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Photochemistry of 17β-Hydroxyestra-5(10),9(11)-dien-3-one. Synthesis of AB Spiro Steroids[1,2]

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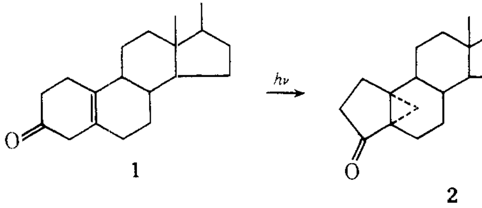
17β-Hydroxyestra-5(10),9(11)-dien-3-one (**3**) was photoisomerized via a 1,3 acyl shift to (10*S*)-17β-hydroxy-3,10-cyclo-3,4-seco-10α-estra-4,9(11)-dien-1-one (**4a**) whose structure was proven by x-ray analysis. Irradiation of **4a** caused photodecarbonylation to 2,10-cyclo-2,3-seco-*A*-norestra-3(5),9(11)-dien-17β-ol (**5a**) plus photoisomerization back to **3**. Acetone photosensitization of **3** did not yield any isolable photoproducts.

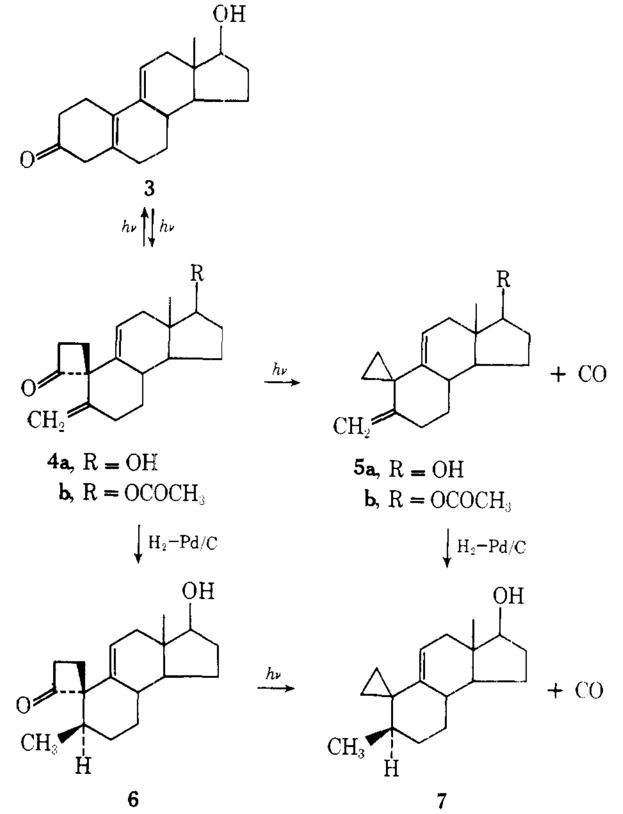
Several years ago the unusual spectroscopic properties of β,γ-unsaturated cyclic ketones caused us to investigate their photochemistry.[3-7] It was found that upon direct irradiation 17β-hydroxyestra-5(10)-en-3-one (**1**) afforded 17β-hydroxy-5α,19-cyclo-*A*-nor-10β-androstan-3-one (**2**) via a 1,2 acyl shift.[5,6] Since direct irradiation of cyclic β,γ-unsaturated ketones usually afforded products resulting from 1,3 acyl shifts, rather than 1,2,[8] it was thought that the "semiplanar" A ring conformation[9] led to this unusual reaction pathway. To test this hypothesis 17β-hydroxyestra-5(10),9(11)-dien-3-one (**3**) was irradiated since **3** contains a similar "semiplanar" A-ring conformation[9] which is now part of a β,γ,δ,ε dienone chromophore.



