plified by visualizing the mechanics of the structures involved. For example, where several coördinating groups are held together in a single molecule in such orientation that they can all simultaneously associate with a given metal atom (as in the second copper complex, above), it seems logical that the probability of complete dissociation of the complex is much less than where the coördinating groups are in separate molecules. Where all the groups are in a single molecule, it is necessary for all the coördinate linkages to be broken simultaneously. On the other hand, where the coördinate groups are in separate molecular units, the dissociation of each coördinate linkage can occur independently. This is the commonly accepted explanation for the great stability of polydentate complexes, *e. g.*, copper phthalocyanine.

However, this phenomenon of the increased stability of complexes involving multiple bonds may also play a role in the formation of the less stable complexes involving hydrogen bonding. For example, in the case of proteins, as pointed out by Pauling,[2] the combined effect of a large number of hydrogen bonds between two adjacent close-fitting large molecules may result in a relatively stable association.

Another example of the effect of multiple bonds occurs in connection with tanning phenomena. Russell and Tebbens[3] have shown that the simple esters of gallic acid do not tan leather, but that polyesters, for example mannitol hexagallate, which contain a multiplicity of gallate groups, have the property of combining with hide substance.

This improbability of dissociation of a complex held together through several points of attachment must be directly reflected in the entropy factor involved in the association-dissociation equilibrium. The further elucidation of this effect to the point where the stability of complexes can be predicted quantitatively presents one of the most important objectives yet to be realized in physical and colloid chemistry.

---

(2) Linus Pauling, *Chem. Eng. News*, **24**, 1375–1377 (1946).

(3) Albert Russell and W. G. Tebbens, Jr., THIS JOURNAL, **64**, 2274–2276 (1942).

CLEVELAND, OHIO R. K. ILER

RECEIVED DECEMBER 12, 1946

5(4)-AMINO-4(5)-IMIDAZOLECARBOXAMIDE, A PRECURSOR OF PURINES

Sir:

An *inhibition analysis* of the effect of purines on the toxicity of sulfanilamide for certain bacteria showed that *p*-aminobenzoic acid functions in the biosynthesis of purines.[1] If sulfanilamide prevents *p*-aminobenzoic acid from functioning as a coenzyme, or from being converted to a coenzyme, involved in the biosynthesis of purines, the precursor preceding this "blocked" enzyme system might be expected to accumulate in the medium during sulfanilamide inhibition when biosynthesis of purines is the limiting factor for growth.

Stetten and Fox[2] isolated an amine formed by bacteria during sulfonamide bacteriostasis and on the basis of chemical studies proposed that the amine was 2-hydroxy-5,6-diaminopyrazine.

The correlation of certain other data suggested to us that 5(4)-amino-4(5)-imidazolecarboxamide, isomeric with 2-hydroxy-5,6-diaminopyrazine, might be a precursor of purines. Since a precursor of purines would be expected to accumulate in the medium under the conditions employed by Stetten and Fox,[2] the amine of Stetten and Fox[2] was isolated by their method for comparison with synthetic 5(4)-amino-4(5)-imidazolecarboxamide and found to be identical with that compound.

Synthesis of 5(4)-amino-4(5)-imidazolecarboxamide was effected by the method of Windaus and Langenbeck[3] except that the free amine instead of the picrate was isolated by hydrogenation of 5(4)-nitro-4(5)-imidazolecarboxamide in absolute ethanol and that Adams platinum catalyst was employed instead of a palladium catalyst. Evaporation of the solvent and recrystallization from absolute ethanol–benzene gave colorless needle-like prisms, m. p. 169.8–171.4° with decomposition when dried at 100° over phosphorus pentoxide. The picrate was prepared by addition of a small amount of alcoholic picric acid to the reduction product. Recrystallization from absolute ethanol gave bright yellow needle-like prisms, m. p. 239.6° with decomposition.

The amine which accumulated during sulfonamide bacteriostasis of *Escherichia coli* was isolated by the procedure of Stetten and Fox[2] as the picrate, bright yellow needle-like prisms, m. p. 239.4° with decomposition, which was converted by their procedure to the free amine, colorless needle-like prisms, m. p. 168.8–170.2° with decomposition when dried at 100° over phosphorus pentoxide.

A mixture of the isolated and synthetic picrates melted at 239.4° with decomposition. The melting points of each picrate and the mixture were determined in Pyrex melting point tubes by inserting the tubes in a bath a few degrees below the decomposition point. Contact with soft glass and time of heating of the picrate affect the decomposition point. A mixture of the isolated amine and synthetic 5(4)-amino-4(5)-imidazolecarboxamide melted at 169.2–170.6° with decomposition.

The results indicate that 5(4)-amino-4(5)-imidazolecarboxamide functions as a precursor of purine bases or is formed from a precursor of purines by the organism and that *p*-aminobenzoic acid or a compound synthesized by the organism from *p*-aminobenzoic acid functions as acoenzym:

---

(1) Shive and Roberts, *J. Biol. Chem.*, **62**, 463 (1946).

(2) Stetten and Fox, *J. Biol. Chem.*, **161**, 333 (1945).

(3) Windaus and Langenbeck, *Ber.*, **56**, 683 (1923).

in converting such a precursor to purines. It appears therefore that this coenzyme functions in combining a single carbon unit into the pyrimidine ring.

