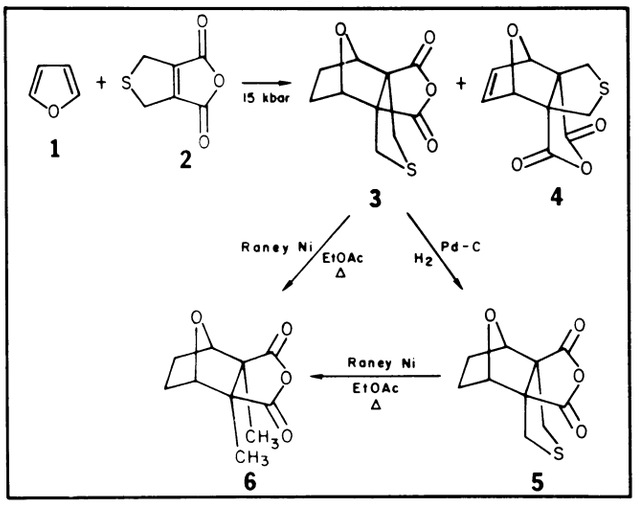
CHEMISTRY

Cantharidin: Success under pressure

Berkeley, Calif., chemists have designed a two-step synthesis of a relatively simple but elusive molecule, cantharidin, whose claims to fame include its effectiveness as a wart remover and ineffectiveness as an aphrodisiac.

Despite its relatively simple structure and lack of enantiomeric (mirror image) forms, cantharidin — the active ingredient in the apocryphal aphrodisiac Spanish fly — has long eluded the organic chemist's grasp. In fact, what looks like the obvious approach to its synthesis — a Diels-Alder type of reaction — was tried unsuccessfully as early as the 1920s.



A Diels-Alder reaction is an addition reaction that occurs when a conjugated diene — a molecule, such as furan (which is labeled "1" in the diagram), with double bonds that alternate with single bonds — reacts with a dienophile ("diene lover"). William G. Dauben and colleagues of the University of California investigated several reasons for chemists' long-standing failure to achieve synthesis of cantharidin with the Diels-Alder reaction. One reason, they hypothesized, was the inadvertent use of a dienophile that would lose its reactivity during the reaction due to steric strain — the crowding together of non-bonded atoms. So the Berkeley group chose a dienophile (2) that would overcome the steric problem. In addition, Dauben and co-workers, who report their synthetic cantharidin victory in the Oct. 22 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, ran the reaction with extremely high pressures — 15,000 atm in the initial experiments. The Berkeley bunch is one of a half dozen or so groups worldwide investigating the use of high pressure as an organic synthesis tool. The synthesis of cantharidin (6), a naturally occurring molecule in a European beetle, represents one of the first successes crafted by that tool.

Surrogate oxygen for cancer therapy

Two new drugs that seem to mimic the effect of oxygen may improve radiation therapy for cancer patients. Radiation therapists know that tumor cells containing little or no oxygen are about three times less susceptible to X-ray death than are oxygen-containing tumor cells. The new drugs, currently under evaluation in laboratory animals, simulate the effect of oxygen in tumor cells (which are usually oxygen-deficient), increasing the likelihood of killing those cancerous cells by X-ray exposure. The chemicals, developed by J. Martin Brown of Stanford University Medical Center and colleagues, are analogs of (but less toxic than) two well-known radiosensitizers—misonidazole and metronidazole.

EARTH SCIENCES

Algerian quake

The Oct. 10 magnitude 7.3 earthquake that destroyed as much as 80 percent of the city of Al Asnam, Algeria, may be the deadliest quake since a 1978 Iran quake killed 15,000, according to the U.S. Geological Survey. While the actual toll may never be known, revised estimates from rescue officials range as high as 10,000. The long-term average for earthquake deaths is about 10,000 per year, according to the Survey, although fewer than 300 persons were killed in 1980 prior to the Algerian quake. Such statistics are skewed, however, by incidents such as the July 27, 1976, Tangshan, China, quake that killed between 250,000 and 600,000 (SN: 9/1/79, p. 150) and the Feb. 4, 1976, Guatemala quake that claimed 23,000 lives.

Geologists believe that the Algerian quake was caused by the relentless march of the African plate toward the Eurasian plate. Al Asnam lies on the boundary of those two plates, where stress builds within the earth's crust as the African plate is forced beneath the Eurasian plate.

Staying out of the ozone

If you're on a Northwest Airlines flight next spring, your route may be determined by a satellite that measures ozone in the stratosphere. When Arlin Krueger of NASA's Goddard Space Flight Center in Greenbelt, Md., saw how much detail there is in the data from the ozone mapping instrument aboard the polar orbiting Nimbus 7 satellite, he began to wonder who could use such information. His first takers are the airlines, who hope to use the satellite information to avoid regions of high ozone and to accurately track the strong, west-to-east jet stream.

The Nimbus 7 instrument looks vertically through the atmosphere and tallies the total ozone at any given spot. In places of low pressure, the ozone-containing stratosphere drops closer to the ground, while in regions of high pressure, the stratosphere is pushed higher. Like water running off a mountain and into a valley, ozone collects in the low-pressure, low-stratosphere regions and is found in lower concentrations in the high-pressure, high-stratosphere areas. This varying thickness of the ozone layer is detected by the instrument. In addition, it is these regions of high and low pressure that set up the flow of the jet stream and determine its location acrosss the continental United States. The fingerprint of the jet stream, therefore, is clearly evident between the regions of high and low ozone, explains co-worker Melvyn Shapiro of the National Center for Atmospheric Research in Boulder, Colo.

Such data are important to commercial airlines for two reasons: Effective next February, ozone levels within an airplane will not be allowed to exceed 0.3 parts per million, according to Krueger. (Usually encountered in high-altitude transcontinental or transoceanic flights, ozone in airplanes has been linked with respiratory and skin problems.) While air filters may be used to remove ozone from aircraft cabins, the Nimbus 7 data might also help planes to avoid pockets of high ozone. Secondly, more precise location of the jet stream would allow more accurate routing that could lead to fuel savings for east-bound flights and to head-wind reduction for west-bound flights. A recent study by Robert Steinberg of NASA's Lewis Research Center in Cleveland, Ohio, concluded that accurate pinpointing and use of the jet stream could lead to an overall fuel savings of 3 to 5 percent.

In order to test these possibilities, NASA plans a study in cooperation with Northwest Airlines and the Federal Aviation Administration. Next spring, which is the season of peak ozone, Northwest Airlines will begin using 6-hour-old ozone mapping data in their route planning, and planes will carry ozone monitoring equipment to check how well the satellite-guided routes avoid ozone pockets.