Meetings

Chemistry: Pure and Applied

While major emphasis was placed on organic chemistry, considerable attention was devoted to certain aspects of inorganic, analytical, and applied chemistry at the 19th International Congress of Pure and Applied Chemistry held in London, 10–17 July 1963. This congress was held immediately after the 22nd Conference of the International Union of Pure and Applied Chemistry (4–9 July) and included over 800 contributed papers and 19 invited lectures.

In his opening address, Lord Todd, the president of the Congress, expressed the view that the recent spectacular advances which seemingly threaten the ecological balance of nature are in reality but another manifestation of the fact, already demonstrated by the development of the atomic sciences, that scientific progress inevitably entails some element of risk. With apparent control of environmental factors within reach and with genetic control of the entire race a distinct possibility, it becomes critically necessary for the chemist to maintain closer liaison with the biologist. Lord Todd further emphasized the vital importance for the governments of the world to have at their disposal politically unbiased, sound advice on scientific matters. In his opinion, advice is possible only through the instruments of the non-political scientific international unions operating within the framework of the International Congress of Scientific Unions. Other international organizations operating under the aegis of the United Nations are essentially political in their orientation, and hence, for the most part, are not suited for providing such unbiased advice. In my opinion, American scientists must take an increasingly active part in such deliberations rather than use the congresses attendant upon general assemblies of the unions as sounding boards for personal scientific contributions.

The general topic of reactive, short-lived intermediates in organic reactions was extensively discussed and was keynoted in one of the opening lectures, by George Wittig (Heidelberg). He reviewed critically the question of the existence and participation of "cycloynes" (small rings containing carbon-carbon triple bonds) as chemical intermediates. By means of ingenious "trapping" experiments in a number of laboratories, a good circumstantial case can be built up for the existence (short-lived) of such compounds, particularly for benzyne, but in the opinion of Wittig, direct proof for their existence is still lacking.

The broad subject of mechanisms in organic reactions formed the basis for the largest single group of presentations. O. A. Reutov (Moscow) summarized (largely for the first time in English) his investigations on rearrangements of the skeletons and hydride transfers encountered with free alkyl radicals and cations in solutions. By use of isotopic labels, a viewpoint has been developed that both types of reactions occur through a single, probably cyclic, transition state. With free radicals the predominant shift involves a 1,3 migration of a skeletal carbon. With cations such migration is frequently accompanied by hydride shifts; a marked isotope effect was noted with deuterium- and tritium-labelled compounds, possibly caused by disruption of the symmetry of the transition state by the presence of the isotopes.

In view of the current interest in inhibition by physical quenchers (for example, naphthalene) and by chemical retarders (mercaptans and disulfides) of nonchain reactions induced by photochemical agents and radiation, S. J. Cohen *et al.* (Brandeis University) discussed the mechanism of action of such retarders on model systems. Naphthalene removes excitation energy from initially formed, short-lived radicals, whereas the sulfur compounds function by conversion of the radicals to their precursors and are not consumed but rather regenerated.

The rapidly developing area of organometallic compounds provided a basis for joint sessions dealing with strictly organometallics and inorganic polymers. Of considerable interest was the preparation and proton NMR (nuclear magnetic resonance) studies of a series of six-membered cycles carrying C_2-functional silicon groups (methyl substituted) and two additional hetero atoms (O, NH, NR, S). Parent compounds were 2-silacyclohexanes, 2,5-disilacyclohexanes and 2,6-disilacyclohexanes (W. Simmler, Farbenfabriken Bayer AG, Leverkusen). From the data presented, definite conclusions as to the variation of the strength of the C-Si bond with different hetero atoms can be drawn.

A novel group of tetrameric alazynes $(C_6H_5AlNAr)_4$ has been prepared by heating the adducts of triphenylaluminum and aniline and certain of their derivatives in boiling benzene or toluene (J. I. Jones and W. S. McDonald, National Chemical Laboratory, Teddington, England). Single crystal x-ray analysis provides strong evidence for a structure for $(C_6H_5AlNC_6H_5)_4$ analogous to that proposed for octaphenylcubane [Freedman and Petersen, *J. Am. Chem. Soc.* **84**, 2837 (1962)]. Thus the skeleton is a cube with alternating aluminum and nitrogen atoms at the corners with each carrying a phenyl substituent.

Developments in organic synthesis provided the basis for another large group of papers highlighted by two plenary lectures by A. Eschenmoser (E. T. H., Zurich) and F. Sondheimer (Weizmann Institute of Science, Rehovoth). Using synthetic approaches to the synthesis of the metal-free heterocyclic peripheral systems of vitamin B_{12} (corrins), Eschenmoser resurrected the long neglected imino ethers of Pinner and developed their syntheses as applied to derivatives of pyrrole. By taking advantage of their enhanced reactivity, particularly towards carbonyl displacements, he has substantially succeeded in constructing the corrin skeleton of the vitamin.

Sondheimer supplemented his description of the synthesis of macrocyclic hydrocarbons with alternating single and double bonds (annulenes) and those containing one or more additional triple bonds (dehydroannulenes) with a study of the aromatic properties as defined by Hückel's rule [$(4n+2)$ π-electrons]. If aromatic, an annulene or a dehydroannulene should sustain an induced ring current of π-electrons, a property measurable by NMR. In agreement with theory, those substances expected to be aromatic (for example, monodehydro-[14]-annulene, [18]-annulene, tridehydro-[18]-annulene) showed NMR spectra, thus indicating the existence of a ring current. Those expected to be non-aromatic (for example, [14]-annulene, [24]-annulene, tetradehydro-[24]-annulene) indicated no ring current. It is interesting that the aromatic annulenes and dehydroannulenes did not show benzene-like chemical behavior or stability.

