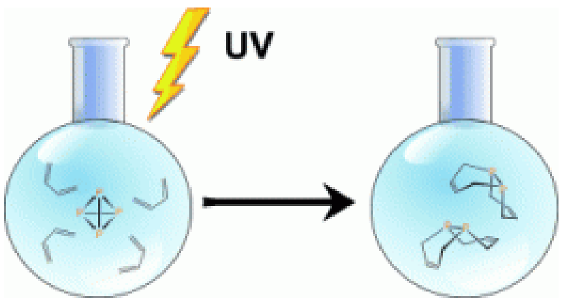
Moving toward greener chemistry

September 3 2010, by Anne Trafton



Phosphorus, a mineral element found in rocks and bone, is a critical ingredient in fertilizers, pesticides, detergents and other industrial and household chemicals. Once phosphorus is mined from rocks, getting it into these products is hazardous and expensive, and chemists have been trying to streamline the process for decades.

MIT chemistry professor Christopher Cummins and one of his graduate students, Daniel Tofan, have developed a new way to attach phosphorus to organic compounds by first splitting the phosphorus with ultraviolet light. Their method, described in the Aug. 26 online edition of *Angewandte Chemie*, eliminates the need for chlorine, which is usually required for such reactions and poses health risks to workers handling the chemicals.

While the new reaction cannot produce the quantities needed for large-scale production of phosphorus compounds, it opens the door to a new field of research that could lead to such industrial applications, says Bertrand, who was not involved in the research.

Extracting phosphorus

Most natural phosphorus deposits come from fossilized animal skeletons, which are especially abundant in dried-up seabeds. Those phosphorus deposits exist as phosphate rock, which usually includes impurities such as calcium and other metals that must be removed.

Purifying the rock produces white phosphorus, a molecule containing four phosphorus atoms. White phosphorous is tetrahedral, meaning it resembles a four-cornered pyramid in which each corner atom is bound to the other three. Known as P_4, white phosphorus is the most stable form of molecular phosphorus. (There are also several polymeric forms, the most common of which are black and red phosphorus, which consist of long chains of broken phosphorus tetrahedrons.)

For most industrial uses, phosphorus has to be attached one atom at a time, so single atoms must be detached from the P4 molecule. This is usually done in two steps. First, three of the atoms in P4 are replaced with chlorine, resulting in PCl_3 — a phosphorus atom bound to three chlorine atoms.

Those chlorine atoms are then displaced by organic (carbon-containing) molecules, creating a wide variety of organophosphorus compounds such as those found in pesticides. However, this procedure is both wasteful and dangerous — chlorine gas was used as a chemical weapon during World War I — so chemists have been trying to find new ways to bind phosphorus to organic compounds without using chlorine.

A new reaction

Cummins has long been fascinated with phosphorus, in part because of its unusual tetrahedral P_4 formation. Phosphorus is in the same column of the periodic table as nitrogen, whose most stable form is N2, so chemists expected that phosphorus might form a stable P_2 structure. However, that is not the case.

For the past few years, Cummins' research group has been looking for ways to break P_4 into P_2 in hopes of attaching the smaller phosphorus molecule to organic compounds. In the new study, Cummins drew inspiration from a long overlooked paper, published in 1937, which demonstrated that P4 could be broken into two molecules of P_2 with ultraviolet light. In that older study, P_2 then polymerized into red posphorus.

Cummins decided to see what would happen if he broke apart P_4 with UV light in the presence of organic molecules that have an unsaturated carbon-carbon bond (meaning those carbon atoms are able to grab onto other atoms and form new bonds). After 12 hours of UV exposure, he found that a compound called a tetra-organo diphosphane had formed, which includes two atoms of phosphorus attached to two molecules of the organic compound.

This suggests, but does not conclusively prove, that P_2 forms and then immediately bonds to the organic molecule. In future studies, Cummins hopes to directly observe the P_2 molecule, if it is indeed present.

Cummins also plans to investigate what other organophosphorus compounds can be synthesized with ultraviolet light, including metallic compounds. He has already created a nickel-containing organophosphorus molecule, which could have applications in electronics.

More information: "Photochemical Incorporation of Diphosphorus

Units into Organic Molecules" by Daniel Tofan and Christopher C. Cummins. *Angewandte Chemie*, 26 August, 2010.

Provided by Massachusetts Institute of Technology