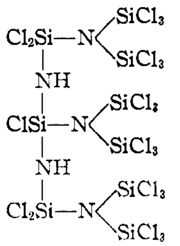
HCl, the following chain structure, corresponding with $Si_9N_5H_2Cl_3$, would result



The agreement here with the analytical results is substantially as good as that given by the first structure, and the molecular weight found is somewhat closer to the calculated value in this case.

The analysis of the solid polymeric residue left after heating the solid reaction products under reduced pressure, to sublime away any ammonium chloride, while not as conclusive as that presented for the silazanes, led to results approaching the requirements of the simple empirical formula, $(Cl—Si{\equiv}N)_x$. One such sample, for example, gave the following data:

Si: 36.5, 35.9; av. 36.3; g.-atoms, 1.1
Cl: 40.9, 40.5; av. 40.7; g.-atoms, 1.0
N: 18.6, 19.4; av. 19.0; g.-atoms, 1.2

Under the conditions of sublimation *in vacuo* any entrapped ammonium chloride would be expected to have been removed; nevertheless, X-ray film of samples thus treated invariably showed lines due to ammonium chloride, which is believed to have resulted from hydrolysis of the sample due to contact with moisture of the air. It is thought, therefore, that the solid is not merely a mixture of either $Si(NH)_2$ or $Si(NH_2)_2NH$, reported by Stock,[3] with ammonium chloride, but rather that it consists essentially of the polymerized chloronitride, $(ClSiN)_x$.

Further studies on the ammonolytic and hydrolytic characteristics of the halides and oxyhalides of silicon, which have been in progress for the past few years, will be presented shortly in a definitive paper.

[3] A. Stock and F. Zeidler, *Ber.*, **56**, 986 (1923).

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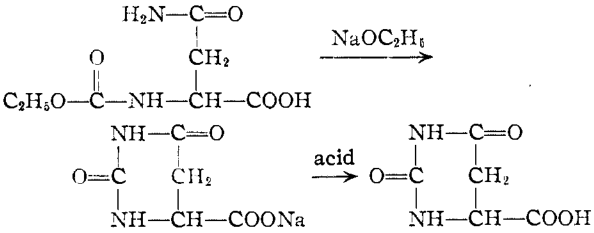
DIHYDROÖROTIC ACID

Sir:

Bachtez and Cavallini[1] have reported a synthesis of "dihydroörotic acid" by fusion of maleic acid and urea. Workers in this laboratory[2] have reported that "dihydroörotic acid" prepared by this method was not active in supporting growth of *Lactobacillus bulgaricus 09* which responds to either ureidosuccinic acid or orotic acid. Recently, Kornberg and co-workers[3] discovered an enzyme system which reversibly converts orotic acid to dihydroörotic acid but which would not utilize "dihydroörotic acid" prepared by the method of Bachtez and Cavallini.

While seeking an answer to this discrepancy, a new synthesis of dihydroörotic acid was devised. D- L- or DL-N$^\alpha$-carbethoxyasparagine was heated under reflux for four hours in an ethanol solution containing 2 molar equivalents of sodium ethoxide to give the corresponding D-, L- or DL-dihydroörotic acid in yields up to 70%. The use of sodium methoxide in methanol gave erratic results.



Heating of dihydroörotic acid with strong mineral acid converts it into 5-hydantoinacetic acid. This reaction apparently goes via ureidosuccinic acid since use of too much acid in the isolation of DL-dihydroörotic acid results in a product contaminated with DL-ureidosuccinic acid.

