Calcd. for $C_{25}H_{24}O_{10}N_4$: C, 55.55; H, 4.48; N, 10.37. Found: C, 55.4; H, 4.60; N, 10.3.

Quinine salt of PCA: m.p. 207–209°. *Anal.* Calcd. for $C_{25}H_{31}O_5N_3$: C, 66.20; H, 6.89; N, 9.27. Found: C, 66.3; H, 6.90; N, 9.3.

Quinine salt of Me N-PCA: m.p. 159–160°. *Anal.* Calcd. for $C_{51}H_{62}O_{10}N_6$: C, 66.65; H, 6.80; N, 9.15. Found: C, 66.5; H, 6.76; N, 9.1.

Acknowledgments.—The authors are grateful for the coöperation of K. J. Palmer on the X-ray studies, F. T. Jones on the optical measurements, and Geraldine Secor and Mary Kilpatrick on the composition analyses.

WESTERN REGIONAL RESEARCH LAB.
ALBANY 6, CALIF.

Reaction of Tantalum with Hydrogen Chloride, Hydrogen Bromide and Tantalum Pentachloride; Action of Hydrogen on Tantalum Pentachloride

BY RALPH C. YOUNG AND CARL H. BRUBAKER, JR.

RECEIVED MAY 19, 1952

Hydrogen Chloride and Tantalum.—When hydrogen chloride gas is passed over tantalum metal at 410° and above, white tantalum pentachloride is formed and can be collected upon a cold-finger condenser. When the temperature is elevated to 600–750°, a thin film of metal, containing dissolved hydrogen, is formed on the heated tube walls. This metal is probably formed by the reduction or thermal decomposition of the pentachloride or some lower chloride, which may begin to form and immediately disproportionate (*cf.* Ruff and Thomas,[1,2] on $TaCl_3$) at the higher temperature. After the reaction has proceeded (600–750°) for a few hours, it is slowed markedly and an olive colored powder forms on the surface of the unreacted metal. Chemical properties and analyses indicate that the olive powder is tantalum dichloride as described by Ruff and Thomas.[1,2]

The tantalum dichloride powder (mixed with metal) was treated with 1 *M* potassium hydroxide and the residual tantalum was filtered away. When the solution was heated, hydrogen bubbled off and a dark flocculent precipitate (presumably $TaO_2 \cdot xH_2O$) formed. The tantalum was oxidized with nitric acid, the pentoxide thus formed was filtered off and chlorine was determined as silver chloride in the filtrate (*Anal.* Cl/Ta = 1.97).

The metallic tantalum films were fused with sodium carbonate and, during the fusion, considerable adsorbed hydrogen gas escaped and burned. The cooled melts were dissolved in water and the solutions were acidified with nitric acid. The weights of pentoxide thus formed indicated the metallic films were tantalum (99.9% Ta or higher.)

Hydrogen Bromide and Tantalum.—If hydrogen bromide is passed over metallic tantalum at 375°, tantalum pentabromide is formed and if the temperature is maintained at 550° or above, some tribromide begins to form, apparently mixed with a still lower bromide or perhaps the metal. *Anal.* Calcd. for $TaBr_3$: Ta, 43.0; Br, 57.0. Found: Ta, 44.7; Br, 55.5.

At higher temperatures (up to 800°) tantalum metal is deposited in the apparatus, probably as the result of reduction or thermal decomposition of the penta- or tribromide. This reaction is also slowed by the formation of a green powder (tantalum tribromide) on the surface of the unreacted metal.

Tantalum Pentachloride and Tantalum.—Schäfer and Pietruck[3] have shown that tantalum pentachloride is not reduced by the metal at 350–400° in an evacuated tube, an observation which was also made in the course of the present work. In the range 475–500°, however, a small amount of a green chloride is formed. If the unreacted pentachloride is sublimed away *in vacuo* and the green material is dissolved in water, one obtains a green solution in which the chlorine to tantalum ratio is 3.35 and the average oxidation state of the tantalum is 3.29. This latter value was obtained electrometrically by use of platinum and saturated calomel electrodes and a potassium nitrate–agar salt bridge. Ceric sulfate was the oxidant. When the inflection in the plot of e.m.f. *vs.* volume of titrant was noted, a brown flocculent precipitate (*cf.* $TaO_2 \cdot xH_2O$) was present in the solution. It was assumed that the tantalum was then in oxidation state (IV). These analyses would indicate the presence of some tantalum in a lower oxidation state (probably III) and possibly a compound such as Ta_3Cl_{10}.

