diate **6b** might also contribute to the observed high selectivity of phosphorylation.

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(35) For compounds **4c** and **4d** a convenient solvent was found in the mixture $CHCl_3$–CH_3OH (4:1) containing a few drops of CH_3COOH. Yields were then estimated spectrophotometrically either directly after dilution of the corresponding aliquot with ethanol or after removal of the volatile solvents from an aliquot by a stream of air, dissolving the residue in 80% CH_3COOH (5% of the final volume), and dilution with 0.01 *N* HCl.

Total Synthesis of Steroids. V.[1] Synthesis of *rac*-3-Methoxy-14α-hydroxy-8α-estra-1,3,5(10)-triene-11,17-dione and Its Derivatives

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The cyclization of 8,14-seco-3-methoxy-11ξ-hydroxyestra-1,3,5,8-tetraene-14,17-dione (**2a**) in the presence of Meerwein reagents led to the formation of tetracyclic products **6a** and **6b**. The stereochemistry of the latter compounds was established by spectral evidence and by their conversion to *rac*-13-isoestrone. Further transformations of **6a** and **6b** led to the new 11-keto compound **19** epimeric at C-14.

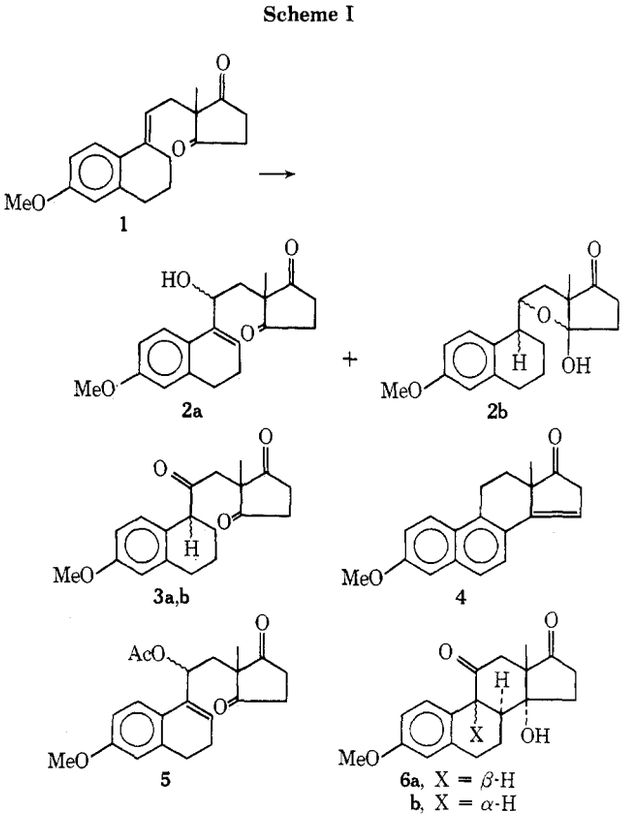
In our first paper on the total synthesis of steroids[2] we reported on the peracid oxidation of Torgov's secodione **1** and now we wish to describe the complete synthesis of the title compound from the same starting material. The secodione **1** was converted as previously described[2] into the mixture of **2a** and **2b**, which was submitted to the action of different acidic reagents in order to produce tetracyclic compounds. The resulting products are presented in Scheme I and listed in Table I. The trione **3**, which did not react further, was obtained in all instances except from the reaction with acetic acid–boron trifluoride. Surprisingly, in three cases 14-dehydroequilenin methyl ether was obtained in substantial amounts. We suggest that this is produced by dehydration of **2a**, leading to an intermediate A, which undergoes an isomerization to the naphthalene derivative B (Scheme II). The latter can cyclize easily to yield **4**, as is known from the literature[3] and as was proved in our previous paper.[4]

We reported previously[2] on the synthesis of the tetracyclic ketones **6a,b**[5] from **2a** in very low yield by the action of boron trifluoride etherate. We have now found that the yield of these required compounds can be increased tenfold by use of Meerwein reagents, *e.g.*, $Me_3O^+BF_4^-$ or $Et_3O^+BF_4^-$ (Scheme III). We did not investigate the course of the reaction of Meerwein reagents with **2a,b** in detail, but we observed on tlc plates the formation of ketal **2c**, which could be isolated and converted in a separate experiment into the triketone **3a,b**. The latter compound is almost always the minor product in the cyclization reaction. Another product formed initially under the influence of $Et_3O^+BF_4^-$ has a polarity similar to that of

