(4) **Z.Ala-Z.Lys-Ala-Ala.OBz** (LDLLL).—The method of preparation of this compound is the same as that of Compounds 1 (a) and 2. The azide solution is prepared from Z.Ala-Z.Lys.$NHNH_2$ (LD, ref. 3, Cmpd. 15) and added to a solution of the tripeptide benzyl ester, prepared from a 50% molar excess of its hydroiodide (ref. 5, Cmpd. 2). A white gelatinous precipitate forms almost immediately. After standing overnight at room temperature, the material is collected and recrystallized from absolute ethanol. Yield of pure product is 62%; m.p. 213–214°.

Anal. Calcd. for $C_{41}H_{52}O_{10}N_6$ (788.9): N, 10.7. Found: N, 10.7.

Peptides (Compounds 5–8).—The peptides are isolated as hydrochlorides which are more or less hygroscopic (Cmpds. 6–8 as monohydrochlorides; Cmpd. 5 as dihydrochloride).

Hydrogenolysis of 0.005 mole of a carbobenzoxy peptide benzyl ester is carried out in 100 cc. of 85% acetic acid, containing 0.005 mole of *N* HCl (0.01 mole *N* HCl in the case of Cmpd. 1), with palladium black as catalyst in a rapid stream of hydrogen, as previously described.[3,4] Concentration of the filtrates *in vacuo* results in oils which crystallize upon dissolving in a small amount of absolute methanol and adding absolute ether. The compounds are recrystallized from a minimum amount of water by the addition of absolute alcohol followed by ether. The pure peptide hydrochlorides are obtained in 70–80% yield. For analysis and rotation measurements they are dried over P_2O_5 at 100° in high vacuum; the data are in Table I.

This work was aided by a contract between the Office of Naval Research, Department of the Navy, and Columbia University (NR 122-260).

DEPARTMENT OF BIOCHEMISTRY
COLLEGE OF PHYSICIANS AND SURGEONS
COLUMBIA UNIVERSITY
NEW YORK 32, N. Y.
RECEIVED DECEMBER 10, 1951

Chemistry of Technetium. II. Preparation of Technetium Metal[1]

BY J. W. COBBLE, C. M. NELSON, G. W. PARKER, W. T. SMITH, JR.,[2] AND G. E. BOYD

Recent large scale separations of technetium from fission product wastes at the Oak Ridge National Laboratory[3] have made chemical studies possible using readily weighable amounts.[4] The preparation of fractional gram quantities of pure metallic technetium was of interest since thus far only microgram amounts have been examined.[5,6] A tetraphenylarsonium perchlorate "process" precipitate containing coprecipitated pertechnetate was the starting material. This precipitate, which is quite stable toward common reagents, may be decomposed with difficulty by perchloric–sulfuric acid digestion. However, an electrolysis of its homogeneous solution in concentrated sulfuric acid afforded a convenient method.

About 0.2 g. of technetium together with 3–4 g. of tetraphenylarsonium perchlorate carrier in approximately one liter of sulfuric acid were electrolyzed for 24 hours with large platinum electrodes (C.D. = 10 ma./cm.^{2}, 2–3 volts). The black, technetium-containing solid which separated was filtered, dried, transferred to an all-glass distilling apparatus and then put into solution by gently warming with a mixture of five ml. each of concentrated nitric, perchloric and sulfuric acids. After the initially vigorous reaction subsided, the technetium was co-distilled with the perchloric acid and collected under dilute ammonium hydroxide. A variety of colors were noted in the acid distillate fractions, presumably owing to complexes similar to those postulated for manganese(VII)[7] and to those observed by us with rhenium(VII). The ammoniacal condensate was made slightly acid with HCl, bromine water was added and technetium sulfide (Tc_2S_7) precipitated with hydrogen sulfide. The coagulation of the slowly-forming, jet-black precipitate may be hastened by conducting operations on a water-bath at *ca.* 100°. The freshly precipitated sulfide dissolved readily in ammoniacal hydrogen peroxide and on evaporation to dryness NH_4TcO_4 and $(NH_4)_2SO_4$ were deposited. Technetium metal was prepared by hydrogen reduction of the latter mixture contained in a platinum boat. The initial reduction at low temperatures produced a black mass (TcO_2 ?) which prevented the loss of NH_4TcO_4 by sublimation. At the final higher temperature (500–600°) the $(NH_4)_2SO_4$ was volatilized leaving the technetium behind. Approximately 0.6 g. of spectrochemically pure metallic technetium has been isolated in the foregoing manner.