Hydrogen and Tantalum Pentachloride.—Although niobium pentachloride is readily reduced with hydrogen to form the trichloride,[4] Schäfer and Pietruck[3] have shown that tantalum pentachloride is not affected at temperatures up to 400°. Studies in the course of the present work resulted in the same conclusions. However, if the reaction is carried out at 500°, some reduction of the pentachloride does occur and a film of the product, tantalum metal, containing dissolved hydrogen, is deposited on the heated walls of the reduction tube. No lower chlorides could be detected. This is in contrast to the reduction of the pentabromide by hydrogen. The formation of tantalum tribromide has been reported by Van Haagen[5] and by Young and Hastings.[6]

---

(1) O. Ruff and F. Thomas, *Ber.*, **55**, 1466 (1922).

(2) O. Ruff and F. Thomas, *Z. anorg. allgem. Chem.*, **148**, 1 (1925).

(3) H. Schäfer and C. Pietruck, *Z. anorg. allgem. Chem.*, **266**, 151 (1951).

(4) C. H. Brubaker, Jr., and R. C. Young, THIS JOURNAL, **73**, 4179 (1951).

(5) W. K. Van Haagen, Thesis, University of Pennsylvania, 1909 (from Friend, "Textbook of Inorganic Chemistry," Vol. VI, p. 195).

(6) R. C. Young and T. H. Hastings, Jr., THIS JOURNAL, **64**, 1740 (1942).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

O^3,O^4,N-Triacetyl-(−)-epinephrine

BY LLEWELLYN H. WELSH

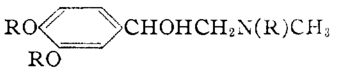
RECEIVED MARCH 21, 1952

The action of excess acetic anhydride on an aqueous solution of ephedrine in the presence of bicarbonate yields the N-monoacetyl derivative.[1] When essentially the same procedure is applied to (−)-epinephrine (Ia), there is obtained a quantitative yield of a crystalline, levorotatory triacetyl

---

(1) L. H. Welsh, *J. Am. Pharm. Assoc.*, **36**, 373 (1947).

derivative, melting, when pure, at 94–95°. Its neutral nature and its failure to give a color reaction in the presence of ferric chloride demonstrate that acylation of the amino nitrogen and phenolic hydroxyl groups has occurred, and permit the identification of the product as O^3,O^4,N-triacetyl-(−)-epinephrine (Ib).[2] Its ultraviolet[3] and infrared[4] absorption spectra are shown in Figs. 1 and 2, respectively.



Ia, R = H
Ib, R = CH$_3$CO

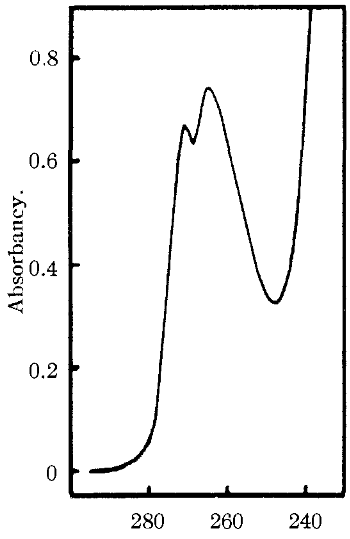


Fig. 1.—Ultraviolet absorption spectrum of triacetylepinephrine taken in 95% ethanolic solution (400 mg./l.) with a model 11 Carey spectrophotometer (1-cm. cell): ϵ_{271} 518, ϵ_{254} 575.

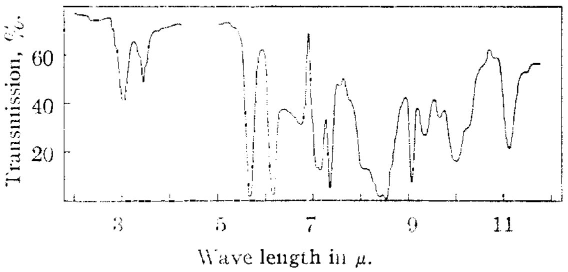


Fig. 2.—Infrared absorption spectrum of triacetylepinephrine taken in carbon tetrachloride (supersaturated 1% soln.) with a model 21 Perkin–Elmer recording spectrophotometer (1-mm. cell).