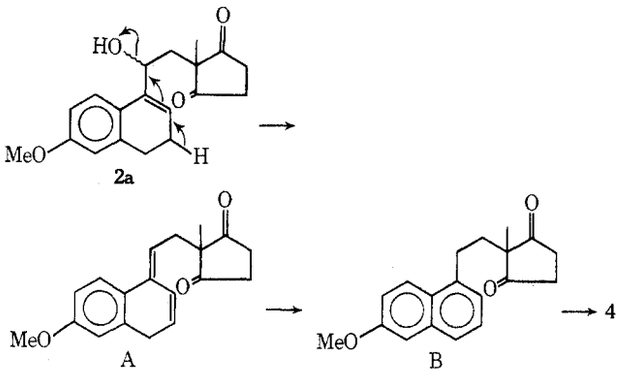
Table I

No.	Acid	Product (yield, %)
1	$SnCl_4$	**3a,b** (95) + traces of other products
2	$CH_3CO_2H + BF_3 \cdot Et_2O$	**3a,b** (50) + **4** (24)
3	$CH_3CO_2H + BF_3 \cdot CH_3CO_2H$	**4** (40) + **5** (41)
4	CF_3CO_2H	**3a,b** (50) + (50)
5	$BF_3 \cdot Et_2O$	**3a,b** (33) + **6a,b** (6.5)
6	Meerwein reagents	**3a,b** (25) + **6a,b** (75)
7	CH_3CO_2H and chlorinated acetic acids	No effect