The metal, which shortly after reduction appeared as a silver-gray spongy mass, tarnished slowly in moist air. It did not dissolve in hot or cold, concentrated or dilute hydrochloric acid, nor was it attacked appreciably by alkaline hydrogen peroxide in agreement with Fried.[5] The metal did dissolve readily in nitric acid and aqua regia, and burned in oxygen to form Tc_2O_7.[4] Its atomic weight from previous chemical analyses on milligram quantities of the oxide was found to be 98.8 ± 0.1 which may be compared with the mass spectrometer value of 98.913.[8] Measurements on an X-ray diffraction pattern taken on the same preparation confirmed in detail the $\sin^2\theta$ and intensity values of Mooney.[9,10]

Whereas the specific activity of pure technetium is not large (*ca.* 20 μc./mg.) it may constitute a radiation hazard in some circumstances. Pure, dry compounds have been found to show about 10 "R"/hr./100 mg. at their surfaces owing to the low energy beta particles emitted (300 kev. maximum energy). These radiations, however, are completely absorbed by ordinary glass laboratory equipment (*i.e.*, beakers, desiccators, etc.). Whether or not technetium is, in addition, a radiological poison is not known. Accordingly, small quantities should be handled with the foregoing facts in mind.

---

[1] This work was performed for the Atomic Energy Commission at Oak Ridge National Laboratory.

[2] University of Tennessee and Consultant, Oak Ridge National Laboratory.

[3] Hot Laboratory Group, Chemistry Division, G. W. Parker, Leader (W. J. Martin, G. M. Hebert, G. E. Creek and P. M. Lantz).

[4] G. E. Boyd, J. W. Cobble, C. M. Nelson and W. T. Smith, Jr., THIS JOURNAL, **74**, 556 (1952).

[5] S. Fried, *ibid.*, **70**, 442 (1948).

[6] R. C. L. Mooney, *Phys. Rev.*, **72**, 1269 (1947).

[7] W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Company, New York, N. Y., 1943, p. 374.

[8] M. G. Inghram, D. C. Hess, Jr., and R. J. Hayden, *Phys. Rev.*, **72**, 1269 (1947).

[9] The authors are indebted to Mr. R. D. Ellison of the Chemistry Division, ORNL, for this X-ray identification.

[10] R. C. L. Mooney, *Acta Cryst.*, **1**, 161 (1948).

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE AND
THE UNIVERSITY OF TENNESSEE
KNOXVILLE, TENNESSEE
RECEIVED DECEMBER 12, 1951

Separation of Keto-acids by Cellulose Columns[1]

BY FREDERICK D. DREW, LAWRENCE M. MARSHALL AND FELIX FRIEDBERG

Because of the instability of keto-acids the separation of these compounds as 2,4-dinitrophenylhydrazones becomes particularly useful. One such separation by column chromatography for biologically important keto-acids has been reported.[2] Cavallini, *et al.*,[3] suggested filter paper chromatography of 2,4-dinitrophenylhydrazones. In this report

---

[1] This investigation was supported in part by research grants from the National Cancer Institute and the United States Public Health Service, and from the Damon Runyan Memorial Fund.

[2] G. A. LePage, *Cancer Research*, **10**, 393 (1950).

[3] D. Cavallini, N. Frontali and G. Toschi, *Nature*, **163**, 568 (1949).

their method has been applied to column chromatography, using a cellulose product (Solka-Floc BW100, supplied by the Brown Company, Berlin, N. H.) and alcohols of different chain length. The order of emergence of the keto-acid derivatives agrees with the R_f values obtained by Cavallini, *et al.*[3] As the R_f values increase longer alcohol chains are needed for adequate resolution.

One to two grams of Solka-Floc was suspended in ammonia saturated *n*-amyl alcohol and introduced into a glass tube of 30-cm. length and 0.6-cm. diameter, the tip of which was plugged with a tuft of cotton. After the column had settled, 0.1 to 0.4 mg. of the hydrazones dissolved in 0.2 ml. of *n*-butanol or ethyl ether were introduced. As soon as the solution had entered the column completely the eluant was added. For satisfactory results, excess moisture must be avoided. Effluent fractions of 0.70 ml. per tube collected on a Technicon collector were diluted to 3.70 ml. with *n*-butanol, then hydrazone concentrations were measured by a Beckman spectrophotometer at 380 mμ. This method of reading hydrazone concentrations at this wave length was found to be not only simpler but 1.5 times more sensitive than alkalization and reading in the visible range.[2] Also, the color of the hydrazones in the butanol diluent was stable for several hours. Whenever there was present any free 2,4-dinitrophenylhydrazine in the sample, the acids were extracted into an ethyl ether and 0.2 ml. was placed on the column in order to effect an adequate separation of the reagent from the hydrazones.

