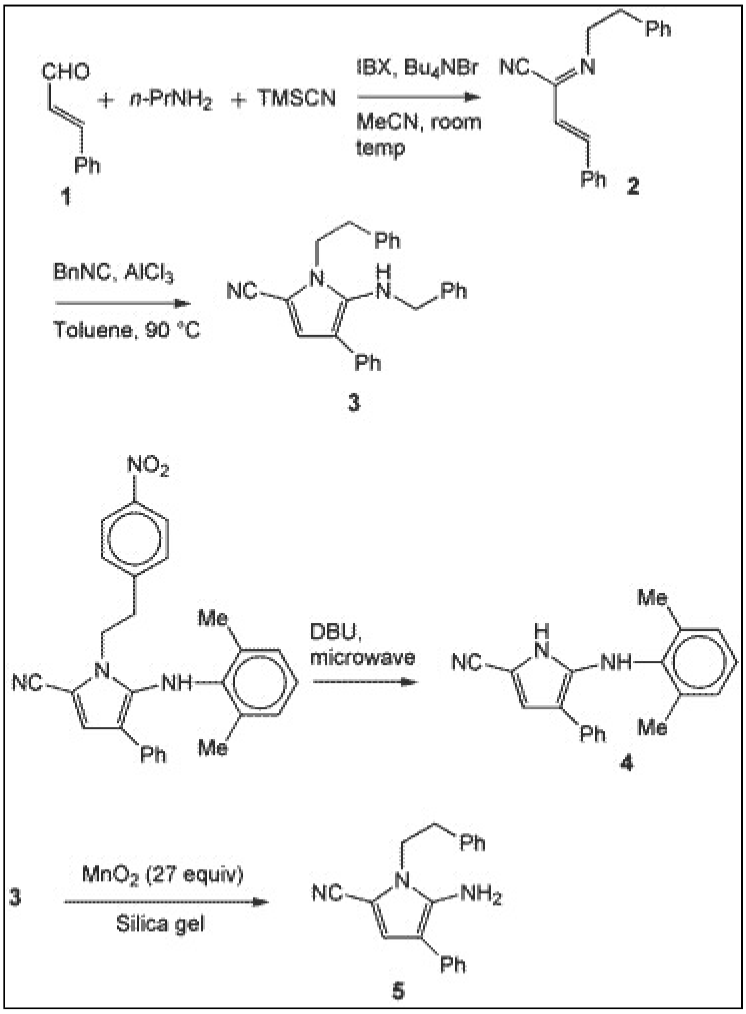
Here's an easy route to highly substituted pyrroles. Substituted 2-aminopyrroles are important structural elements in bioactive compounds and natural products. P. Fontaine, G. Masson*, and J. Zhu* at the Institute of Natural Substance Chemistry (Gif-sur-Yvette, France) note that no convenient synthesis is available for unsymmetrical polysubstituted 2-aminopyrroles. They report an innovative multicomponent reaction that leads to 2-amino-5-cyanopyrroles in two steps from simple starting materials.



The authors' starting components were α,β-unsaturated aldehydes (**1**), primary amines, and cyanotrimethylsilane (TMSCN). These reactants undergo an oxidative Strecker reaction to form intermediate α-imino nitriles (**2**). The oxidant 2-iodoxybenzoic acid (IBX) and Bu_4NBr are essential for this stage of the synthesis to proceed.

Compounds such as **2** provide an ideal configuration for $AlCl_3$-mediated [4 + 1] cycloaddition with an isocyanide that leads to the densely functionalized pyrrole **3** in generally high yields. In all cases, the pyrroles are obtained as the only product, uncontaminated by competing rearrangement processes.

The authors also developed methods for deprotection of the pyrrole nitrogen and the nitrogen on the alkyl amine substituent, illustrated by products **4** and **5**. DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene.

The scope of this reaction sequence makes it possible to introduce substituents at the C–3 and C–4 positions on the pyrrole ring, in addition to the C-2 and C-5 substituents. The presence of the nitrile substituent provides a convenient reactive site for synthesizing other nitrogen-containing heterocycles. (*Org. Lett.* **2009,** *11*, **1555–1558**; **W. Jerry Patterson**)

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