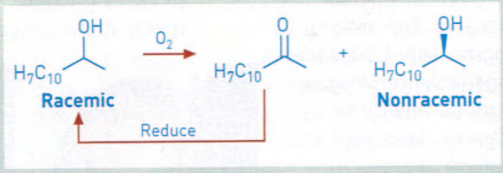
CONCENTRATES

Enantioselective oxidations of secondary alcohols with oxygen

Two research groups have developed methods for catalytic, enantioselective oxidations of secondary alcohols using molecular oxygen as the terminal oxidant. These methods can be used to resolve racemic mixtures of secondary alcohols and to break the symmetry of meso-diols. Assistant chemistry professors Brian M. Stoltz at Caltech and Matthew S. Sigman at the University of Utah and their coworkers have accomplished the feat independently and at about the same time [*J. Am. Chem. Soc.*, **123**, 7475 and 7725 (2001); manuscripts were received a week apart]. Both groups use palladium(II) catalytic systems with the chiral diamine (–)-sparteine as a ligand. After two cycles, a preparative-scale oxidative resolution of racemic α-methyl-2-naphthalenemethanol (shown) by the Caltech group resulted in 68% yield of the optically enriched product in 99% enantiomeric excess. Both groups demonstrate desymmetrization of meso-diols in comparable yields but slightly lower enantiomeric excesses.



Monolayer photoreactivity revisited

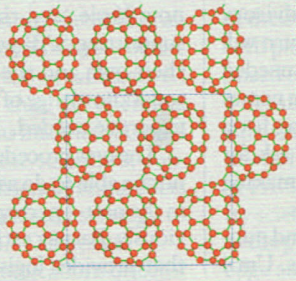
Photodegradation of self-assembled monolayers (SAMs) has potential applications in photolithography. A new study shows that photodegradation of alkylsiloxane SAMs on silicon oxide involves UV-generated, short-lived oxygen-containing radicals [*Langmuir*, **17**, 4497 (2001)]. These findings, by assistant chemistry professor Eric Borguet and coworkers at the University of Pittsburgh, are in marked contrast to those regarding alkanethiol SAMs (C&EN, March 30, 1998, page 31). Other researchers have shown that such SAMs on a metal surface are degraded by ozone. Degradation begins at defect sites, which permit ozone to enter deep into the monolayer, allowing attack from the base. The involvement of ozone, which could diffuse, was thought to be a problem in using such SAMs for photolithography. Now, the Pittsburgh chemists show that with alkylsiloxane SAMs on silicon dioxide, degradation begins at the tips of the alkyl chains and progresses in a top-down fashion. The noninvolvement of ozone suggests that higher resolution patterns may be achievable with alkylsiloxane SAMs than with alkanethiol SAMs, Borguet tells C&EN.

Array probes yeast protein interactions

Scientists have developed a yeast "proteome chip" containing 5,800 yeast proteins that can be used to probe protein interactions [*Science*, published July 26, *Science Express*, http://www.sciencemag.org/feature/express/expresstwise.shl]. The team was led by Michael Snyder, a professor in the departments of molecular, cellular, and developmental biology and of molecular biophysics and biochemistry at Yale University. The proteins are attached to a nickel-coated glass slide through a tag at their amino termini. Protein-protein interactions were probed using biotinylated calmodulin, a calcium-binding protein involved in many cellular processes. Dye-labeled streptavidin was used to identify the proteins that bound calmodulin. The assay found 33 previously unknown potential calmodulin-binding partners. The microarray can also be used to monitor protein-lipid interactions. Six liposomes were used to identify 150 protein targets, including 52 uncharacterized proteins. The authors suggest that it is possible to prepare arrays with as many as 100,000 proteins.

C_{70} polymerized

Although polymeric forms of C_{60} are well known, numerous attempts to polymerize the elongated fullerene C_{70} have yielded only dimers. Now, an international team has succeeded in coaxing C_{70} to form zigzagging polymeric chains [*Science*, **293**, 680 (2001)]. Physicist Alexander V. Soldatov of Harvard University and his colleagues subjected hexagonally packed C_{70} single crystals to 300 °C and 2 gigapascals of pressure (almost 20,000 atm). X-ray diffraction and spectroscopic studies of the polymeric product indicate that the C_{70} cages "are linked via four-membered rings in a 2 + 2 cycloaddition between double bonds close to polar pentagons of the C_{70} cages," according to the paper. This synthesis works, Soldatov tells C&EN, because "the hexagonal packing has the symmetry required to form zigzag chains, and the orientation of the C_{70} molecules also facilitates polymerization." He points out that the C_{70} polymer is the first fullerene polymer whose structure has been resolved at the atomic level.



ADAPTED FROM *SCIENCE*

Knocking out enzyme lowers pain sensitivity

Although smoking mari-juana can help treat the pain, nausea, and appetite loss experienced by some cancer and AIDS patients, its use is controversial. New studies in mice hint at an alternative way to achieve some of marijuana's useful effects. Benjamin F. Cravatt, assistant professor in the Skaggs Institute for Chemical Biology at Scripps Research Institute, and colleagues find that mice lacking the gene to produce a specific catabolic enzyme—fatty acid amide hydrolase (FAAH)—show many of the same physiological effects, including reduced sensitivity to pain, as animals treated with Δ^9-tetrahydrocannabinol (THC), the active ingredient in marijuana [*Proc. Natl. Acad. Sci. USA*, **98**, 9371 (2001)]. The enzyme degrades anandamide, a brain lipid long suspected to be the endogenous ligand for the brain receptors that are activated by THC. Anandamide has a half-life of only minutes in normal mice, which has made its functions difficult to study. But by eliminating FAAH, the researchers increase the levels of anandamide 15-fold and reduce the animals' sensitivity to pain. That makes FAAH an attractive drug target for pain treatment, they suggest.