1 2

Results and Discussion

Direct irradiation of **3** in benzene with a medium pressure mercury arc (Hanovia 450W) through a Pyrex filter gave two products plus recovered **3** (53%) which were separated by chromatography on alumina. The first photoproduct (**4a** 36%) was acetylated to aid in crystallization and yielded 17β-acetoxy-3,10-cyclo-3,4-seco-10α-estra-4,9(11)-dien-1-one (**4b**) on the basis of the following data. Elemental analysis of the acetate **4b** indicated that the alcohol **4a**, from which it was derived, was isomeric with **3**. The infrared spectrum of **4a** showed a hydroxyl band at 3610 cm^{-1}, and **4a** showed an ester carbonyl at 1725 cm^{-1}. Both spectra contained absorption



3

4a, R = OH
b, R = OCOCH3

5a, R = OH
b, R = OCOCH3

6

7

bands at 1770 cm^{-1} characteristic of a cyclobutanone. The NMR spectra of **4a** and **4b** both showed a multiplet centered at δ 5.40 and 5.47, respectively, due to the olefinic C-11 hydrogens, and two singlets at δ 4.78 and 4.64 each integrating for one proton, due to the exocyclic methylene hydrogens on C-4. It is interesting to note that the exocyclic methylene hydrogens in **4b** have different chemical shifts and are moved upfield from their absorption in photoproduct **5b**. This may be explained by the stereochemistry of the spiro system in **4b**. The exocyclic hydrogens in **4b** are positioned in the shielding cone of the cyclobutanone carbonyl as one was much closer than the other. This effect was also noticed in the NMR spectrum of 6-methylenespiro[4,5]decan-1-one.[7]

The second product, formed in 7% yield, was also acetylated and afforded 2,10-cyclo-2,3-seco-*A*-norestra-3(5),9(11)-dien-17β-acetate (**5b**). Elemental analysis of **5b** showed that carbon monoxide had been lost from **4b**. Furthermore, the cyclobutanone carbonyl had disappeared from the infrared spectrum of **4b** leaving only that of the acetate at 1720 cm^{-1}. The absence of an ultraviolet absorption maximum above 220 nm further supported the loss of the carbonyl group. The NMR spectrum of **5b** showed a multiplet at δ 5.44 due to the olefinic C-11 hydrogen, a multiplet centered at δ 4.98 due to the C-17 hydrogen, and a two-hydrogen singlet at δ 4.85 due to the exocyclic methylene hydrogens on C-4. A broad multiplet from δ 0.72 to 0.22 integrating for four hydrogens was assigned to the cyclopropyl group that would result when carbon monoxide was lost from the cyclobutanone. The infrared spectrum of **5b** showed absorption at 3060, 1645, and 890 cm^{-1} characteristic of olefinic and cyclopropyl hydrogens. Irradiation of the photoproduct **4a** also gave a mixture of **3**, **4a**, and **5a** in which **3** was again the major product. This indicates that **3** and **4a** are in a photochemical equilibrium. The photoreversibility of this reaction and the spectral data of the photoproduct establish its structure as the spirocyclobutanone **4a**. The structure of the second photoproduct is the cyclopropyl compound **5a** due to its spectral properties and mode formation from **4a**. Furthermore, the photoisomerization of **3** to **4a** followed by photodecarbonylation to **5a** has recently been reported by other workers.[10] In a closely related study Nakanishi et al. has observed a photochemically induced 1,3 acyl shift to yield a cyclobutanone followed by photodecarbonylation to a cyclopropyl compound.[11]

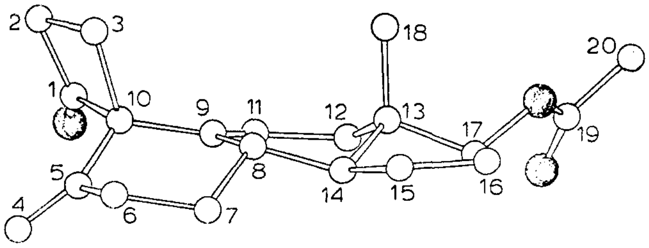


Figure 1. X-ray analysis structure of photoproduct **4b**.

