7α-Methylsulfinyltestosterone Acetate. Isolation of Two Epimers. Epimer A.—7α-Methylthiotestosterone acetate (1 g.) was treated with monoperphthalic acid by the general procedure for sulfoxide preparations described above. Evaporation of the methylene chloride solvent gave a solid which was dissolved in hot acetone. To the refluxing acetone solution petroleum ether (b.p. 60–70°) was added to the point of crystal formation. The mixture was then chilled and the solid was filtered to give 418 mg. (40%) of product with m.p. 148–150° (gas). (The mother liquor was further investigated; see below.) This product was recrystallized once from methylene chloride–ether and then three times from acetone–petroleum ether (b.p. 60–70°) to a constant m.p. at 142–145°; $[\alpha]^{25}D$ −36.2° (0.6% in chloroform); $\lambda_{max}^{CH_3OH}$ 248 mμ (ε 12,800); λ_{max}^{KBr} 5.75, 6.00, 6.16, 8.0–8.06, 9.55, 9.63 μ, also weak bands at 7.71 and 8.84 μ indicating the presence of some sulfone; $R_f^6 = 0.42$.

Anal. Calcd. for $C_{22}H_{32}O_4S$: C, 67.32; H, 8.22; S, 8.17; O, 16.31. Found: C, 66.85; H, 8.31; S, 7.87; O, 16.64.

Similar material prepared in another experiment with 0.75 molar equivalents of monoperphthalic acid (37% yield) had m.p. 149–151°; $[\alpha]^{25}D$ −6.8° (1.0% in chloroform); $R_f^6 = 0.42$; $\lambda_{max}^{CH_3OH}$ 247 mμ (ε 11,000); infrared spectrum was essentially the same as that above except that the sulfone bands were almost absent. This product was different (mixture melting point and papergram mobility comparisons) from the 7α-methylthiosulfinyltestosterone acetate obtained by Holmlund and co-workers[4] by a microbiological procedure.

Epimer B.—The acetone–petroleum ether mother liquor from the 418-mg. preparation (above) gave, after partial evaporation, a second product (202 mg., 20%) with m.p. 171–173° (gas). Recrystallization from acetone–petroleum ether (b.p. 60–70°) three times to constant melting point gave material with m.p. 175–176° (gas); $[\alpha]^{25}D$ +15.5° (0.6% in chloroform). Further purification of this product was accomplished by partition chromatography on Celite[7] diatomaceous earth using the solvent system cyclohexane–dioxane–water (60:40:8) according to a procedure developed by C. Pidacks and described previously.[8] In the second holdback volume a small amount of 7α-methylsulfonyltestosterone acetate was obtained and in the fourth holdback volume the desired 7α-methylsulfinyltestosterone acetate which was identical by mixed melting point and paper chromatographic comparisons with the microbiological product of Holmlund and co-workers[4] (presumed epimer B) was obtained. This material had the following constants: m.p. 170–171° (gas), $[\alpha]^{25}D$ +11.3° (0.97% in chloroform). $R_f^6 = 0.56$; $\lambda_{max}^{CH_3OH}$ 242 mμ (ε 10,800); λ_{max}^{KBr} 5.75, 5.97, 6.18, 8.05, 9.78 μ (no sulfone bands).

Anal. Calcd. for $C_{22}H_{32}O_4S$: C, 67.32; H, 8.22; S, 8.17. Found: C, 66.97; H, 8.36; S, 8.24.

General Procedure for the Preparation of Steroidal C-7 and C-21 Methyl Sulfones.—The steroidal C-7 or C-21 methyl sulfoxide was dissolved or suspended in 75 ml. of methylene chloride per 0.01 mole of steroid and treated with 1.1 mole equivalents of ethereal monoperphthalic acid according to the procedure described above for the preparation of the steroidal sulfoxides, except that the reaction time was extended to 48 hr. The product obtained was recrystallized from the same solvents described above. The compounds thus prepared by this general procedure are shown in Table II.

