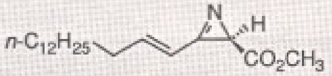
SCIENCE/TECHNOLOGY CONCENTRATES

Cytotoxic compound with highly strained ring system synthesized

Enantioselective synthesis of (*R*)-(–)-dysidazirine (shown below), an antibiotic containing the highly strained 2*H*-azirine system, has been carried out by chemists at Drexel University, Philadelphia [*J. Am. Chem. Soc.*, **117**, 3651 (1995)]. A natural product of the marine sponge *Dysidea fragilis*, dysidazirine is cytotoxic and inhibits the growth of yeast and gram-negative bacteria.



The work was carried out by organic chemistry professor Franklin A. Davis, postdoctoral associate G. Venkat Reddy, and graduate student Hu Liu. They prepared dysidazirine from a *cis-N*-sulfinylaziridine-2-carboxylic acid. When (2*R*,3*R*)-(–)-*N*-(*p*-toluenesulfinyl)-2-carbomethoxy-3-(1-pentadecenyl)aziridine is treated with lithium diisopropylamide followed by iodomethane, a 42% yield of (*R*)-(–)-dysidazirine is obtained after isolation by flash chromatography. The aziridine precursor is formed by treatment of (*R*)-(–)-*N*-(*E*-2-hexadecenylidene)-*p*-toluenesulfinimine with the lithium enolate of methyl bromoacetate via a Darzens-type reaction. According to Davis, methods developed for synthesis of 2*H*-azirines are not readily adaptable to their asymmetric syntheses. "This new protocol opens the rich chemistry of this class of compounds to asymmetric transformations," he says.

Organic syntheses via nitrogen fixation rendered catalytic

Medicinal chemists at Hokkaido University, Sapporo, Japan, have developed a catalytic method to make a variety of heterocyclic compounds by fixation of molecular nitrogen [*J. Org. Chem.*, **60**, 1480 (1995)]. Their results extend the use of nitrogen gas at 1 atm as an inexpensive reagent in organic synthesis. Chemistry professor Miwako Mori and graduate student Masanori Hori used titanium tetrachloride to catalyze the reaction of nitrogen gas with lithium and trimethylsilyl chloride to form a mixture containing tris(trimethylsilyl)amine and a titanium trimethylsilylnitride. Those species react with diketones to yield substituted pyrroles and pyridines. For example, 1-phenylhexane-2,5-dione gives 2-benzyl-5-methylpyrrole, and 2-(3-oxobutyl)-2-cyclohexen-3-ol-1-one reacts to form a partially reduced 2-methyl-4-quinolone.

Low-pressure aerogels open up commercial applications

Aerogels—superlight organic and inorganic materials normally produced under extremely harsh conditions—can now be made at ambient pressures [*Nature*, **374**, 439 (1995)]. With air composing up to 99.9% of their volume, aerogels are the most porous solids known. An aerogel starts out as a wet gel in which a liquid supports a network of long-chain molecules. To produce the aerogel, the fluid is removed to leave a dried molecular mesh. However, supercritical temperatures and pressures normally are needed during this process to avoid capillary forces that would irreversibly collapse the gel. The expense and danger of such processing conditions have made commercial development of aerogels impractical. Now, C. Jeffrey Brinker and coworkers at the University of New Mexico and Sandia National Laboratories, Albuquerque, report that, if the hydroxylated surfaces of inorganic gels are derivatized with organosilanes, the inorganic network of the gel doesn't cross-link as the material collapses. Thus, the walls of the pores don't "stick" to each other, which allows the gel to "spring back" to its original porous state when drying is complete. The aerogels produced by the New Mexico scientists have porosities of up to 98.5%, more than adequate for pursuing commercial applications such as dielectric materials or catalyst supports.

Catalytic antibody used to synthesize natural product

A catalytic antibody has been used for the first time in the total synthesis of a natural product. Subhash C. Sinha and Ehud Keinan of the department of chemistry at Technion-Israel Institute of Technology, Haifa, used an antibody that speeds the hydrolysis of a variety of organic substrates to catalyze an enantioselective reaction in a synthetic pathway to the natural product (–)-α-multistriatin [*J. Am. Chem. Soc.*, **117**, 3653 (1995)]. (–)-α-Multistriatin (shown at right) is an essential component of the aggregation pheromone of the European elm bark beetle, an insect responsible for severe damage to elm trees.

Most previous syntheses of (–)-α-multistriatin have used enantiomerically pure natural products to supply the compound's four asymmetric centers. But in the synthesis developed by Sinha and Keinan, all four asymmetric centers originate from an antibody-catalyzed reaction in which a nonchiral enol ether starting material is converted to an enantiomerically pure ketone. According to the researchers, "The key point . . . is not simply that one can make α-multistriatin, or even that this is now the best way to synthesize the compound, but rather that catalytic antibodies perform competitively in the important testing ground of natural product synthesis."

Soil conditions affect escape of methyl bromide from fields

Factors such as soil pH and moisture affect how much methyl bromide escapes to the atmosphere after agricultural fields are treated with the fumigant, according to a report in *Science* [**267**, 1979 (1995)]. Those findings indicate conditions could be manipulated to minimize emissions of the ozone-depleting compound, according to Ralph J. Cicerone and coworkers at the department of earth system science at the University of California, Irvine, and at the National Institute of Agro-Environmental Science in Tsukuba, Japan. Production of methyl bromide will be banned in the U.S. on Jan. 1, 2001, and a worldwide phaseout is being debated by countries party to the Montreal Protocol on Substances That Deplete the Ozone Layer. In field experiments, the researchers measured the flux of methyl bromide into the atmosphere, the amount of the gas in the soil at varying depths, and the bromide content of the soil before and after fumigation. They find that less of the fumigant escapes to the atmosphere with higher soil pH, greater moisture content and organic matter in the soil, and greater injection depth.