To determine whether the carbonyl group in **4** was α or β, an x-ray analysis was done on **4b**. The results of this analysis[12] (see Figure 1) prove that the steroid **4** has the 10*S* configuration.

Inspection of a Dreiding model of **4** showed the spatial arrangements of the carbonyl and olefinic groups to be such that the optical rotatory dispersion rule for β,γ-unsaturated ketones cannot be applied in this case.[3c,13] Furthermore, the ORD curve of **6** $[\Phi]_{330}$ −11, [Φ] +68, shows an extremely weak negative Cotton effect similar to those previous observed for this configuration.[3c] Catalytic reduction of **4a** should proceed from the less hindered side. In the above case this is the α side (see Figure 1) and yields the reduction product **6**. Photodecarbonylation of **6** yielded **7** prepared by catalytic reduction of **5a**.

The photoisomerization of **3** to **4** proceeds via a singlet or short-lived triplet state, since the reaction could not be quenched with 2,5-dimethylhexa-2,4-diene or 1,3-cyclohexadiene. Photosensitization experiments with acetone or acetophenone led to the disappearance of starting material, but no triplet product could be isolated. Similar results have been observed for other β,γ-unsaturated ketones.[14]

The conformation of the chromophore in **3** is planar, the same as that for 17β-hydroxy-5(10)-estren-3-one (**1**), based on the results of hydride reduction products,[15] strain-energy minimization calculations,[16] and x-ray analyses.[9] Therefore, if conformation was the controlling factor in their photoreactivity, they should both exhibit the same photochemistry.[7] However, they do not and other factors must be involved.[8] Photolysis of **3** proceeds from either an excited singlet state or a short-lived triplet state via a 1,3 acyl shift to afford **4a**. On the other hand, photolysis of **1** proceeds from the excited triplet state via a 1,2 acyl shift (oxadi-π-methane rearrangement) to afford the cyclopropyl ketone **2**.[7] These results support the previously reported generalizations concerning the photochemistry of β,γ-unsaturated ketones,[8] which have been rationalized by spin density distribution arguments[17] and molecular orbital calculations.[18]

Photolysis of **3** affords a convenient entry into AB spiro steroids which have recently attracted attention for their androgenic activity.[19] The presence or absence of alkyl groups on C-10 has greatly affected their physiological properties,[20] and this synthesis of a spiro structure at C-10 while still retaining functionality at C-5 and C-11 should offer a ready access to a number of very interesting spiro steroids.

Experimental Section

Ir spectra were recorded on Perkin-Elmer 137 and 225 spectrometers. Uv absorption spectra were measured in methanol solution with a Cary 14 spectrophotometer. NMR spectra were recorded at 100 MHz on a Varian XL-100 spectrometer. Chemical shifts are reported in δ (ppm) from the internal standard Me_4Si. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. VPC analyses were performed on an F and M Model 700 gas chromatograph using a 3-ft, 3% OV-17 on 100–120 mesh Gas-Chrom Q column at 150 °C. Elemental analyses were performed by Micro-Analysis Inc., Wilmington, Del.

17β-Hydroxyestra-5(10),9(11)-dien-3-one (3). 17β-Hydroxy-5(10)-estren-3-one[21] (880 mg) was brominated and dehydrobrominated according to the method of Levine and Eudy[14] previously used for the 17β-acetate. The intermediate 17β-hydroxyestra-4,9-dien-3-one was crystallized from petroleum ether–acetone (1:1) as chunky crystals: mp 176 °C; NMR ($CDCl_3$) δ 5.80 (s, 1, H-4) and 0.72 (s, 3, H-18). 3,3-Dimethoxyestra-5(10),9(11)-dien-17β-ol was isolated as a gum: uv max (EtOH) 238.5 nm (ϵ 21 800); ir ($CHCl_3$) 3620 cm^{-1} and no carbonyl absorption; NMR ($CDCl_3$) δ 5.51 (m, 1, H-11), 3.18 (s, 6, OCH_3), and 1.74 (s, 3, H-18).