L-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-L-asparagine had the properties: decomposed at 266°; $[\alpha]^{25.3}D$ +33.23° (c 1.992)[4] in 1% $NaHCO_3$. *Anal.* Calcd. for $C_5H_6O_4N_2$: C, 37.98; H, 3.83; N, 17.72. Found: C, 38.18; H, 3.97; N, 17.69.[5]

D-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-D-asparagine had the properties: decomposed at 266°; $[\alpha]^{25.3}D$ −31.54° (c 2.01) in 1% $NaHCO_3$. *Anal.* Found: C, 37.69; H, 4.03; N, 17.71. A sample of this material was converted to the brucine salt which was recrystallized to constant decomposition point (268°) and constant optical rotation [$[\alpha]^{25}D$ −32.15° (c 1.039) in water]. The brucine salt was decomposed with acid and the dihydroörotic acid obtained freed from brucine by repeated recrystallization from water. Its properties were $[\alpha]^{26.5}D$ −34.29° (c 2.488) in 2.5% $NaHCO_3$ and decomposition at 267–268°.

DL-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-DL-asparagine decomposed at 259° and was optically inactive. *Anal.* Found: C, 38.23; H, 3.85; N, 17.67.

DL-Dihydroörotic acid prepared from N$^\alpha$-carbethoxy-DL-asparagine has been found to differ in melting point, infrared spectrum and solubility with material prepared by the method of Bachtez and Cavallini. An attempt to resolve the material prepared by the method of Bachtez and Cavallini into D and L isomers by recrystallization of its brucine salt was unsuccessful.

Microbiological tests carried out in these labora-

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[1] M. Bachtez and G. Cavallini, *Ber.*, **66B**, 681 (1933).

[2] D. S. Spicer, K. V. Liebert, L. D. Wright and J. W. Huff, *Proc. Soc. Exptl. Biol. Med.*, **79**, 587 (1952).

[3] J. Lieberman and A. Kornberg, *Federation Proc.*, **12**, 239 (1953).

[4] We are indebted to H. C. Zell for the optical measurements.

[5] We are indebted to Joyce Pyett, Arthur Fadenrecht and Kermit B. Streeter for the microanalyses.

tories with *Lactobacillus bulgaricus 09*[6] have shown that L-dihydroörotic acid and DL-dihydroörotic acid prepared by the new procedure will support growth and that the activity of these substances as well as of orotic acid and ureidosuccinic acid are reversibly inhibited by D-dihydroörotic acid.

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[6] L. D. Wright, C. A. Driscoll, C. S. Miller and H. R. Skeggs, *Proc. Soc. Exptl. Biol. Med.*, in pr

BOOK REVIEWS

Radiocarbon Dating. By Willard F. Libby, Professor of Chemistry, Institute of Nuclear Studies, University of Chicago. The University of Chicago Press, Chicago 37, Illinois. 1952. vii + 124 pp. 16 × 24 cm. Price, $3.50.

An undergraduate elective course gave this reviewer a side interest in geology and the seemingly unanswerable question: "How long has geology been a-making?" Five years later as a doctorate candidate in analytical chemistry he was exposed to a geochemical infection by contact with the late Alfred C. Lane, and helped to date several uranium-containing specimens. The uranium–thorium–lead method put reliable dates into the range of historical geology down to the most recent 100 million years; of this remaining recent void, the last 20,000 holds much of the interest, and now Professor Libby's group has made possible the radiocarbon dating of pre- and post-ice age materials. Hess' discovery of cosmic radiation in 1911 meant little to the nuclear chemist of those days, but the discovery of the neutron, its production by cosmic ray action in the atmosphere, and the reaction $N^{14} + n = H^1 + C^{14}$ all combined to give us radiocarbon dating, the C^{14} half-life of 5568 ± 30 years setting a practical limit of about 20,000 years, and with thanks to the long-gone plants which fixed the radioactive carbon dioxide and the animals which helped the plants to preserve it for use by Libby's testers.

In Chapter I the author presents the nuclear background, which is more complex than indicated above, and carefully cites and evaluates the many pertinent variables: the long-period constancy of cosmic radiation, the earth's radiocarbon inventory, its cycle of distribution and utilization, and the problem of reliable choice of reliable specimens. Chapter II continues the study, bringing up the question of the vertical and horizontal variations of neutron intensity, rate of exchange between atmospheric and fixed carbon dioxide (in ocean and land compounds), the mixing of the ocean reservoir, and the constancy of cosmic radiation during recent millennia. Chapter III deals with the method of arriving at the half-life value of carbon-14.