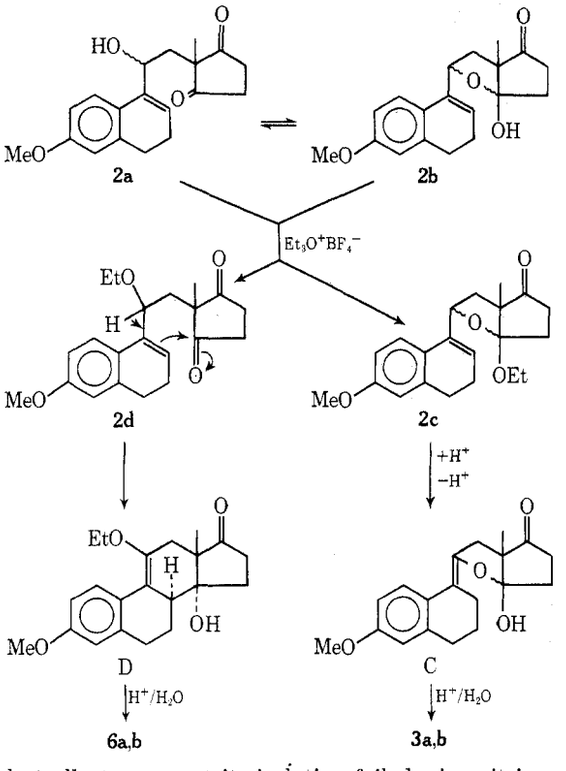
Scheme I



Scheme II



Scheme III



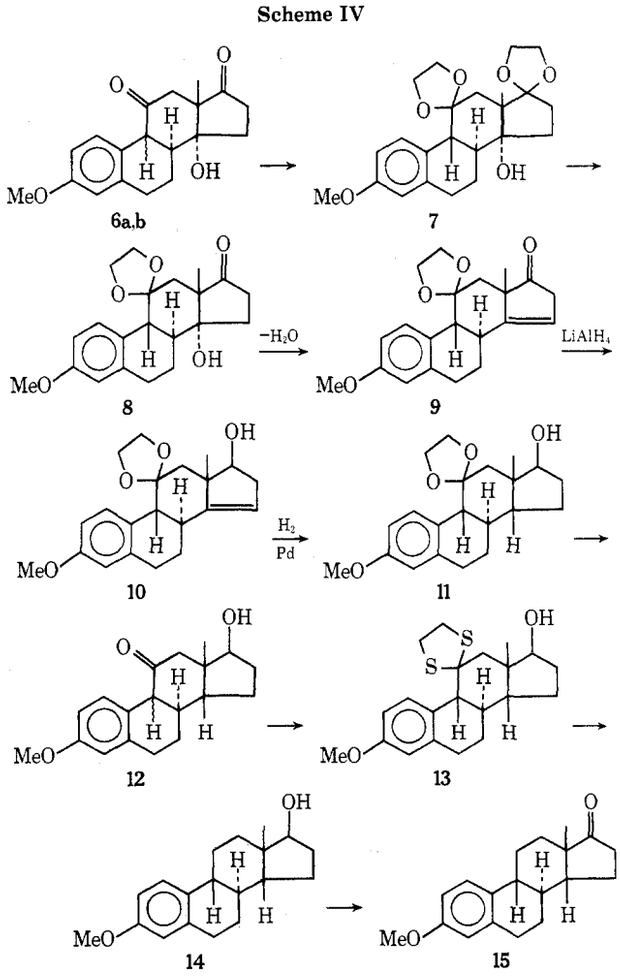
2c, but all attempts at its isolation failed, since it is converted very rapidly into **6a,b**. We suggest that it may have the isomeric structure **2d**. In compound **2c** one keto group is blocked by ketal formation, and the other keto group is too far from the "cyclization center," *i.e.*, from carbon atom C-9. Consequently, the most probable reaction is the isomerization to an enolic ether ketal C. The hydrolysis of C produces the triketone **3a,b**. The possible intermediate **2d** formed from **2a**, however, can cyclize directly to a tetracyclic intermediate D, and the hydrolysis of the latter yields the diketones **6a** and **6b**. Furthermore, we found that the first cyclization product is **6a**. Examination of Dreiding models of the starting material **2a** and the products **6a,b** leads to the conclusion that the attack of Meerwein reagents or BF_3, respectively, has to follow from the α side. Consequently trans C/D ring junction is formed and ring C assumes the boat conformation in **6a** after hydrolysis of the initially formed 11-enol ether. Prolongation of the reaction time causes its conversion into the epimeric **6b** with cis junction of ring B and C. In a separate experiment we confirmed the greater stability of **6b** in alkaline or acidic medium.

The yield of the tetracyclic ketones depends strongly on the concentration of the reactants; higher yields were obtained in dilute solutions. At higher concentrations of **2a,b** the formation of **3a,b** predominates. Best yields of the tetracyclic products **6a,b** were obtained in dilute acetone, whereas the yield of the intermediate **2c** can be increased to *ca.* 50% by carrying out the reaction in chloroform. Compounds **6a** and **6b** also show the expected uv and ir absorption. The assignment of the geometry of **6a**, or **6b**, respectively, was based mainly on their pmr spectra as well as on their conversion to compounds with known geometry as will be described later.

The pmr spectrum of **6a** exhibits, in addition to the expected methyl resonances, a doublet at 4.1 ppm which is ascribed to H-9, whose large coupling constant (J = 12 Hz) suggests that the B/C ring junction is trans. On the other hand, H-9 in **6b** is coupled to H-8 by only 6.5 Hz, thus proving that the B/C ring junction is cis. Furthermore, H-1 in **6a** gives rise to a doublet at 7.15 ppm (J = 8.5 Hz) whereas in **6b** the same signal is shifted by 0.4 ppm upfield and superimposed on the signals of H-2 and H-4. This difference in chemical shift is caused by the paramagnetic shielding effect of the 11-carbonyl group, which is especially pronounced in the case of a B/C cis compound.