To a solution of the entire ketal (800 mg) in 24 ml of acetone was added with stirring at room temperature 440 mg of malonic acid in 3.5 ml of H_2O and 26 ml of acetone and the solution was let stir for 3 h. The reaction mixture was diluted with 60 ml of benzene and 20 ml of 10% $NaHCO_3$, and the organic layer was separated and washed twice with 50 ml of $NaHCO_3$, dried (Na_2CO_3), and freed of solvent under reduced pressure leaving 500 mg of amorphous products.[22a,b] Crystallization from acetone–hexane gave 17β-hydroxyestra-5(10),9(11)-dien-3-one (**3**) as chunky crystals: mp 119–120 °C; uv max (EtOH) 240 nm (ϵ 21 000), 297 (160); ir ($CHCl_3$) 3620 (OH), 1720 cm^{-1} (3-one); NMR ($CDCl_3$) δ 5.51 (m, 1, H-11) as expected for 17β-hydroxyestra-5(10),9(11)-dien-3-one (**3**).

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.89. Found: C, 78.98; H, 8.80.

Photolysis of 17β-Hydroxyestra-5(10),9(11)-dien-3-one (3). A solution of **3** (250 mg) in benzene (250 ml) stirred with a stream of N_2 was irradiated with a 450-W Hanovia lamp through a Pyrex filter. The reaction, which reached an equilibrium in about 4 h, was monitored by VPC. Evaporation of the solvent in vacuo yielded a gum (280 mg). A total of 1.0 g of this crude gum from combined runs was chromatographed over alumina (activity III, 85 g). Initial elution with 200 ml of petroleum ether–acetone (92:8) afforded 70 mg of 2,10-cyclo-2,3-seco-*A*-norestra-3(5),9(11)-dien-17β-ol (**5a**) in 7% yield, which resisted crystallization: ir ($CHCl_3$) 3610 (OH), 3060 cm^{-1} and no carbonyl absorption; NMR (C_6D_6) δ 5.54 (m, 1, H-11), 4.69 (s, 1, H-3), 4.62 (s, 1, H-3), and 0.65–0.41 (m, 4, cyclopropyl). Acetylation of the alcohol **5a** gave 2,10-cyclo-2,3-seco-*A*-norestra-3(5),9(11)-diene 17-acetate (**5b**) as needles: mp 129 °C; ir (KBr) 3060, 1645, 1720 (acetate), 890 cm^{-1} (exo methylene); NMR (C_6D_6) δ 5.44 (m, 1, H-11), 4.98 (m, 1, H-17), 4.85 (s, 2, H-3), 0.95 (s, 3, H-18), and 0.72–0.22 (m, 4, cyclopropyl).

Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.41; H, 9.49. Found: C, 78.98; H, 9.53.

Further elution with 350 ml of petroleum ether–acetone (88:12) yielded 360 mg (36%) of **4a** as an amorphous product, which resisted crystallization: uv (MeOH) 305 nm (ϵ 65); ir ($CHCl_3$) 3610 (OH), 1770 (cyclobutanone), and 900 cm^{-1}; NMR ($CDCl_3$) δ 5.52 (m, 1, H-11), 4.68 (s, 1, H-4), 4.61 (s, 1, H-4) exocyclic methylene. Acetylation of the alcohol **4a** afforded (10*S*)-17β-acetoxy-3,10-cyclo-3,4-seco-10α-estra-4,9(11)-dien-1-one (**4b**) as long needles: mp 124–125 °C; uv 305 nm (ϵ 65); ir (KBr) 1770 (cyclobutanone), 1725 cm^{-1} (acetate); NMR ($CDCl_3$) δ 5.47 (m, 1, H-11), 4.78 (s, 1, H-4), 4.64 (s, 1, H-4), 2.95 (s, 2, H-2, J = 8 Hz), and 0.78 (s, 3, H-18).

Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.37; H, 8.23. Found: C, 76.66; H, 7.93.

Further elution with the same solvent yielded starting material, **3a** (530 mg, 53%), which was very unstable due to autoxidation.