THE CLAYTON BIOCHEMICAL INSTITUTE AND THE DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
AUSTIN, TEXAS

WILLIAM SHIVE
W. W. ACKERMANN
MALCOLM GORDON
M. E. GETZENDANER
ROBERT E. EAKIN

RECEIVED MARCH 5, 1947

PARTIAL HYDROLYSIS OF SILICON TETRACHLORIDE

Sir:

The existence of an homologous series of silicon oxychlorides of the general formula $Si_nO_{n-1}Cl_{2n+2}$ was established, and the first seven members isolated and identified in 1941 by Schumb and Holloway.[1] Single members, including the cyclic tetramer, $Si_4O_4Cl_8$, had also been prepared by others by various means,[2,3,4] but the method referred to[1] gave a complete series of homologs which were separable by distillation.

More recently it was mentioned in a review article[5] that the first two members of the series of oxychlorides had been prepared in this Laboratory by the partial hydrolysis of silicon tetrachloride in dilute, anhydrous diethyl ether solution by means of addition of moist ether, according to the equations

$$2SiCl_4 + H_2O = Si_2OCl_6 + 2HCl$$
$$3SiCl_4 + 2H_2O = Si_3O_2Cl_8 + 4HCl$$

Half a mole of silicon tetrachloride was dissolved in about 200 g. of anhydrous ether in a three-necked flask immersed in ice water. One quarter mole of water measured from a buret was separately dissolved in the minimum amount of anhydrous ether (about 350 g.). The wet ether was introduced by means of a separatory funnel, into the silicon tetrachloride solution at a rate of about two drops a second, with constant stirring.

There was no observable change within the flask during the reaction, but on standing overnight a very small deposit of a white solid, presumably silica, accumulated in the flask. The ether was evaporated off on a steam-bath, leaving about twenty milliliters of oily residue. This oil was fractionated at a pressure of fifteen mm. Two of the fractions were analyzed gravimetrically for chloride.

Fraction	Boiling point, °C.	%Cl Found	Calculated
II	50–53	76.69	76.76 for Si_2OCl_6
III	75.5–76.5	70.90	70.94 for $Si_3O_2Cl_8$

Better yields of higher boiling residue were obtained when the reaction was carried out at the temperature of solid carbon dioxide.

All attempts to carry out the partial hydrolysis of silicon tetrachloride in the vapor phase were unsuccessful.

The partial alcoholysis of $SiCl_4$ in ether solution with ethyl alcohol has also been accomplished in a similar manner, to give the following compounds.

Compound	Boiling point, °C.	%Cl Found	%Cl Calculated
$C_2H_5OSiCl_3$	102–104	58.83	59.28
$(C_2H_5O)_2SiCl_2$	137–138	37.59	37.52
$(C_2H_5O)_3SiCl$	156.5	17.53	17.86

Similar reactions with ammonia, dihydric alcohols, such as ethylene glycol, and hydrogen sulfide, in place of water, are to be attempted, as well as the partial hydrolysis, thiohydrolysis, ammonolysis, and alcoholysis of other non-metal halides, such as boron trichloride.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INST. OF TECH.
CAMBRIDGE, MASSACHUSETTS

W. C. SCHUMB
A. J. STEVENS

RECEIVED MARCH 1, 1947

---

(1) Schumb and Holloway, THIS JOURNAL, **63**, 2753 (1941).

(2) Friedel and Ladenberg, *Compt. rend.*, **66**, 539 (1868); *Ann.*, **147**, 355 (1868).

(3) Troost and Hautefeuille, *Bull. soc. chim.*, [2] **13**, 213 (1870); **16**, 243 (1871); **19**, 255 (1873) **35**, 360 (1881); *Ann. chim. phys.*, [5] **7**, 452 (1876).

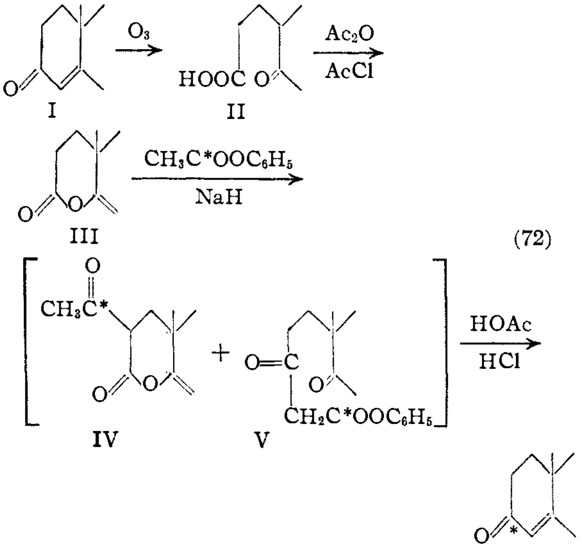
(4) Rheinboldt and Wisfeld, *Ann.*, **517**, 197 (1935).

(5) Schumb, *Chem. Rev.*, **31**, no. 3, 590 (1942).

RADIOACTIVE CHOLESTENONE[1]

Sir:

In connection with recent studies of the intermediary metabolism of the steroid hormones and the relation of these substances to various forms of cancer,[2] a method has been devised for the preparation of steroids containing isotopic carbon in ring A. Cholestenone was used as a model in the following series of reactions in which C^{14} was employed.



The yield of keto acid II obtained by ozonization of cholestenone (I) was considerably im-

---

(1) This work was supported by funds provided by the American Cancer Society on the recommendation of the Committee on Growth of the National Research Council.

(2) (a) Dobriner, *et al.*, *Science*, **99**, 494 (1944); (b) Heilman and Kendall, *Endocrinology*, **34**, 416 (1944).