Compounds **6a** and **6b** possess four chiral centers at carbon atoms 8, 9, 13, and 14, and therefore eight diastereoisomers are possible. In order to establish the correct geometry of the compounds **6a** and **6b** the series of reactions shown in Scheme IV was carried out. The mixture of

Scheme IV



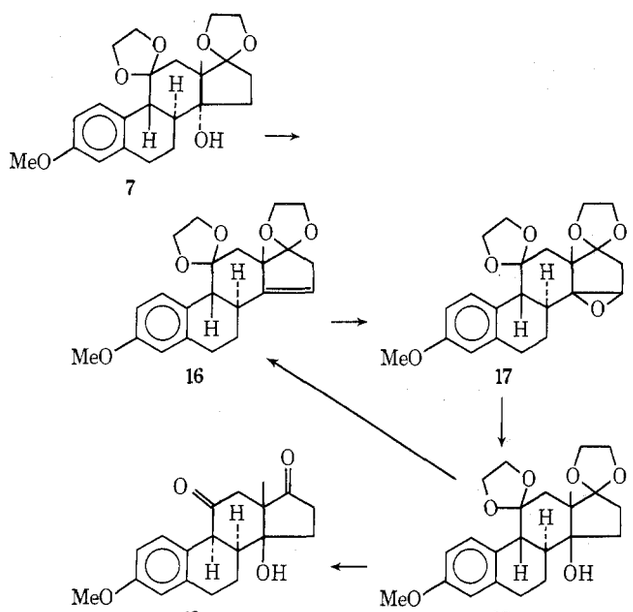
6a and **6b** was converted into a single diketal **7**, which was selectively hydrolyzed to the 17-keto compound **8**. After dehydration of the latter with thionyl chloride in pyridine

and subsequent reduction with $LiAlH_4$ the unsaturated alcohol **10** was obtained. Further reduction of the double bond with hydrogen on palladium catalyst gave the saturated alcohol **11**. Catalytic reduction of steroidal systems with an aromatic ring A always leads to a C/D cis junction, regardless of how C-17 is substituted.[6] Acid hydrolysis of the ketal **11** yielded the hydroxy ketone **12**, which was transformed to the thioketal **13**. Reduction of the latter with Raney nickel and subsequent oxidation with Jones reagent[7] at C-17 produced the 3-methyl ether of *rac*-13-isoestrone. Its properties were identical with those reported by Johnson, *et al.*[8] Since 13-isoestrone has a trans B/C ring junction, we assumed that our diketal **7** had the same geometry.

Further inspection of Dreiding models of the above compounds leads to the conclusion that although the diketones **6** and **19** preferentially assume B/C cis geometry (in the case of **19** this seems to be the only existing form), their 11-ketals or 11-thioketals, respectively, are pure B/C trans isomers for steric reasons. In this way we have proved the stereochemistry of compounds **6a** and **6b** on carbon atoms 8, 9, and 13.

The stereochemistry of the hydroxyl group at C-14 was elucidated in the manner illustrated in Scheme V. The di-

Scheme V



ketal **7** was dehydrated with thionyl chloride in pyridine to the unsaturated diketal **16**. The double bond at C-14 was subsequently epoxidized with *m*-chloroperbenzoic acid to yield the β-epoxide **17**, where it has been assumed that the attack of perbenzoic acid took place in the same manner as in the case of catalytic reduction. Reduction of the epoxide with $LiAlH_4$ produced a new 14-hydroxy compound **18** whose alcohol function should have β geometry. Compound **18** was different indeed from the starting diketal **7**; acid hydrolysis produced the diketone **19**, which was different from the starting diketones **6a** and **6b**. According to its pmr spectrum it has a cis B/C ring junction, since the coupling constant between the protons 8 and 9 was only 7 Hz. The new diketal **18** was dehydrated with thionyl chloride in pyridine to the same diketal **16** as obtained from **7**, and not as expected to a compound with an 8(14) double bond. This can be explained only by assuming a twisted conformation of the C/D ring system caused by the interactions of the substituents at C-11, C-13, C-17, and C-14, which consequently facilitates more the trans diaxial elimination of water from C-14 and C-15 than from C-14 and C-8.

The sequence of reactions just described indicates that the 14-hydroxyl group in compounds **6a** and **6b** had the α geometry, *i.e.*, trans to the angular methyl group.

Further reactions of the new estrone derivatives, *i.e.*, their conversion into 19-norandrostanes, will be published shortly.

Experimental Section

Melting points were measured on a micro hot plate, and are not corrected. Ir spectra were determined in KBr tablets with an Infracord instrument, and pmr spectra were measured with a Jeol 100-MHz spectrometer in $CDCl_3$ solution (accuracy ±0.5 Hz). The microanalyses were performed in our microanalytical laboratory (head: Z. Celler, M.Sc.).

