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EXPANDING THE SCOPE OF CARBON−CARBON BOND FORMATION

Cross-coupling chemistry is a well-developed field, particularly for syntheses that form a carbon−carbon bond by breaking a carbon−halide bond. Approaches for carbon−carbon bond formation by breaking a carbon−nitrogen bond are far less explored. Abigail Doyle and Chung-Yang Huang expand the scope of cross-coupling reactions by describing a new method to synthesize β,β-disubstituted alkylamines through nickel-catalyzed ring-opening reactions between 2-arylaziridines and organozinc reagents (DOI: 10.1021/ja3013825).

Other synthetic methods for alkylations of aziridines—three-membered rings containing a single nitrogen atom—require strong nucleophiles and lack regioselectivity. Doyle and Huang's cross-coupling reaction occurs at room temperature under mild conditions and with complete regioselectivity. The reaction uses a catalytic system made up of an air-stable nickel catalyst that is inexpensive and commercially available. In addition, the reaction is compatible with a wide variety of functional groups on both the aziridine and organozinc reagent.

Doyle and Huang provide an accessible way to make β,β-disubstituted alkylamines, which include substituted phenethylamines. Derivatives of phenethylamine can be bioactive compounds like stimulants, psychedelics, and antidepressants. Perhaps more importantly, the authors have created a general method that can be applied to many types of reactions to produce a diverse range of molecules. **Yun Xie, Ph.D.**

STUCK ON YOU: NANOTUBE FUNCTIONALIZATION AT THE MOLECULAR LEVEL

Research has suggested that attaching other molecules to the walls of single-walled carbon nanotubes (SWCNTs) can tailor the unique optical and electrical properties of these materials to specific applications, such as creating novel drug delivery vehicles or molecular sensors. Recent work indicates that SWCNTs first need to be decorated with surfactants that influence access to the nanotube surface, but it has been unclear exactly how these surfactants affect functionalization at the molecular level.

To get a better idea of how surfactants operate at the nanotube surface, Daniel Blankschtein and co-workers use a combination of computer simulations, experiments, and calculations (DOI: 10.1021/ja301635e). They studied the reaction of diazonium salts with SWCNTs that had been decorated with one of three different surfactants.

The charged head groups of the surfactants influence whether the diazonium ion is attracted to or repelled by the nanotube surface. The authors note that understanding the functionalization process better through simulation and modeling could eventually help optimize techniques to modify SWCNTs. **Christen Brownlee**

PUTTING THE PRESSURE ON BENZENE TO BOND

Roald Hoffmann and co-workers apply high-level calculations on benzene to reveal four new species of benzene dimers that have yet to be synthesized (DOI: 10.1021/ja302597r). It is remarkable that, given much previous work on benzene dimers, the proposed molecules had escaped theoretical or experimental notice.

The researchers found the new dimers by bringing together two benzenes to an uncomfortably close distance. Most of the time they flew apart, occasionally they formed known dimers (a good check on the computational method), and sometimes they relaxed into ground-state $(C_6H_6)_2$ structures entirely unknown. The four new dimers identified in this way are 50−99 kcal/mol less stable than two non-interacting benzene molecules. Even though the molecules are relatively unstable, they are also resistant to fragmenting back to two benzenes. The calculated activation energies for fragmentation of the dimers range from 27 to 36 kcal/mol.

The study by the Cornell group is unique in the care they have taken to examine computationally a plethora of escape routes potentially available to such dimers—because the four dimers are relatively high in energy, they could find reaction pathways that result in more stable products. For example, the dimers could undergo reactions such as hydrogen shifts or electrocyclic reactions, or dimerize themselves. Hundreds of reactions were examined, and the researchers postulate that it could be possible to make and isolate one or more of the four proposed dimers. **Yun Xie, Ph.D.**

A SUGAR-SENSING MOLECULAR LOGIC GATE? SWEET!

Logical functions such as AND, OR, and NOT manipulate and evaluate binary values. Researchers have implemented these logic gates in both silicon and molecular forms, developing systems that respond to electrical and chemical inputs. Now Alexander Schiller and colleagues describe a molecular system that can perform a logical function called IMP ("implication") (DOI: 10.1021/ja303214r).

In an IMP gate, "either input p implies input q or vice versa." The authors implemented such a gate using a fluorescent dye, water-soluble perylenediimide (WS-PDI), and the boronic acid-containing viologen BBV (input p). The second input is fructose (q). In aqueous solution, WS-PDI fluoresces on its own ($p = 0$, $q = 0$, output = 1) and also in the presence of fructose ($p = 0$, $q = 1$, output = 1). BBV quenches that fluorescence ($p = 1$, $q = 0$, output = 0)—unless fructose, which reacts with the boronic acid, is also present ($p = 1$, $q = 1$, output = 1). The authors monitored the reaction using fluorescence correlation spectroscopy on a confocal microscope.

The result is both a logic circuit and a sugar sensor—a system containing both dye and BBV will not fluoresce unless fructose (>0.5 mM) is also present, producing a signal in less than a second. "This work demonstrates ways by which Boolean logic can process information in the field of sugar diagnostics," the researchers write. **Jeffrey M. Perkel**

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NONLINEAR OPTICAL PROBE FOR METAL ION IDENTIFICATION

Selective detection and identification of metal cations is important, for example in environmental monitoring and testing, so analytical chemists are continually looking for improved means of identifying and quantifying metal ions in solution. Benoît Champagne and co-workers have undertaken an ab initio study of a system that may be effective for metal cation identification across alkali, alkaline earth, and transition metal ions (DOI: 10.1021/ja302395f).

The authors use a switchable spiropyran/merocyanine system that isomerizes upon complexation of a metal cation. This molecule has second-order nonlinear optical (NLO) properties, which means that the dielectric polarization responds nonlinearly to light.

Ab initio calculations predict that the hyperpolarizability of the merocyanine molecule is quite different for various bound metal cations in this system, indicating that each ion will have a unique response to an incident laser. By measuring the NLO response, researchers can identify metal cations. The results reported here provide a new method that analytical chemists can add to their toolbox for detecting and identifying metal cations. **Polly Berseth, Ph.D.**