Figure 1 shows the separation of pyruvic, oxalacetic and α-ketoglutaric acid hydrazones, using *n*-amyl alcohol saturated with ammonia as eluant. Figure 2 shows that of pyruvic, α-ketobutyric, and α-keto-γ-methiolbutyric acid hydrazones, using *n*-decyl alcohol saturated with ammonia as eluant.

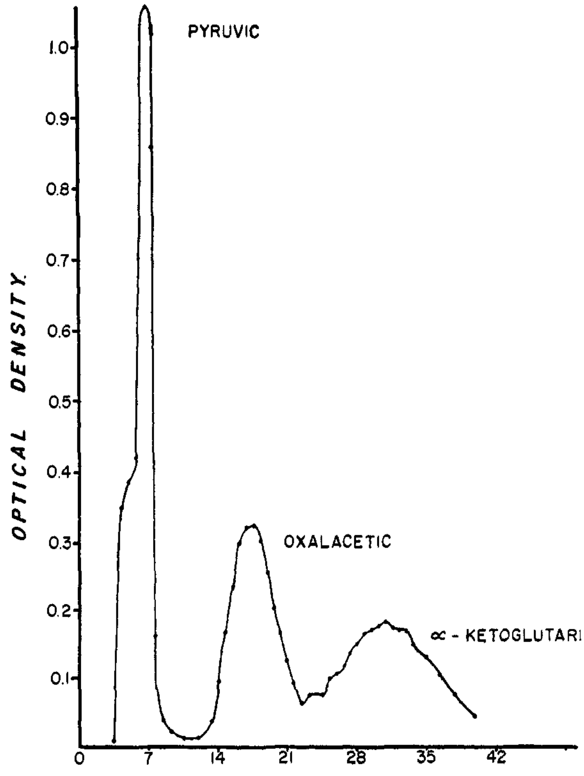

Fig. 1.—Chromatograph of pyruvic, oxalacetic and α-ketoglutaric acid hydrazones.

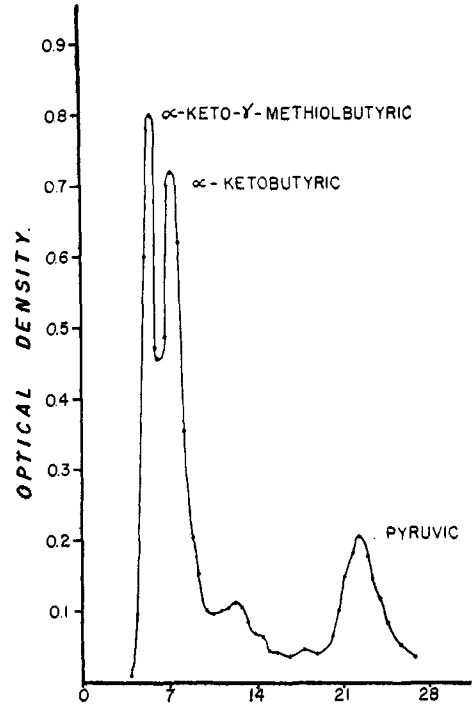

Fig. 2.—Chromatograph of pyruvic, α-ketobutyric and α-keto-γ-methiolbutyric acid hydrazones.

It was found that in conditions of best resolution, there was a separation of the pyruvic acid hydrazone into two bands, as reported by LePage.[2] All five acids may be separated on one chromatographic run by the use of a developing liquid delivered from a reservoir so arranged that the *n*-butyl-*n*-decyl alcohol mixture will gradually and automatically increase with respect to the concentration of the *n*-butyl alcohol.[4] The acids emerge in the following order: γ-methiol-α-ketobutyric, α-ketobutyric, pyruvic, oxalacetic and α-ketoglutaric. By this method, recovery of the hydrazones ranged from 75 to 90%, being highest for the pyruvic acid hydrazone. For identification, the emerging hydrazones were mounted on NaCl crystals and examined in the infrared spectrum between 1800 and 1400 cm.$^{-1}$

(4) K. Donaldson, V. Tulane and L. M. Marshall, *Anal. Chem.* (in press).

DEPARTMENT OF BIOCHEMISTRY
SCHOOL OF MEDICINE
HOWARD UNIVERSITY
WASHINGTON, D. C.

RECEIVED DECEMBER 6, 1951

The Photochemical Chlorination of Methylsilicones

BY J. R. ELLIOTT AND E. M. BOLDEBUCK

The photochemical reaction of ferric chloride with organic materials such as alcohols,[1] acids,[2] al-

---

(1) M. Prasad and P. S. Limaye, *J. Indian Chem. Soc.*, **10**, 91, 101 (1933).

(2) J. C. Ghosh and R. M. Purakayastha, *ibid.*, **6**, 827 (1929).