Synthesis of 3-Methoxy-14α-hydroxy-8α,9β-estra-1,3,5(10)-triene-11,17-dione (6a) and 3-Methoxy-14α-hydroxy-8α,9α-estra-1,3,5(10)-triene-11,17-dione (6b). To a solution of 10 g (32 mmol) of the mixture **2a,b** in 1 l. of acetone the solution of 12.1 g (64 mmol) of Et_3OBF_4 in 10 ml of acetone was added and left at room temperature for 16 hr. The solvent was then removed *in vacuo*, the residue was dissolved in 100 ml of chloroform and shaken with 2 *N* aqueous sodium carbonate (3 × 50 ml), the organic layer was washed neutral, dried with anhydrous $MgSO_4$, and filtered, and the solvent was evaporated *in vacuo*. Trituration with benzene yielded the crystalline mixture of **6a** and **6b**. Repeated crystallization from chloroform–*n*-hexane (4:1) yielded two reaction products.

A. A 5.75-g (57.5% yield of **3-methoxy-14α-hydroxy-8α,9β-estra-1,3,5(10)-triene-11,17-dione (6a):** mp 190–191°; λ_{max} (ethanol) 276 nm (ϵ 1700) and 283 (1630); ν_{max} 3500 (OH), 1740 (CO at C-17), 1700 cm^{-1} (CO at C-11); δ 1.15 (s, 3 H, CH_3), 4.10 (d, 1 H, H-9, $J_{9,8}$ = 12 Hz), 7.15 ppm (d, 1 H, H-1, $J_{1,2}$ = 8.5 Hz). *Anal.* Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.60; H, 7.07.

B. A 1.85-g (18.5%) yield of **3-methoxy-14α-hydroxy-8α,9α-estra-1,3,5(10)-triene-11,17-dione (6b),** mp 215–216° (from MeOH) or 192–194° (from C_6H_6). The spectroanalytical data of this compound were different for both crystalline modifications.

6b crystallized from MeOH: mp 215–216°; λ_{max} 278 and 284 nm (ϵ 1715 and 1580); ν_{max} 3530 (OH), 1730 cm^{-1} (CO at C-11 and C-17); δ 1.15 (s, 3 H, CH_3), 3.78 (s, 3 H, OCH_3), 3.95 (d, 1 H, H-9, $J_{9,8}$ = 6.5 Hz), 6.60–6.85 ppm (m, 3 H, aromatic protons).

6b crystallized from C_6H_6: mp 192–194°; λ_{max} as above; ν_{max} 3450 (OH), 1730 (CO at C-17), and 1700 cm^{-1} (CO at C-11); δ[$(CD_3)_2CO$] 1.10 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 4.22 (d, 1 H, H-9, $J_{9,8}$ = 6.3 Hz), 6.82 (d, 1 H, H-1, $J_{1,2}$ = 8.7 Hz), 6.6–6.7 (m, 2 H, H-2, H-4), 7.55 ppm (s, 6 H, C_6H_6).

14-Ethoxy-3-methoxy-11,14-oxido-8,14-secoestra-1,3,5(10),8-tetraen-17-one (2c). To a solution of 1.0 g (3.2 mmol) of the alcohol **2** in 100 ml of chloroform the solution of 1.41 g (7.5 mmol) of $Et_3O^+BF_4^-$ in 50 ml of chloroform was added with stirring at room temperature. After the substrate disappeared (*ca.* 15 min.) from the reaction mixture, 0.2 l. of water was added, the mixture was shaken vigorously, and the organic layer was separated, dried with anhydrous $MgSO_4$, filtered, and evaporated *in vacuo*. Trituration with 5 ml of MeOH produced 0.48 g of crystalline **2c:** mp 133–134°; λ_{max} 271 nm (ϵ 13,870); ν_{max} 1740 cm^{-1} (CO at C-17); δ 1.15 (s, 3 H, CH_3), 1.28 (t, 3 H, OCH_2CH_3), 3.82 (q, 2 H, OCH_2CH_3), 3.85 (s, 3 H, OCH_3), 5.05 (t, 1 H, H-11), 5.98 ppm (t, 1 H, H-8).