Treatment of 17β-Acetoxy-7α-methylsulfonyl-4-androsten-3-one with 0.5% Methanolic Potassium Hydroxide to Give 6-Dehydrotestosterone Acetate.—A suspension of 56 mg. of 17β-acetoxy-7α-methylsulfonyl-4-androsten-3-one in 5 cc. of 0.5% methanolic potassium hydroxide was stirred under nitrogen for 3 min. when solution was completed. After an additional 1 min., the solution was acidified with acetic acid. Dilution with water and filtration afforded 40 mg. (89%) of 6-dehydrotestosterone acetate,[9] m.p. 137–140°. Admixture with an authentic sample did not depress the melting point. The infrared spectra for the two samples were identical.

Acknowledgment.—We wish to thank Mr. L. Brancone and staff for the microanalyses and Mr. W. Fulmor and staff for the spectral and polarimetric determinations.

(6) The solvent system used was benzene, acetic acid, petroleum ether (b.p. 90–100°), water in the volume ratio 13:16:7:4. We thank Dr. Holmlund and his colleagues for these determinations.

(7) Celite is the trademark of Johns Manville Corp. for diatomaceous earth.

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Formation and Oxidation of 2-(9′-Fluorenyl)-fluorene[1]

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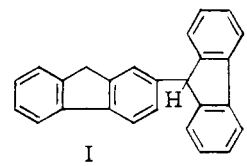
In an earlier paper it was reported that reaction of fluorene and sodium amide yielded two products which were isomers of 9,9′,9′,9″-terfluorene since more than two moles of fluorenone were obtained by oxidation of these products.[2] In the present work, the preparation and oxidation of a related compound, 2-(9′-fluorenyl)fluorene (I) are described. I was isolated as a by-product in the Clemmensen reduction of 9-fluorenol in toluene, was also produced when 9-fluorenol was boiled with fluorene in acetic acid in the presence of sulfuric acid, or was obtained by Friedel-Crafts reaction between fluorene and 9-bromofluorene in carbon disulfide.



I

On oxidation with sodium dichromate in acetic acid, I gave *o*-(fluorenone-2-carbonyl)benzoic acid and 13*H*-indeno[1,2-*b*]anthracene-6,11,13-trione (*lin*-phthaloylfluorenone), but no fluorenone, indicating that two molecules of fluorene were condensed at the 2- and 9- positions, respectively. I gave fluorene by zinc dust distillation, and its ultraviolet absorption spectrum differed from those of dibiphenyleneethane,[3] tribiphenylenepropane,[3] and 2,2′-difluorenyl.[4]

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Barnett's[5] method was employed to synthesize the *lin*-phthaloylfluorenone. *o*-(Fluorenone-2-carbonyl)benzoic acid was formed by oxidation of *o*-(fluorene-2-carbonyl)benzoic acid and was esterified in ethanol.

Experimental[6]

2-(9′-Fluorenyl)fluorene (I).—9-Bromofluorene (2.44 g.) and fluorene (1.66 g.) were dissolved in carbon disulfide (30 ml.). Anhydrous aluminum chloride (1.35 g.) was added in small portions with stirring at the boiling point. The reaction color immediately turned greenish blue and hydrogen chloride gas was evolved. After warming for 0.5 hr. on the water bath, the mixture was cooled and poured into water. The carbon disulfide layer was separated, washed with water, and evaporated to dryness to give colorless needles 1.5 g., m.p. 225–226° (from benzene), soluble in hot benzene, acetic acid, and ethyl acetate, and stable at the melting point. Ultraviolet absorption spectra: $\lambda_{max}^{CHCl_3}$ mμ (log ε); 272.5 (4.52), 296 (4.15), 307 (4.22), 323 (3.27).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49; mol. wt., 330. Found: C, 94.15; H, 5.68; mol. wt., 325.