With the background theory and experiment covered, Chapter IV considers the preparation of the sample for measurement, with its problems of inorganic and organic combination, alteration of original substances by putrefaction, heat and possible exchange. Acceptable sample materials are charcoal, wood, grasses, peat, antlers and hairy materials, and shell. More or less thoughtfully planned and executed preparation is needed before any sample (in amount to yield 12 to 5 g. of final carbon) is ready for combustion to carbon dioxide, processing of the gas and reduction of the gas to carbon by hot magnesium. This carbon product requires further treatment to give the final carbon powder, which even yet contains some 10% of ash as magnesium oxide.

Chapter V describes the measurement of the radioactivity of the carbon, by an apparatus using a modified Geiger counter, and includes considerable discussion of apparatus and operational details which might have effects on the answers. For measurement the carbon powder is made into a mush which is spread thinly and evenly on the inside of the measuring cylinder; the water is dried out with pumping to the micron range, and an atmosphere of poorly adsorbed ethylene and argon is introduced. The cylinder is now ready for measurement. in an apparatus in which it is surrounded by a screen-wall of plain Geiger counters to reduce the activity background. The actual measuring run-time is 48 hours, with further time for background determinations.

Chapter VI lists materials measured and dates assigned for work done prior to late 1951, a total of 218 different samples. The specimens are from all parts of the globe, and represent relics of "literate" and illiterate recent and early man, of plant life related to pre- and post-glacial periods, of logs buried in the sands of time, and ancient vegetation gone to sodden peat in arctic and temperate climes. The ages found vary from a juvenile 712 ± 200 to the ancient "at least 21,000" years. The whole list is a wonderful help and factual spiritual lift to the time-counting archeologist, geologist and palynologist, as Frederick Johnson makes clear in Chapter VII. These last fifteen pages serve to interrelate the radiocarbon datings with previous chronology, showing how many perplexities are resolved, even though some remain and a few new ones are created. Just as uranium-lead ratios showed that thus measurable geologic time began some 2,000,000,000 years ago, that the Cambrian period went back 850,000,000 years and the youngest rocks with measurable ratios are maybe 100,000,000 years old, so now we know that Folsom man made arrow points 10,000 years past, the Mankato glacial period dates only 11,000 instead of 25,000 years back, it is 6500 years since Mt. Mazama blew its crown to dust to give us bottomless Crater Lake, and some nameless aborigines trapped fish 5700 years ago on Boylston Street, Boston.

It is only a little book but good things often come in small packages, and this one is good reading for all sorts of ordinary non-nuclear chemists.

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Chemistry and Methods of Enzymes. Third Edition. By James B. Sumner, Professor of Biochemistry, Cornell University, and G. Fred Somers, Chairman, Dept. of Agricultural Chemistry and Associate Director, Agricultural Experiment Station, University of Delaware. Academic Press, Inc., 125 East 23rd Street, New York 10, N. Y. 1953. xvi + 462 pp. 16.5 × 23.5 cm. Price, $7.50.

In this, the 3rd edition, out 5 years after the 2nd, the authors have added new and dropped old material keeping the size of the book fairly unchanged. Since Sumner crystallized the first enzyme, urease, in 1926, a large number of enzymes from animal and plant tissues, from bacteria and molds have been crystallized and all proved to be proteins. In fact, the authors turn the sentence around and state that probably most proteins are enzymes. Enzyme chemistry has become a part of protein chemistry, in which determination of specific activity provides a particularly sensitive method for determination of purity and native state of the protein. The methods of purification still depend largely on art, with few generally applicable rules. Throughout the book one finds observations and remarks testifying to the long laboratory experience of the authors. This gives the