TABLE I

Compound	M. p.,[a] °C.	Yield, %	Formula	N analyses,[b] % Calcd.	Found
5-Chloro-2-thiophenesulfonamide	113.5	57	$C_4H_4ClNO_2S_2$	7.09	7.08
Sodium N-chloro-5-chloro-2-thiophenesulfonamide	124.5 dec.	71	$C_4H_2Cl_2NNaO_2S_2 \cdot 3H_2O$	4.53	4.53
N-Methyl-5-chloro-2-thiophenesulfonamide	44	33[c]	$C_5H_6ClNO_2S_2$	6.64	6.40
N-Ethyl-5-chloro-2-thiophenesulfonamide	52[d]	33[e]	$C_6H_8ClNO_2S_2$	6.22	6.20
N-Propyl-5-chloro-2-thiophenesulfonamide	14[f]	9	$C_7H_{10}ClNO_2S_2$	5.82	5.57
N-(1-Methylethyl)-5-chloro-2-thiophenesulfonamide	41	18	$C_7H_{10}ClNO_2S_2$	5.82	5.83
N-Butyl-5-chloro-2-thiophenesulfonamide	19[f]	22	$C_8H_{12}ClNO_2S_2$	5.59	5.36
N-Amyl-5-chloro-2-thiophenesulfonamide	32	31	$C_9H_{14}ClNO_2S_2$	5.25	5.05
N-Hexyl-5-chloro-2-thiophenesulfonamide	47	42[e]	$C_{10}H_{16}ClNO_2S_2$	4.98	4.96
N-Heptyl-5-chloro-2-thiophenesulfonamide	46	46	$C_{11}H_{18}ClNO_2S_2$	4.75	4.72
N-Phenyl-5-chloro-2-thiophenesulfonamide	83[g]	28	$C_{10}H_8ClNO_2S_2$	5.12	5.09

[a] All melting points are corrected. [b] Analyses by semi-micro Kjeldahl method. [c] Recrystallized from methanol–water. [d] Benzene used instead of ether as solvent. [e] Recrystallized from ethanol–water. [f] Liquid at room temperature; decomposed slowly on standing. [g] Recrystallized from 50% ethanol.

5-Chloro-2-thiophenesulfonamide was prepared by heating for fifteen minutes on a steam-bath a stirred mixture of 8.5 g. (0.039 mole) of 5-chloro-2-thiophenesulfonyl chloride and excess dry ammonium carbonate. After addition of a small amount of ice-water the mixture was extracted with ether. The residue after evaporation of the ether was dissolved in hot water, treated with Norit A, filtered and cooled, yielding the sulfonamide.

Sodium N-chloro-5-chloro-2-thiophenesulfonamide was prepared by adding to 1 g. (0.00506 mole) of 5-chloro-2-thiophenesulfonamide 9 g. (0.00607 mole) of 5.25% sodium hypochlorite solution and 15 ml. of saturated sodium chloride solution. The precipitate was filtered, washed with saturated salt solution, and extracted with absolute ethanol. The ethanol solution was filtered and allowed to evaporate, yielding sodium N-chloro-5-chloro-2-thiophenesulfonamide trihydrate.

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RECEIVED SEPTEMBER 6, 1949

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COMMUNICATIONS TO THE EDITOR

A NEW VALENCE STATE OF AMERICIUM, AM(VI)[1]

Sir:

Evidence has been obtained for the existence of americium in the formal valence of plus six:

1. Americium(III) is completely oxidized by ammonium peroxydisulfate in 0.2 *M* nitric or chloric acids to a non fluoride-precipitable state. At a concentration of 200 μg of element per 100 microliters (2 g./l.), the characteristic pink of Am(III) changes to a strong yellow color.

2. The absorption spectrum of such an oxidized solution was measured with a Beckman model DU spectrophotometer using quartz micro cells and 0.1 sensitivity scale. The solution shows no Am(III) absorption at 504 and 811 mμ, or Am(V) absorption at 514 and 714 mμ. There is a narrow and prominent peak at 991–992 mμ, and strong ultraviolet absorption. The decrease with time of these new absorption peaks is attended by a growth of Am(V) absorption but no increase in the Am(III) absorption. The rate of decrease of the 991 peak is much greater in the absence of sulfate, and the ultraviolet absorption is altered.

3. By the addition of sodium acetate, a yellow compound of tetrahedral structure was obtained which was isomorphous with the analogous $NaMO_2Ac_3$ compounds (M is U or Pu). The refractive index of sodium americyl acetate has the expected value of 1.528 (compared with 1.501 and 1.518 for the uranium and plutonium compounds, respectively). There were no Am(III) or Am(V) absorption lines in this compound. The compound was dried with acetone, treated with excess ferrous ammonium sulfate and back-titrated with ceric sulfate. The amount of americium was determined by radio-assay. A value of 2.9 was obtained for the number of equivalents on reducing Am(VI) to Am(III).

4. X-Ray analysis showed a cubic structure with an a_0 of 10.6 which is the same as that of the uranium and plutonium analogs.

5. Ether extraction after removal of sulfate with barium and salting with ammonium nitrate and nitric acid gave essentially complete extraction.

6. Hexone (methyl isobutyl ketone) extraction was also successful, but less complete, apparently due to reduction by the solvent.

7. Addition of sulfuric acid (sufficient to make 4 *M* sulfuric acid) to a solution of Am(V) in 0.3 *M* perchloric acid caused rapid disappearance of

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[1] This document is based on work performed at the Los Alamos Scientific Laboratory of the University of California under AEC contract W-7405-eng-36.

