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.

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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