the fractions obtained by ozonolysis of parthenin at room temperature, which also results in the formation of formic acid, gave a positive iodoform test and the n.m.r. spectrum of parthenin had no signal corresponding to the $=\!C\!-\!CH_3$ peaks present, for example, in the n.m.r. spectra of dihydroparthenin (II), anhydroparthenin (VI), neotenulin and santonin.

One of the several reduction products of VI, hexahydroanhydroparthenin (VII), proved to be identical with tetrahydroambrosin.[7,8] This provides proof for the previously assumed structure of ambrosin (VIII)[7] and shows that I and VIII have the same stereochemistry at C_4, C_5, C_6 and C_7. The rotatory dispersion curve[9] of III is almost superimposable on that of tetrahydrohelenalin which suggests the absolute configuration at C_1, C_4 and C_5.

Acknowledgment.—This investigation was supported by a grant from the United States Public Health Service (RG-5814).

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(8) We wish to thank Dr. V. Herout for carrying out the comparison.

(9) Kindly determined by Professor C. Djerassi.

(10) Recipient of a Fulbright Travel Grant 1958–1959.

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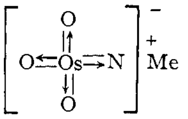
RECEIVED OCTOBER 2, 1959

ORGANIC OSMIAMATES[1]

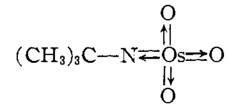
Sir:

Osmiamates (I)[2] in which the osmium is octovalent are not known in Organic Chemistry. We wish to report the synthesis of two organic osmiamates: *t*-butyl osmiamate (II) and 1,1,3,3-tetramethylbutyl osmiamate (III) which were obtained as a result of our general studies on the reaction of osmium tetroxide with various groups of organic compounds.[3,4] *t*-Butyl osmiamate was prepared by allowing osmium tetroxide (1.0 g.) in 50 cc. of pure ligroin to drop slowly with stirring at 0° and preferably in a nitrogen atmosphere into a ligroin solution (25 cc.) of excess (7.0 g.) of *t*-butylamine. Stirring was continued for 24 hours whereby an orange precipitate separated out and was removed by filtration. This was recrystallized several times from hot pure *n*-pentane at −10° into hair-like, orange-yellow crystals which agglomerated like cotton fibers; yield, 65%; m.p. 110°. This compound also can be prepared in aqueous solutions.



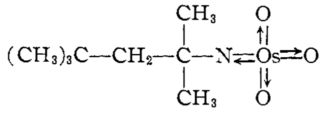
$$\left[\mathrm{O}\leftrightarrows\overset{\mathrm{O}\atop\uparrow\downarrow}{\underset{\downarrow\uparrow\atop\mathrm{O}}{\mathrm{Os}}}\rightrightarrows\mathrm{N}\right]^{-}\overset{+}{\mathrm{Me}}$$

I



$$(\mathrm{CH_3})_3\mathrm{C}\!-\!\mathrm{N}\rightleftarrows\overset{\mathrm{O}\atop\uparrow\downarrow}{\underset{\downarrow\uparrow\atop\mathrm{O}}{\mathrm{Os}}}\rightleftarrows\mathrm{O}$$

II



$$(\mathrm{CH_3})_3\mathrm{C}\!-\!\mathrm{CH_2}\!-\!\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\!-\!\mathrm{N}\rightleftarrows\overset{\mathrm{O}\atop\uparrow\downarrow}{\underset{\downarrow\uparrow\atop\mathrm{O}}{\mathrm{Os}}}\rightleftarrows\mathrm{O}$$

III

Anal. Calcd. for $C_4H_9NO_3Os$: N, 4.53; Os, 61.48; mol. wt., 309. Found: N, 4.68; Os,[5,6] 60.08; mol. wt., 303 (cryoscopic in benzene).

With the thiourea reagent[3] *t*-butyl osmiamate gave an immediate pink coloration characteristic for octovalent osmium. A paper chromatogram developed with ligroin–*t*-butyl alcohol mixture, 90:10 v./v., gave an R_f of 0.68 (32°). An infrared spectrum 10% in $CHCl_3$ showed a strong band, absent in the infrared spectrum of the amine, at 910–915 cm.$^{-1}$ compared with that of osmium tetroxide at 951 cm.$^{-1}$. Bands usually attributed to the amino or hydroxyl hydrogens were absent. An ultraviolet spectrum in *t*-butyl alcohol gave a maximum at 323 mμ; ϵ, 4066.

1,1,3,3-Tetramethylbutyl osmiamate (III) was prepared in exactly the same way as the *t*-butyl osmiamate; yield, 69%; m.p. 51.5° (*n*-pentane).

Anal. Calcd. for $C_8H_{17}NO_3Os$: N, 3.83; Os, 52.04. Found: N, 3.80; Os, 51.89.

This osmiamate also gave an immediate pink color with the thiourea reagent and on a paper chromatogram an R_f value of 0.87 (32°). The infrared spectrum 10% in $CHCl_3$ showed a strong band at 910–915 cm.$^{-1}$ with the amino and hydroxyl hydrogen bands absent. The ultraviolet spectrum in *t*-butyl alcohol showed a strong band with a maximum at 323 mμ; ϵ, 3650.

Both osmiamates react with dilute sulfuric acid to give osmium tetroxide and the sulfates of the original amines. They deflagrate spontaneously on a hot plate and show strong oxidizing properties; they react with olefins in the same manner as osmium tetroxide. These and other reactions of osmiamates are now being investigated and will be reported later.

Acknowledgment.—The authors are indebted to Dr. Shin-ichi Sasaki and Mrs. J. A. Hilton for technical assistance, to Dr. S. Nagy for the nitrogen analysis and to Rohm and Haas for a supply of 1,1,3,3-tetramethylbutylamine.

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(1) Supported by NIH Contract B-1493(C1).

(2) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, 1950, p. 1507.

(3) N. A. Milas, J. H. Trepagnier, J. T. Nolan, Jr., and M. I. Iliopulos, THIS JOURNAL, **81**, 4730 (1959).

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(6) R. Criegee, *Ann.*, **522**, 75 (1936); R. Criegee, B. Marchand and H. Wannowius, *ibid.*, **550**, 99 (1942). Criegee, *et al.*, indicated that osmium analyses gave always low values.

(7) NIH Postdoctorate Research Associate, Fulbright Traveling Fellow.

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RECEIVED OCTOBER 13, 1959

THE BIOLOGICAL CONVERSION OF SYNTHETIC METHOSTENOL-4-C^{14} TO CHOLESTEROL[1]

Sir:

We have reported recently that sodium acetate-1-C^{14} injected into rats intracardially becomes incorporated into the methostenol (4α-methyl-Δ^7-cholesten-3β-ol) of the skin and liver–small in-

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(1) This investigation was supported by a research grant (H-2458-C3) from the National Institutes of Health, Public Health Service.