Am(V) absorption which was accompanied by a rapid growth of the 991 peak (Am(VI)) and Am(III) absorption. Insufficient evidence has been accumulated to establish whether this disproportionation gives Am(IV) in observable amounts.

The authors would like to express appreciation to E. Staritzky for the crystallographic identification and to F. H. Ellinger for the X-ray analysis.

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RECEIVED FEBRUARY 6, 1950

THE TOTAL SYNTHESIS OF ESTRONE AND THE REMAINING STEREOISOMERS

Sir:

As early as 1935[1] extensive research programs directed toward the total synthesis of the female sex hormone estrone were well under way. These studies have since been continued with increasing interest in laboratories all over the world. In 1942 Bachmann, Kushner and Stevenson[2] succeeded in synthesizing a stereoisomer of the hormone, "estrone a." Using essentially the same synthetic scheme as Bachmann, *et al.*, Anner and Miescher[3] recently were able to isolate additional stereoisomers including *dl*-estrone. Six of the eight possible racemic forms, estrone, a-f, have now been reported.[4]

In the present communication we are reporting a completely new synthesis which has yielded, in addition to the natural product (estrone b), the two remaining stereoisomers g and h. The potassium salt of *m*-methoxyphenylacetylene (prepared from *m*-hydroxyacetophenone) was added to 1,5-decalindione[5] in a 1:1 molecular ratio. The acetylenic bond of the resulting carbinol was hydrogenated over palladium catalyst and the product dehydrated with formic acid. The unsaturated ketone, produced in 70% over-all yield from the diketone, was cyclized with hydrogen chloride and aluminum chloride in benzene, giving an oily mixture from which were crystallized in about equal amounts two stereoisomeric 1-keto-8-methoxy-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysenes: α-form, m. p. 168.4–170° (*Anal.* Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.60; H, 8.37) and β-form, m. p. 153.4–154.8° (*Anal.* Found: C, 80.11; H, 8.13). The β-isomer gave a benzal derivative,[6] m. p. 152–153.1° (*Anal.* Calcd. for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 83.49; H, 7.66), which on treatment with potassium *t*-butoxide and methyl iodide afforded two angularly methylated stereoisomers,[6] β^1, m. p. 146.6–147.2° (*Anal.* Calcd. for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 83.88; H, 7.83) and β^2, m. p. 147.0–147.8° (*Anal.* Found: C, 84.01; H, 7.85). Oxidation of the β^2 benzal derivative[7] with ozone afforded *dl*-homomarianolic acid methyl ether, m. p. 225.2–227.5° (reported,[3] 225–227°), which on heating with lead carbonate yielded *dl*-estrone methyl ether, m. p. 143.2–144.0° (reported,[3] 143–144°). A comparison of the crystals with natural estrone methyl ether[8] indicated that they possess identical form and optical properties. Infrared spectrographic analysis[9] gave identical curves for the two materials. Demethylation with pyridine hydrochloride afforded *dl*-estrone, m. p. 252.8–254.8° (reported,[3] 251–254°), which showed 50% of the activity of U.S.P. estrone in ovariectomized rats.[10] Resolution *via* the *l*-menthoxyacetate gave *d*-estrone *l*-menthoxyacetate, m. p. 132–135°, undepressed on admixture with the ester (m. p. 133.5–135°) prepared from natural estrone.

The β^1 benzal derivative yielded a new stereoisomer, estrone g (presumably *dl* lumiestrone), m. p. 238.5–240° (*Anal.* Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.80; H, 8.22); methyl ether, m. p. 109–110° (*Anal.* Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.25; H, 8.44). Similar studies in the α-series yielded what is apparently estrone d, m. p. 180.6–181.4° (reported,[4] 184–186°), methyl ether, m. p. 115–116.2° (reported,[4] oil), derived from the homomarrianolic acid methyl ether, m. p. 169.8–170.5° (reported,[4] 170–171°); and the new estrone h, m. p. 197.0–198.1° (*Anal.* Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.14; H, 8.19), methyl ether, m. p. 67–68.3° (*Anal.* Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.19; H, 8.49).

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[1] See for example, Robinson and Schlittler, *J. Chem. Soc.*, 1288 (1935).

[2] Bachmann, Kushner and Stevenson, THIS JOURNAL, **64**, 974 (1942).

[3] Anner and Miescher, *Experientia*, **4**, 25 (1948); *Helv. Chim. Acta*, **31**, 2173 (1948).

[4] Anner and Miescher, *ibid.*, **32**, 1957 (1949).

[5] Prepared from 1,5-dihydroxynaphthalene by a modification of the method of Hudson and Robinson, *J. Chem. Soc.*, 691 (1942).

[6] *Cf.* Johnson, THIS JOURNAL, **65**, 1317 (1943).

[7] *Cf.* Johnson *ibid.*, **66**, 215 (1944).

[8] The crystallographic examinations were kindly performed by Dr. R. L. Clarke of the Sterling-Winthrop Research Institute.

[9] Kindly carried out by Dr. R. N. Jones of the National Research Council, Canada.

[10] Tests kindly performed by Drs. R. K. Meyer and E. G. Shipley of the Zoology Department, University of Wisconsin.

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THE DIELECTRIC CONSTANT OF TRIFLUOROACETIC ACID

Sir:

The dielectric constant of trifluoroacetic acid has been found to increase with increasing temperature in the range of −10 to +30°. This appears to be an unusual property for a liquid, as a search of the literature has failed to disclose any other substances showing this property to this extent.

The dielectric cell had cylindrical electrodes of nickel and had a calibration of 61.5 microfarads. The substitution method was employed