The filtrate was chromatographed on 50 g of silica gel column, and elution with benzene–acetone (96:4) yielded in the first fractions 0.1 g of the secotrione **3a,b:** mp 116–117°; λ_{max} 278 and 285 nm (ϵ 2070 and 1650); ν_{max} 1720 (CO at C-14 and C-17) and 1700 cm^{-1} (CO at C-11); δ 0.97 (s, 3 H, CH_3), 2.80 (s, 4 H, 2 H-15, 2 H-16), 3.68 ppm (s, 3 H, OCH_3). *Anal.* Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.46; H, 7.27.

Further elution with the same solvent system gave 0.31 g of the mixture **6a,b**. The yield of all reaction products was 89%. The compound **2c** left in chloroform solution with $Et_3O^+BF_4^-$ for several hours yielded the secotrione **3a,b**, mp 115–117°, in quantitative yield.

3-Methoxy-14α-hydroxy-11,11,17,17-bis(ethylenedioxy)-8α,9β-estra-1,3,5(10)-triene (7). The solution of 2 g (6.4 mmol) of **6a** or the mixture **6a,b** in 100 ml of benzene was refluxed with 0.54 ml of ethylene glycol and 0.02 g of *p*-toluenesulfonic acid for

10 hr with water separation. The solution was then treated with charcoal, filtered through Celite, and evaporated *in vacuo*. Crystallization from benzene gave 2.48 g (96.5% yield) of diketal **7**: mp 217–219°; ν_{max} 3550 (OH), 1200, 1150, and 1040 cm^{-1} (OC bands from ketal grouping); δ 1.18 (s, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 3.98 ppm (s, 4 H, OCH_2CH_2O at C-17). *Anal.* Calcd for $C_{23}H_{30}O_6$: C, 68.70; H, 7.46. Found: C, 69.10; H, 7.58.

3-Methoxy-14α-hydroxy-11,11-ethylenedioxy-8α,9β-estra-1,3,5(10)-trien-17-one (8). The solution of 2 g (5 mmol) of diketal **7** in 150 ml of benzene–acetone–water (9:20:1) mixture was left at 40° for 1 hr with 0.01 g of *p*-toluenesulfonic acid. Acetone was then distilled off and the benzene layer was washed with 2 *N* aqueous Na_2CO_3 solution and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent *in vacuo* the residue was crystallized from methanol, yielding 1.62 g (91% yield) of monoketal **8**: mp 232–235°; ν_{max} 3500 (OH) and 1730 cm^{-1} (CO at C-17); δ 1, 16 (s, 3 H, CH_3), 3.78 (s, 3 H, OCH_3), 6.6–6.8 (m, 2 H, H-2 and H-4), 7.35 ppm (d, 1 H, H-1). *Anal.* Calcd for $C_{21}H_{26}O_5$: C, 70.40; H, 7.30. Found: C, 70.43; H, 7.28.

Dehydration of the Monoketal 8 to 3-Methoxy-11,11-ethylenedioxy-8α,9β-estra-1,3,5(10),14-tetraen-17-one (9). The solution of 1.5 g (4.2 mmol) of monoketal **8** in 100 ml of pyridine was left at room temperature with 1 ml of thionyl chloride for 1 hr. The reaction mixture was then poured into 2 l. of water and filtered. Recrystallization of the precipitate from MeOH gave 1.31 g (92% yield) of the unsaturated monoketal **9**: mp 162–163°; λ_{max} 278 and 286 nm (ϵ 1705 and 1680); ν_{max} 1740 cm^{-1} (CO at C-17); δ 1.45 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 5.88 ppm (s, 1 H, H-15). *Anal.* Calcd for $C_{21}H_{24}O_4$: C, 74.20; H, 7.00. Found: C, 74.20; H, 7.10.

Reduction of 9 to 3-Methoxy-11,11-ethylenedioxy-17β-hydroxy-8α,9β-estra-1,3,5(10),14-tetraene (10). **9** (1.3 g, 4 mmol) dissolved in 100 ml of ether was reduced with 0.04 g of $LiAlH_4$ at room temperature. Standard work-up yielded 1.1 g (85% yield) of 3-methoxy-11,11-ethylenedioxy-17β-hydroxy-8α,9β-estra-1,3,5(10),14-tetraene (**10**): mp 154–156°; λ_{max} 278 and 285 nm (ϵ 1740 and 1630); ν_{max} 3500 cm^{-1} (OH); δ 1.28, (s, 3 H, CH_3), 3.88 (s, 3 H, OCH_3), 4.10 (t, 1 H, H-17), 5.48 (s, 1 H, H-15), 6.68–6.85 (m, 2 H, H-2, H-4), 7.47 ppm (d, 1 H, H-1).

