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HIGHLY REACTIVE MOLECULES KNOWN AS CARBENES HAVE GONE FROM UNSTABLE INTERMEDIATES WITH NANOSECOND LIFETIMES TO POWERFUL TOOLS IN SYNTHETIC CHEMISTRY.

Taming Carbon's Wild Side
WHAT WE KNOW BY **CRISTINA LUIGGI** / NOVEMBER 30, 2009

In the early days of organic chemistry—the branch of science that deals with the seemingly endless interactions involving carbon atoms—the forces that governed carbon's atomic and molecular behavior weren't fully understood; anything seemed possible. With the blinkered determination and optimism of their alchemist predecessors, chemists set their sights on isolating and synthesizing a wide array of compounds—some observed in nature, others dreamt up by their imaginations.

One such chemical species, methylene, was the focus of French chemist Jean-Baptiste Dumas in the early 1830s. Methylene is the simplest member of a class of organic molecules known as carbenes, which contain an atom of carbon only bonded to two other atoms, in this case, a pair of hydrogen atoms.

Dumas' quest was driven by scientific curiosity rather than the promise of any practical applications. He observed that other one-carbon molecules, such as methane (the principal component of natural gas), carbon dioxide, and the toxic carbon monoxide were readily found in nature. It seemed reasonable to expect methylene to be easily synthesized in a lab. Dumas figured he could do this by dehydrating the one-carbon alcohol, methanol. But he failed.

Over the next century, a procession of chemists tried their luck at isolating methylene and other types of carbenes. Each and every one of them failed. By the 1960s, a general consensus was etched into the foundation of organic chemistry: Carbenes were too unstable for isolation. While they took part in many reactions, carbenes would forever remain transient intermediates with lifetimes of mere nanoseconds. The conclusion was that no one would ever be able to bottle them up and that scientists should stop wasting their careers in such pursuits.

All atoms strive to be in the most stable state possible, which is generally when their outermost shells have exactly eight electrons. Chemical bonding involving the sharing of electrons between atoms helps individual atoms achieve this stability. The reason for carbene instability—not known in Dumas' time—is that their carbon atoms have a rare electronic configuration.

A carbon atom has two electrons in its inner shell and four in the outer, and is most stable when it shares those four outermost electrons with other atoms. By forming four bonds, a carbon atom is in turn welcoming four electrons into its outer shell, making eight. Because the carbon atoms in carbenes have only two bonds, they are missing two electrons. The electron-deficient carbon atom is therefore highly reactive; it is looking to borrow a pair of electrons in a bond with other atoms or molecules.

But in the early 1990s, a chemist working for DuPont, Anthony Arduengo, figured out how to stop these elusive molecules from reacting further. Arduengo was working on the commercial production of a catalyst to be used in making environmentally friendly automobile paints. Considering that the reaction involved a carbene intermediate, he was surprised at how efficiently he was able to produce the catalyst in an industrial setting, under less stringent conditions than would normally be employed in a research lab . This led him to believe that carbenes were much sturdier than previously thought. The type in question, an N-heterocyclic carbene, or NHC, has a ring of two nitrogen atoms and three carbon atoms, one of which has only two bonds. Arduengo thought he could isolate it, but DuPont higher-ups met his inkling with skepticism. Even though he was told to find another research goal, Arduengo went about trying to stabilize the NHC anyway.

Arduengo's gamble paid off. In 1991, more than 150 years after the first attempt, he became the first chemist to successfully crystallize a carbene by placing the two-bonded carbon between the two nitrogen atoms. Electrons from the latter can provide the carbon with the most stability.

But Arduengo wasn't alone in his breakthrough. Three years earlier, French chemist Guy Bertrand had managed to create an oily substance that exhibited carbene-like reactivity through a slightly different approach. Whether he had managed to isolate a "true" carbene, however, was still under dispute. Nevertheless, both Bertrand and Arduengo shook the organic chemistry community to the core and spawned a renaissance in carbene chemistry.

Twenty years later, numerous labs around the world have joined Bertrand and Arduengo in synthesizing almost a thousand stable carbenes with a staggering diversity in structures. In a recent issue of *Science*, Bertrand reported the synthesis of a novel type of carbene that was stable at room temperature as both a solid and in solution. "The role of scientists is to challenge the rules which have been established by their predecessors," Bertrand says. "There are still many families of reactive intermediates, the isolation of which have been impeded by the belief that they are inherently unstable." But even when in the late 1980s he was hell-bent on proving that carbenes could be stabilized enough to be isolated, he never imagined they would find so many useful applications within just a few years.

Carbenes have since been identified as some of the most powerful organic catalysts. Earlier this year, scientists led by Yugen Zhang at the Institute of Bioengineering and Nanotechnology in Singapore reported the use of N-heterocyclic carbenes to catalyze the transformation of carbon dioxide into methanol. This reaction—highly desirable as it could convert a prevalent greenhouse gas into fuel—is extremely challenging in part because carbon dioxide is so thermodynamically stable and resistant to chemical reactions. This stability is no match for NHCs, however. They form transient bonds with the carbon in CO2, making it more willing to bond with hydrogen ions, eventually resulting in the production of methanol.

The catalyst's stability allowed the reaction to take place under ambient conditions while using air as the source for CO2. It is cheap, renewable, and has low toxicity—a catalytic dream by the standards of environmentally friendly chemistry.

Dumas' methylene may forever remain too unstable for isolation, but this new generation of stable, "bottleable" carbenes has and will continue to push the boundaries of chemical stability further, realizing the vision of more than a century's worth of chemists.