In the area of inorganic chemistry, major attention was focused on high temperature chemistry of inorganic salt systems and on inorganic polymers. Progress in the first area was summarized by H. Bloom (University of Tasmania, Australia). Interest in such systems has received much impetus recently from the use of molten salts in the extraction of minerals, and their potential use in the development of atomic energy, rocket propulsion, and fuel cells. Apart from the industrial value of molten salt systems, they are of great theoretical interest since they are the only class liquids in which the structural units are ions.

In the analytical chemistry sessions major emphasis was placed on neutron activation analysis, a technique particularly adapted to determination of trace impurities. Analysis of the germanium, arsenic, antimony, copper, chromium, molybdenum, silver, indium, zinc, and palladium content of 67 iron meteorites was reported by A. A. Smalos and D. Mapper (Atomic Energy Research Establishment, Harwell, England). Statistical analyses indicated significant correlations for a number of the elements. Important similarities have also emerged, particularly among the hexahydrite group.

Actions taken by the Council of IUPAC at the conference included the adoption of revised statutes for the Union. It is hoped this action will permit broader participation by the member nations. Viet Nam and South Korea were admitted to the Union. Lord Todd (Great Britain) was elected president for 1963–1965, succeeding W. Albert Noyes (United States); W. Klemm (Germany) was elected to the new office of president-elect; and John C. Bailar, Jr. (United States) succeeded Sir Charles Dodds as honorary treasurer. The complete plenary lectures will be published by Butterworth, probably in November.

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Health Physics

Health physics, as a specialized profession concerned with the prevention and control of hazards from ionizing radiation and radioactive materials, is now in its third decade. The wide range of its concerns was apparent at the 1963 annual meeting of the Health Physics Society held on 10–13 June at New York City. Included were sessions on studies of the Hiroshima and Nagasaki survivors, radiation biology, radiation physics, dosimetry, and fallout. Also included, but perhaps mostly of specialized interest to the profession were sessions on air monitoring, bioassay, instrumentation, nuclear safety, personnel monitoring, waste disposal, and standards.

Shields Warren, who introduced the first session of invited papers on dosimetry and medical effects of the nuclear bombings of Hiroshima and Nagasaki, observed that the studies are a reversal of the health physicists' usual role in that they are a study of a planned maximum exposure. Stuart Finch (Yale), a former member of the Atomic Bomb Casualty Commission, summarized its medical findings to date. These include an increase of one case per million persons per rad in the leukemia rate which seems linear with dose down to the general Japanese population background rate; an increase in lenticular opacities, an alteration of 1 percent in the sex-ratio of the F_1 generation, and some evidence of micro-encephaly in the offspring of mothers who were in the first trimester at the time of exposure. Little evidence of accelerated aging, loss of visual acuity, and increase in non-neoplastic disease, or malformed offspring had been found. Emphasis is currently shifting to a study of the borderline evidence for an increased cancer incidence and for some retardation in the natural ossification processes in the F_1 generation.

Most of the dosimetry of the Hiroshima and Nagasaki exposures has been by retrospective estimation. J. Auxier (Oak Ridge National Laboratory) reviewed the current efforts of Project Ichiban to improve the precision of these dose estimates. Data from 1962 Nevada experiments (employing the bare Health Physics Research Reactor) should reduce the present uncertainty from ± 50 to ± 27 percent. C. S. White (Lovelace Foundation) presented information on blast and thermal radiation effects. An overpressure in the range of 50 to 55 pounds per square inch is an LD_{50} for man (that is, it kills 50 percent of those exposed). The pathological effects of overpressure are observed at the junction of tissues of different densities. White's data indicated that reflection may increase the overpressure in a foxhole or fallout shelter kind of enclosure and that the range of these "conventional" effects increases with yield faster than the nuclear dose.

In the radiation biology session, A. H. Sparrow (Brookhaven National Laboratory) presented data on the continued exposure of plants which showed a close correlation between nuclear volume and radiosensitivity. Many of the gymnosperms have an LD_{50} below 1000 rads. In 20 generations of mice, the males of which had been given one 200-r exposure 24 hours after birth, J. P. Spalding *et al.* (Los Alamos Scientific Laboratory) observed a decline in litter size but an increase in period of productivity and number of conceptions in the F_{10} generation. The mean survival time of the irradiated F_{22} generation was reduced under continued gamma exposure from 38.4 to 30.4 days. Most of this decrement could be eliminated by cross breeding with the control line.

The hypothesis of a simple equivalence between radiation damage and that due to aging was not supported in studies made by W. T. Ham *et al.* (Medical College of Virginia) on the eyes of rabbits exposed to x-rays. A 25 to 50 percent protective effect was demonstrated by mice which had been administered 10 μmoles of 2-aminoethylisothiouronium bromide-hydrobromide and 1 μmole of 5-hydroxytryptamine creatinine sulfate 5 to 10 minutes prior to 1200-r x-irradiation (J. L. Leitch, U.C.L.A.). β-aminoisohotyric acid, an end product of the normal break-down of the DNA in the cell nucleus, has been suggested as a sort of "built-in" dosimeter. H. Smith and J.