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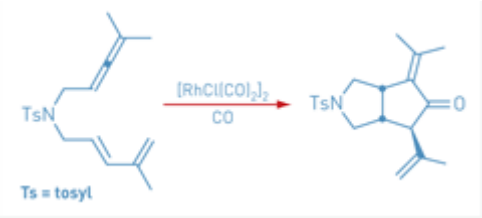
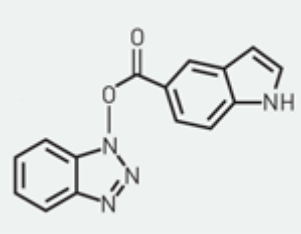
Diene is key to novel cycloaddition



The first [2+2+1] cycloaddition reaction of a 1,3-diene, an allene, and carbon monoxide has been reported by chemists at Stanford University (*Angew. Chem. Int. Ed.* 2006, *45*, 2459). Paul A. Wender Mitchell P. Croatt, and Nicole M. Deschamps developed the reaction (shown), which offers an efficient and selective route to highly substituted alkylidenyl cyclopentanones. Others have attempted similar cycloadditions in the past—using an unactivated alkene rather than a diene—with little success. Rather than undergo cycloaddition, in those instances the alkene and allene moieties simply cycloisomerized to a seven-membered ring. By replacing the alkene with a 1,3-diene, the Stanford group was able to coax the cycloaddition reaction to take place under mild conditions in the presence of a rhodium catalyst. The reaction is chemoselective, targeting only the olefin closest to the allene, and appears to be accelerated in the presence of a BrØnsted acid. The chemists report excellent yields and no evidence of the cycloisomerization

that plagued earlier efforts with alkenes.

Potent SARS inhibitors identified



Small-molecule agents that represent the most potent inhibitors yet known of the protease of severe acute respiratory syndrome virus have been identified. SARS, a contagious and potentially fatal respiratory condition caused by a coronavirus, was first reported in Asia several years ago and still cannot be effectively treated. Its protease plays an essential role in viral replication and is thus a promising target for anti-SARS therapeutics. Although a few inhibitors have been found, none are highly potent (that is, none have activities in the low nanomolar range), and no preclinical testing of the agents has been reported. Now a series of potent small-molecule inhibitors, like the 7.5-nM agent shown, have been identified by Po-Huang Liang of Academia Sinica, Taipei, Taiwan; Chi-Huey Wong of Scripps Research Institute; and coworkers (*Chem. Biol.* 2006, *13*, 261). The benzotriazole esters act as suicide inhibitors by bonding irreversibly to a key site on the virus.

Frictionless pirouettes in solution

Given the proper push, a diatomic molecule in solution can spin with so little friction that it acts as if it were in the gas phase. That finding is the first example of nearly frictionless rotation in a room-temperature liquid (*Science* 2006, *311*, 1907). The University of Southern California's Stephen E. Bradforth, Brown University's Richard M. Stratt, and coworkers found that when they photodissociated a flowing film of an aqueous iodine cyanide solution with ultrashort, high-energy laser pulses, they could make the resulting cyanide radical spin so quickly that it essentially wipes out any frictional force on the molecule. The spinning diatomic radical creates a shock wave that throws back the water molecules

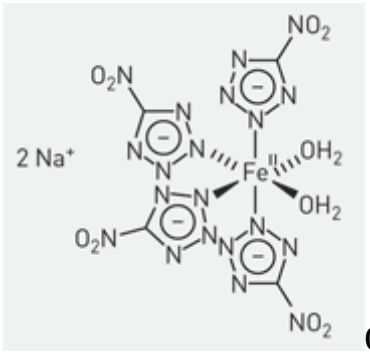
that surround it. It continues to spin nearly frictionlessly for about 10 picoseconds until the shock dissipates and the water rushes back into its space. Bradforth and Stratt say the discovery contradicts what's expected from the physics of molecules in solution and suggests chemists may need to rethink how molecules move energy around in liquids.

Self-catalytic activity found in genomic DNA

Catalytic activity has beenfound for the first time in a natural DNA sequence. The self-catalytic activity shows "that DNA is not merely the inert information tape for storing hereditary information, as has been thought for half a century, but that it also has the intrinsic capacity to modify itself," says Jacques R. Fresco of Princeton University, who made the discovery with coworkers Olga A. Amosova and Richard Coulter (*Proc. Natl. Acad. Sci. USA* 2006, *103*, 4392). Sidney Altman of Yale University and Thomas R. Cech of Howard Hughes Medical Institute discovered catalytic RNA, work for which they shared the 1989 Nobel Prize in Chemistry. And catalytic activity has been identified in synthetic DNA, such as in DNA oligomers created in in vitro evolution experiments. Now, the Princeton group has discovered self-catalyzed guanine-depurinating activity in short natural DNA sequences as well. These sequences are widely distributed in human and other genomes, suggesting that self-catalyzed depurination of guanine may play a key biological role.

Safe 'green' explosives

Environmentally friendly and safe substitutes for lead-based primaries have been developed by researchers at the University of North Carolina, Chapel Hill, and Los Alamos and Lawrence Berkeley National Laboratories. Primaries are small explosive charges used to detonate larger charges, ranging from propellants for bullets to explosives used in mining. Most are lead-based and therefore potentially harmful for the environment and for people exposed to the residue after primaries explode. These materials



can also detonate accidentally. Finding a replacement has been difficult, because the substitutes also have defects, including instability or toxicity. Now, UNC chemistry professor Thomas J. Meyer and his colleagues have synthesized four green primary explosives that meet all of the criteria needed to replace those containing lead (*Proc. Natl. Acad. Sci. USA* 2006, *103*, 5409). Based on complex metal dianions and environmentally benign cations, the compounds (one of which is shown) can be desensitized by storage in water and release no harmful residues when they blow up.

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