Irradiation[23] for 4 h of the photoproduct **4a** also gave a mixture of **3, 4a,** and **5a** in which **4a** was again the major product.

Sensitization and Quenching Experiments. Samples of **3** (10 mg) in benzene (10 ml) with sufficient benzophenone to capture >95% of the incident light were irradiated in sealed, degassed test tubes. VPC analysis indicated that **3** disappeared but no photoproducts were observed. Similar results were obtained using acetone as the solvent. When 2,5-dimethylhexa-2,4-diene and 1,4-cyclohexadiene were used in 0.01, 0.1, and 2.0 M concentrations as quenchers, no quenching of the formation of **4a** and **5a** was observed, according to VPC analyses of the solutions.

(10*S*)-17β-Hydroxy-3,10-cyclo-3,4-seco-10α-estra-9(11)-en-1-one (6). To a solution of cyclobutanone **4a** (50 mg) in benzene (10 ml), 5% platinum on Darco G-60 catalyst (50 mg) was added, and the mixture hydrogenated at room temperature in a Parr series 3910 low-pressure hydrogeation apparatus at a starting pressure of 60 lb. One equivalent of hydrogen was consumed after 2 h. After removal of catalyst by filtration, the filtrate was evaporated under reduced pressure and afforded 46 mg (92% yield) of **6:** mp 145–146 °C; uv (CH_3OH) 290 nm (ϵ 98); ir 1770 cm^{-1} (cyclobutanone); NMR (C_6H_6) δ 5.80 (m, 1, H-11), 4.91 (m, 1, H-17), 2.78 (t, 2, H-2, J = 8 Hz), 1.27 (d, 3, H-4, J = 7 Hz), 0.93 (s, 3, H-18).

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.78; H, 9.55. Found: C, 78.74; H, 9.59.

2,10-Cyclo-2,3-seco-*A*-norestra-9(11)-en-17β-ol (7). A solution of **5a** (20 mg) in benzene was hydrogenated and worked up as described above. The solvent was evaporated at a reduced pressure, and afforded 18 mg (90% yield) of **7** as colorless needles: mp 135–136 °C; ir (KBr) 3260, 3060 cm^{-1} and no carbonyl absorption; NMR (C_6D_6) δ 5.45 (m, 1, H-11), 3.69 (m, 1, H-17), 1.25 (d, 3, H-3, J = 7 Hz), 0.89 (s, 3, H-18), 0.75–0.40 (m, 4, cyclopropyl).

Anal. Calcd for $C_{17}H_{26}O$: C, 82.61; H, 10.63. Found: C, 82.79; H, 10.61.

Photolysis of (10*S*)-17β-Hydroxy-3,10-cyclo-3,4-seco-10-estra-9(11)-en-1-one (6). A solution of **6** (25 mg) in benzene (25 ml), stirred with a stream of N_2, was irradiated[23] for 7 h; the reaction was monitored by VPC. Evaporation of solvent at a reduced pressure yielded a gum (23 mg), which was chromatographed on an alumina plate (1000 μ) developed with 50 ml of petroleum ether–acetone (9:1). Elution with methanol afforded 15 mg (79% yield) of crystalline product. After several recrystallizations colorless needles were obtained, the ir and NMR spectra of which were identical with those of **7**, melting point and mixture melting point 135–136 °C. Also two very minor products were observed.

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Registry No.—**3,** 5218-51-9; **4a,** 56296-11-8; **4b,** 58576-63-9; **5a,** 56250-04-5; **5b,** 60538-75-2; **6,** 60538-76-3; **7,** 60538-77-4; 17β-hydroxy-5(10)-estren-3-one, 1089-78-7; 17β-hydroxy-4,9-dien-3-one, 6218-29-7; 3,3-dimethoxyestra-5(10),9(11)-dien-17β-ol, 53303-90-5; 2,5-dimethylhexa-2,3-diene, 36721-80-9; 1,4-cyclohexadiene, 628-41-1.

References and Notes

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