In contrast to Ia, Ib is quite stable, and easily soluble in chloroform. These characteristics of the substance, and the ease with which it is formed, suggest that the acetylation reaction may be employed to advantage in the isolation, identification and estimation of epinephrine.

Resistance of the alcoholic hydroxyl group of ephedrine and epinephrine toward acetylation under the experimental conditions appears noteworthy. In the presence of as much as 15 to 30 molecular proportions of anhydride, this functional group remains virtually, if not literally, intact while the amino and phenolic functions are quantitatively acetylated.

Experimental

Finely powdered (−)-epinephrine[5] (2.00 g., 0.0109 mole) was added to a mixture of 60 g. of sodium bicarbonate and 200 cc. of water in a 1-l. erlenmeyer flask. While the system was vigorously stirred by a motor-driven wire stirrer, 30 cc. (0.32 mole) of reagent grade acetic anhydride was added cautiously in 4 equal portions. Violent foaming was controlled by the addition of a few drops of ether. When the evolution of carbon dioxide had ceased after the last addition of anhydride, the mixture was allowed to stand about five minutes then extracted with six 100-cc. portions of chloroform. The filtered extracts were concentrated on the steam-bath to an oil which was induced to crystallize by adding ether and triturating. The yield of almost white product was quantitative (3.35 g.); m.p. 91–93° (cor.). It was recrystallized with 90% recovery by dissolving it in acetone (1.3 cc./g.) and adding 7 volumes of ether. Thrice-recrystallized material had m.p. 94–95° (cor.), $[\alpha]^{21}_{D}$ −94.7° (U.S.P. CHCl$_3$, *c* 1.01).

Anal. Calcd. for C$_{15}$H$_{19}$NO$_6$: C, 58.24; H, 6.19; N, 4.53. Found: C, 58.17, 58.28; H, 6.10, 6.08; N (Kjeldahl),[6] 4.45, 4.53.

From acetone–ether, the substance crystallizes as platy or tabular prisms: *refractive indices*, α = 1.516, β = 1.527, γ = 1.572 (all ± 0.002); *optic sign*, biaxial positive; *optic angle*, $2V$ = 52° (from microscopic observation of interference figure and calculated from refractive indices); *extinction*, both parallel and inclined; *system*, probably monoclinic.[7]

---

[2] The racemic substance, along with other products, including the tetracetyl derivative, results from the action of acetyl chloride on racemic epinephrine: see H. Bretschneider, *Monatsh.*, **76**, 355 (1947).

[3] Determination by Lee S. Harrow, Division of Cosmetics, Food and Drug Administration.

[4] Determination by Jonas Carol, Division of Pharmaceutical Chemistry, Food and Drug Administration.

[5] Prepared from Winthrop-Stearns synthetic (−)-epinephrine bitartrate by precipitation with ammonia: $[\alpha]^{20}_{D}$ −51.1° (*c* 2 in 0.5 N hydrochloric acid).

[6] Determinations by Charles Graichen, Division of Cosmetics, Food and Drug Administration.

[7] Optical crystallographic properties determined by Wm. V. Eisenberg and A. H. Tillson, Division of Microbiology, Food and Drug Administration.

DIVISION OF PHARMACEUTICAL CHEMISTRY
FOOD & DRUG ADMINISTRATION
FEDERAL SECURITY AGENCY
WASHINGTON 25, D. C.

NEW COMPOUNDS

Aryl Esters of Pivalic Acid

Five new esters of pivalic acid were prepared by the method given below.

One-quarter mole of pivalyl chloride was added to a solution of one-quarter mole of the phenol in 50 ml. of pyridine, and the solution was heated on the steam-bath for three hours. The solution was poured into a large excess of water and the aqueous mixture was extracted with ether. The ether extracts were washed with 10% sodium hydroxide solution to remove pivalic acid or pivalyl chloride, washed with 5% hydrochloric acid to remove pyridine, and finally washed with water. The ether solution was dried and concentrated, and the ester was then distilled under reduced pressure through a Vigreux column.