Clemmensen Reduction of 9-Fluorenol.—A mixture of amalgamated zinc (10 g.), water (10 ml.), toluene (40 ml.), concd. hydrochloric acid (35 ml.), and 9-fluorenol (10 g.) was refluxed briskly for 24 hr. Hydrochloric acid was added every 6 hr. After the reaction, fluorene (8 g., m.p. 113–114°) was obtained by steam distillation. A residual product was filtered and recrystallized from ethyl acetate to yield I, 0.8 g., m.p. 224–227°.

Reaction of Fluorene and 9-Fluorenol.—9-Fluorenol (0.8 g.) and fluorene (0.73 g.) in acetic acid (7 ml.) and two drops of concd. sulfuric acid were refluxed for 5 hr. After pouring into cold water, the white amorphous product was filtered off giving 0.8 g. of I, m.p. 224–226° (from benzene).

Oxidation of I.—A solution of I (1.0 g.) in glacial acetic acid (10 ml.) was refluxed with sodium dichromate (3 g.) and concd. sulfuric acid (1 drop) for 3 hr. After cooling and diluting the solution with cold water, the yellow amorphous precipitate was filtered and treated with dilute sodium hydroxide (10%). Acidification of the alkali soluble part gave a precipitate which was recrystallized from acetic acid to yield yellow prisms of *o*-(fluorenone-2-carbonyl)benzoic acid (0.2 g.), m.p. 257–258°, identical with that obtained by oxidation of *o*(fluorene-2-carbonyl)benzoic acid.

Anal. Calcd. for $C_{21}H_{12}O_4$: C, 76.82; H, 3.68. Found: C, 76.67; H, 3.77.

The alkali-insoluble part was recrystallized from acetic acid to afford small orange-red needles, m.p. 367°, 0.5 g., which gave a blue color test with concd. sulfuric acid. This was identical with the *lin*-phthaloylfluorenone which was prepared by Barnett's method.[5]

Anal. Calcd. for $C_{21}H_{10}O_3$: C, 81.28; H, 3.25. Found: C, 81.17; H, 3.47.

Ethyl *o*-(Fluorenone-2-carbonyl)benzoate.—The acid was esterified in the usual manner to give yellow crystals, m.p. 108–110° (from alcohol).

Anal. Calcd. for $C_{23}H_{16}O_4$: C, 77.51, H, 4.53. Found: C, 77.15; H, 4.61.

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(6) All melting points are uncorrected.

Fries Rearrangement of 3-Nitrophenyl Butyrate

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Few examples of the Fries isomerization of nitrophenyl esters are reported in the literature.[1–10] The reduced tendency of these esters to undergo Fries rearrangement must be associated with the retarding effect of the nitro substituent in the phenyl ring.[11–16]

The Fries reaction of 3-nitrophenyl acetate,[2,3] propionate,[6] phenylacetate, and benzoate[10] has already been realized. In the present work 3-nitrophenyl butyrate has been subjected to the Fries rearrangement by heating it for 2.5 hr. in the absence of a solvent in the presence of aluminum chloride at 140°. The isomerization yielded 3.5–5% of the so far unknown 4-nitro-2-hydroxybutyrophenone, which was characterized by its phenylhydrazone. The structure of this new ketone was proved by oxidation which gave 4-nitro-2-hydroxybenzoic acid.

Experimental[17]

3-Nitrophenyl butyrate was prepared in 80% yield from sodium 3-nitrophenoxide (obtained from 3-nitrophenol and sodium ethoxide in benzene) and butyryl chloride in benzene. After the removal of the solvent the residual ester[18] was used without further purification, as it decomposed on distilling. The ester (10.5 g., 0.05 mole) was mixed with aluminum chloride (6.55 g., 0.05 mole,) in a flask protected against moisture and heated in an oil bath at 135–140° for 150 minutes. At the beginning of the reaction hydrogen chloride was evolved. The solidified product was dissolved

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