

(4) **Z-Ala-Z-Lys-Ala-Ala.OBz (LDLL)**.—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.NHNH₂ (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 C₄₁H₅₂O₁₀N₈ (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 carbobenzyloxy 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 P₂O₅ at 100° in high vacuum; the data are in Table I.

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Chemistry of Technetium. II. Preparation of Technetium Metal¹

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Recent large scale separations of technetium from fission product wastes at the Oak Ridge National Laboratory³ 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

(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).

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 (Tc₂S₇) 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 NH₄TcO₄ and (NH₄)₂SO₄ 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 (TcO₂?) which prevented the loss of NH₄TcO₄ by sublimation. At the final higher temperature (500–600°) the (NH₄)₂SO₄ 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 Tc₂O₇.⁴ 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 sin² θ 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.

(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).

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Separation of Keto-acids by Cellulose Columns¹

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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).