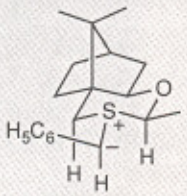
Aniline found to be best solvent for extracting metallofullerenes

Japanese chemists have reported what they call a breakthrough in the extraction of C_{60}-based endohedral metallofullerenes. Many compounds of the type $M@C_{60}$—where M is a metal atom inside the fullerene cage—have been prepared. But they could not be isolated because of the difficulty of extracting these "filled buckyballs" from the sooty mixture that is produced during their synthesis using electric arcs or laser vaporization. Pyridine was previously shown to extract $Ca@C_{60}$, but no one has reported a general solvent for extracting metallofullerenes—until now. Yoshihiro Kubozono, a research associate in Okayama University's chemistry department, and his coworkers tried to extract $Ca@C_{60}$ with 48 solvents, and besides pyridine, had success with only one: aniline. They then showed that aniline could be used to extract seven other $M@C_{60}$ molecules, where M is yttrium, barium, lanthanum, cerium, praseodymium, neodymium, or gadolinium [*J. Am. Chem. Soc.*, **118,** 6998 (1996)]. Mass spectrometry was used to demonstrate the presence of these molecules in the extracts. "Aniline is a better extraction solvent than pyridine," Kubozono tells C&EN. Using aniline as eluent, his group also has isolated $Ca@C_{60}$ using HPLC.

Sulfur ylide yields chiral epoxides from aldehydes

A new method for transforming aldehydes into chiral epoxides gives the highest enantioselectivity yet reported, according to researchers in England. Varinder K. Aggarwal, professor of chemistry at the University of Sheffield, and coworkers employ catalytic quantities of an easily accessible chiral sulfide that reacts with phenyldiazomethane to form a sulfur ylide in the presence of copper acetylacetonate. The ylide attacks the aldehyde, yielding the desired epoxide and splitting out the original sulfide, which then reenters the catalytic cycle [*J. Am. Chem. Soc.*, **118,** 7004 (1996)]. For example, from benzaldehyde the researchers obtained a 73% yield of *trans*-stilbene with 93% enantioselectivity using the ylide (above). The method can be used for both aliphatic and aromatic aldehydes, and the neutral reaction conditions are suitable even for base-sensitive compounds.



Antibody perturbs structure, properties of metal complex

Researchers have found that an antibody can compress a copper complex and thereby cause an immunochromic effect, a change in the complex's spectral and chemical properties. The work was reported last week by Ehud Keinan and coworkers in the department of molecular biology at Scripps Research Institute, La Jolla, Calif., and the department of chemistry at Technion-Israel Institute of Technology, Haifa [*Nature,* **382,** 339 (1996)]. The findings help confirm the feasibility of the controversial "entatic state" hypothesis of enzyme action developed in the late 1960s by Bert L. Vallee of Harvard University Medical School and R. J. P. Williams of the University of Oxford, England. According to the hypothesis, a metalloenzyme's protein moiety imposes steric constraints on the enzyme's metal-containing active site. These constraints change the complex's chemical properties and increase the enzyme's catalytic activity. It has been difficult to model this behavior to prove or disprove the hypothesis. Keinan says the study by his group—in which antibody binding perturbs the structure and UV-visible spectrum of a copper complex—provides strong evidence in support of the entatic state hypothesis. "These results lead us closer to a long-desired goal of achieving antibody catalysis of nonnatural transformations, in particular of organometallic reactions," says Keinan.

Mild hydrothermal synthesis of complex fluorides devised

Syntheses of complex fluorides—which exhibit piezoelectric characteristics, photoluminescence, and other interesting properties—have traditionally relied on solid-state reactions at high temperatures. Chemists in China now have prepared two complex fluorides using mild hydrothermal conditions [*Chem. Commun.*, **1996,** 1641]. The group at Jilin University and Changchun Institute of Applied Chemistry prepared crystalline $KMgF_3$ by mixing KF and MgF_2 with deionized water, adding hydrofluoric acid, and heating at 120 to 240 °C under pressure for several days. $LiBaF_3$ was synthesized in the same way from either a reaction mixture of LiF, BaF_2, and water, or from LiOH and $Ba(OH)_2$ solutions to which NH_4HF_2 was added. The crystalline fluorides were characterized by X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, and IR spectroscopy. Results show that the fluorides crystallize in cubic systems with perovskite structures. The group, led by Shouhua Feng, professor of chemistry at Jilin University, states that "the hydrothermal synthesis route to complex fluorides appears advantageous in terms of lower synthesis temperature, high purity, and crystallinity with no evidence of insertion of oxygen."

Biotechnology patent could lead to polyester harvests

Scientists at Massachusetts Institute of Technology have received a U.S. patent (5,534,432) that could lead to harvesting polyesters from plants. The patent covers insertion of genes for polyhydroxybutyrate polymerase into bacteria and crop plants. It is the sixth in a series of biotechnological patents for making biodegradable polyester resins to be obtained by biology professor Oliver P. Peoples and former MIT research fellow Anthony J. Sinskey. Sinskey is now vice president for research and development at Metabolix in Cambridge, Mass., which has licensed the patents. The patents cover insertion of thiolase genes that mediate condensation of acetate to acetoacetate, and reductase genes for conversion of acetoacetate to β-hydroxybutyrate, as well as the polymerase genes. Harvesting polyhydroxybutyrate from transgenic corn could lower production costs of the polyester, according to Metabolix. The transgenic bacteria and plants also can copolyesterify β-hydroxybutyrate with β-hydroxyalkanoates up to C_{12}. Monsanto currently produces the Biopol brand of β-hydroxybutyrate/valerate copolyester by fermentation of *Alcaliginese eutrophus*, a process originally invented by ICI.