Photochemical Behavior of Δ^4-3-Oxo, Δ^5-7-Oxo, and Δ^1-3-Oxo Steroids in Concentrated Acid Solution[1]

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Irradiation with UV light of 5α-androst-1-en-3-one (**9**) in concentrated sulfuric acid leads to **15** and **16**; similarly 4a-methyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1*H*)-one (**10**) gives **17** and **18**. The formation of the four products is rationalized in terms of a photochemically induced 1,2-alkyl shift to the positively charged positions of the starting carbenium ions. On the other hand, irradiation under the same conditions of **4**, **8**, **7**, and **11** yields, quantitatively, unchanged starting material, while the analogous bicyclic compound $\Delta^{1,9}$-10-methyl-2-octalone (**1**) has been reported to yield photorearrangement products. The lack of reactivity of **7** and **11** can be explained according to the proposed mechanism for the photorearrangement of **1**. In the case of **4** and **8**, the presence of the steroid rings C and D prevents the photorearrangement, but the mechanistic explanation of this effect cannot be determined from the present experimental data.

The irradiation of $\Delta^{1,9}$-10-methyl-2-octalone (**1**) in concentrated sulfuric acid has been reported to yield an interesting photoisomerization by the efficient rearrangement of the generated hydroxycarbocation:[2] **1** → **1H** → **2H** → **3H** → **3** (Scheme I). The importance of this result in relation with steroid chemistry has been emphasized,[2,3] since **1** represents the common "half-molecule" of many steroid hormones.[4] Steroidal conjugated cyclohexenones and cyclohexadienones (Chart I: **4**, **5**, **6**) have certainly received much attention as chromophores for photorearrangements in neutral media,[5] nevertheless, in order to study their behavior in strong acid solution, one must bear in mind two important facts: first, all functional groups and substituents at position 17 of the steroid skeleton are acid labile[6] and, therefore, should be removed in order to avoid unnecessary complications. Second, in strong acid solution, $\Delta^{1,5}$-androstadiene (**6**) tends to isomerize to its $\Delta^{1,4}$ isomer **5**,[7] which reacts further to give a complex mixture of compounds arising mainly from a dienone–phenol rearrangement.[7] When irradiated in concentrated sulfuric acid, **5** yields compounds that are not detected by GC analysis in the absence of light.[7] and whose investigation is under way.

In this paper we report our results obtained by irradiating, in concentrated sulfuric acid, the four steroidal derivatives 4-androsten-3-one (**4**), 4-estren-3-one (**7**), 5-androsten-7-one (**8**), and 5α-androst-1-en-3-one (**9**) and the two octalones 4a-methyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1*H*)-one (**10**) and 4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (**11**) (Chart I).

Scheme I

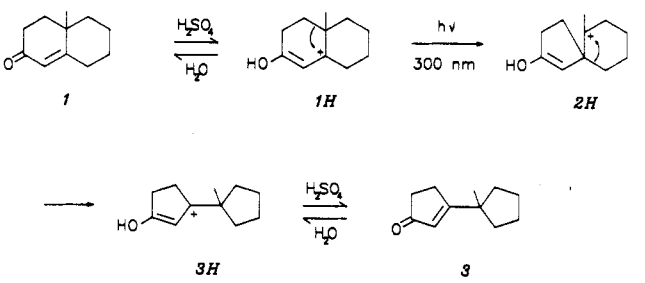
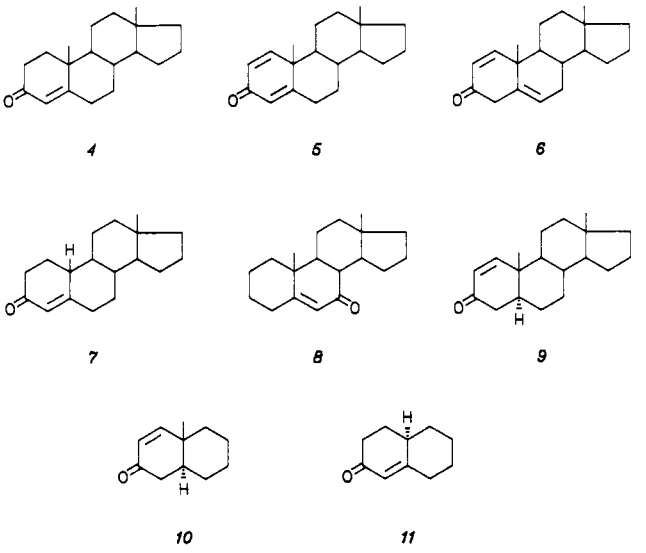