Catalytic Reduction of 10 to 3-Methoxy-11,11-ethylenedioxy-17β-hydroxy-8α,9β,14β-estra-1,3,5(10)-triene (11). **10** (1.10 g, 3.2 mmol) dissolved in 250 ml of toluene was shaken in H_2 atmosphere in the present of 1.1 g of 10% Pd/C. After the theoretical amount of hydrogen was consumed (*ca.* 2 hr), the catalyst was removed and the solvent was evaporated *in vacuo*. The residue, recrystallized from MeOH, gave a quantitative yield of **11**: mp 161–164°; λ_{max} 278 and 285 nm (ϵ 1770 and 1650); ν_{max} 3400 cm^{-1} (OH); δ 1.30 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 6.70–6.88 (m, 2 H, H-2 and H-4), 7.58 ppm (d, 1 H, H-1, $J_{1\text{-}2}$ = 10 Hz). *Anal.* Calcd for $C_{21}H_{28}O_4$: C, 73.40; H. 8.15. Found: C, 73.70; H, 8.28.

Hydrolysis of the Saturated Ketal 11. The solution of 1.0 g (2.9 mmol) of **11** in 100 ml of MeOH and 10 ml of 10% aqueous HCl was left at room temperature for 2 hr. Standard work-up yielded 0.63 g (73% yield) of **3-methoxy-17β-hydroxy-8α,9β,14β-estra-1,3,5(10)-trien-11-one (12)**: mp 140–144°; ν_{max} 3500 (OH) and 1700 cm^{-1} (CO at C-11); δ 1.15 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 3.55 (d, 1 H, H-9, $J_{9,8}$ = 11 Hz), 3.92 (t, H-17), 6.68–6.95 (m, 2 H, H-2 and H-4), 7.40 ppm (d, 1 H, H-1).

11-Thioketal of 3-Methoxy-17β-hydroxy-8α,9β,14β-estra-1,3,5(10)-trien-11-one (13). To the solution of **12** (100 mg, 0.3 mmol) in ethanedithiol (0.5 ml), BF_3·Et_2O (0.5 ml) was added and the mixture was left at room temperature for *ca.* 10 min. The solution was then diluted with 100 ml of ether and washed with 1 *N* NaOH solution until the odor was eliminated. Further standard work-up yielded the crude mercaptal **13** (120 mg, 96% yield), recrystallized from MeOH: mp 130–137°; λ_{max} 280 and 285 nm (ϵ 1600 and 1490); δ 1.15 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 4.00 (t, 1 H, H-17), 6.50–6.75 (m, 2 H, H-2 and H-4), 8.47 ppm (d, 1 H, H-1). *Anal.* Calcd for $C_{21}H_{28}O_2S_2$: C, 67.00; H, 7.45. Found: C, 67.09; H. 7.55.

Desulfurization of the Mercaptal 13. Freshly prepared Raney nickel (from 2 g of alloy) was added to the solution of the thioketal **13** (70 mg) in methanol (30 ml) and the resulting suspension was refluxed with stirring for *ca.* 0.4 hr. Nickel was then filtered off and the solvent was evaporated *in vacuo*, yielding 47 mg (88% yield) of **3-methoxy-17β-hydroxy-8α,9β,14β-estra-1,3,5(10)-triene (14)**: mp 111–113° (from benzene–hexane); λ_{max} 278 and 285 nm (ϵ 2340 and 2150); δ 0.97 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 4.17 (t, 1 H, H-17), 6.50–6.72 (m, 2 H, H-2 and H-4), 7.20 ppm (d, 1 H, H-1). *Anal.* Calcd for $C_{19}H_{26}O_2$: C, 79.80; H, 9.10. Found: C, 80.76; H, 9.69.

The oxidation of 40 mg of the above product **14** with Jones reagent[8] under standard conditions yielded 30 mg (76% yield) of the methyl ether of ***dl*-13-isoestrone (15)**, mp 108–110° (from MeOH) (lit. mp 109–110°). The other physical data were also in good agreement with the literature.[6]

Dehydration of the Diketal 7. **7** (2.5 g, 6.2 mmol) was dehydrated with thionyl chloride in pyridine as described previously and worked up in the same manner. A 2.38-g (quantitative yield of **3-methoxy-11,11,17,17-bis(ethylenedioxy)-8α,9β-estra-1,3,5(10),14-tetraene (16)** was obtained: mp 142–144°; ν_{max} 1610, 1500 (aryl), 1155, 1140, 1100, 1050 cm^{-1} (OC from ketal; δ 1.38 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 4.00 (s, 4 H, OCH_2CH_2O at C-17), 5.55 ppm (s, 1 H, H-15). *Anal.* Calcd for $C_{23}H_{28}O_5$: C, 71.90; H. 7.29. Found: C, 71.82; H, 7.30.

Epoxidation of 16. To a solution of 2 g (5.2 mmol) of **16** in 200 ml of chloroform a solution of 0.89 g (5.2 mmol) of *m*-chloroperbenzoic acid in 100 ml of chloroform was added at −50°. The solution was then left for 12 hr, and the temperature was permitted to rise slowly up to 10° (for the last 3 hr). The reaction mixture was then washed several times with aqueous Na_2CO_3 to remove the acids and subsequently worked up in the usual manner to give 1.79 g (86% yield) of **3-methoxy-14β,15-epoxy-11,11,17,17-bis(ethylenedioxy)-8α,9β-estra-1,3,5(10)-triene (17)**: mp 183–190°; ν_{max} 1610, 1510 (aryl), 1120, 1100, 1080 (OC from ketal), 840, 800 cm^{-1} (epoxide); δ 1.40 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 4.00 (s, 4 H, OCH_2CH_2O at C-17). *Anal.* Calcd for $C_{23}H_{28}O_6$: C, 69.00; H. 7.00. Found: C, 69.30; H, 6.96.

Reduction of the Epoxide 17. **17** (2 g, 5 mmol) dissolved in 100 ml of THF was reduced with 0.08 g of $LiAlH_4$ at room temperature. The reaction product was isolated in the usual manner, and 1.9 g (95% yield) of **3-methoxy-14β-hydroxy-11,11,17,17-bis(ethylenedioxy)-8α,9β-estra-1,3,5(10)-triene (18)** was obtained: mp 203–204°; ν_{max} 3500 (OH), 1600 and 1500 cm^{-1} (aryl); δ 1.38 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 4.00 (s, 4 H, OCH_2CH_2O at C-17), 4.48 ppm (s, 1 H, OH).

The above product **18** (1.5 g) was hydrolyzed with 10% aqueous HCl in methanol and the standard work-up gave 1.0 g (85.5% yield) of **3-methoxy-14β-hydroxy-8α,9α-estra-1,3,5(10)-triene-11,17-dione (19)**: mp 195° dec; ν_{max} 3450 (OH), 1740 (CO at C-17), 1700 cm^{-1} (CO at C-11); δ 0.96 (s, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 4.3 ppm (d, 1 H, H-9, $J_{9,8}$ = 7 Hz). The dehydration of compound **18** with thionyl chloride in pyridine gave back **3-methoxy-11,11,17,17-bis(ethylenedioxy)-8α,9β-estra-1,3,5(10),14-tetraene (16)**, mp 141–144°, identical in all respects with the compound obtained previously.

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Registry No.—2a, 51606-66-7; **2b**, 51510-09-9; **2c**, 51510-10-2; **3a,b**, 30041-29-3; **6a**, 51606-67-8; **6b**, 51606-68-9; **7**, 51510-11-3; **8**, 51510-12-4; **9**, 51510-13-5; **10**, 51510-14-6; **11**, 51510-15-7; **12**, 51606-69-0; **13**, 51510-16-8; **14**, 51606-70-3; **16**, 51510-17-9; **17**, 51510-18-0; **18**, 51606-71-4; **19**, 51606-72-5.

References and Notes

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