Chart I



Results

Behavior of the Enones in Concentrated Sulfuric Acid. When dissolved in concentrated sulfuric acid, the

(1) Taken in part from the Ph.D. Dissertation of P.L., Instituto Químico de Sarriá, October, 1984. Photochemical Reactions. 21. For part 20, see: Lupón, P.; Grau, F.; Bonet, J. J. *Helv. Chim. Acta* **1984**, *67*, 332.
(2) Cornell, D. G.; Filipescu, N. *J. Org. Chem.* **1977**, *42*, 3331.
(3) Bryce-Smith, D. *Specialist Periodical Reports. Photochemistry*; The Chemical Society: London, 1979; Vol 10, p xxi.
(4) Fieser, L. F.; Fieser, M. *Steroids*; Reinhold: New York, 1959.
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(6) (a) Miura, T.; Takagi, H.; Kimura, M. *Chem. Pharm. Bull.* **1979**, *27*, 783 and previous papers in the series. (b) Jones, H. A. *Can. Spectrosc.* **1971**, *16*, 10.
(7) Izuzquiza, C.; Nieto, A.; Palomer, A.; Canals, F.; Bonet, J. J., unpublished results.

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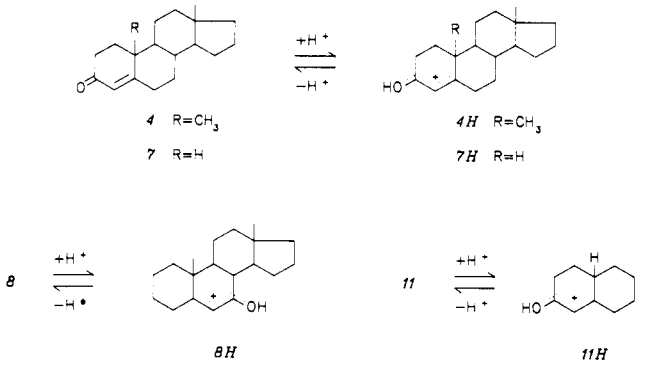
Scheme II



Scheme III

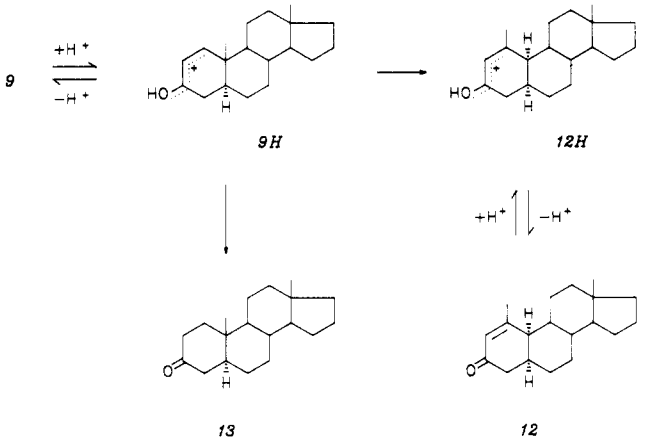


Table I. Product Distribution on Treatment of 9 with Sulfuric Acid

conditions	time, h	yield, % 9	12	13
H_2SO_4 (97%), 20 °C, *c* 9 mg/4 mL	144	83.7	15.1	
H_2SO_4 (97%), 45 °C, *c* 9 mg/4 mL	2	86.4	11.5	
	4	79.6	20.3	
	8	69.9	28.3	
	22	39.7	57.9	
	48	17.0	83.0	
	72	10.8	89.2	
H_2SO_4 (80%), 45 °C, *c* 10 mg/5 mL	48	68.0	16.0	11.0

steroidal enones **4**, **7**, and **8** and the octalone **11** formed stable solutions of the hydroxy carbocations **4H** (λ_{max} = 297 nm), **7H** (λ_{max} = 293 nm), **8H** (λ_{max} = 287 nm) and **11H** (λ_{max} = 288 nm), respectively (Scheme II). The UV spectra of these solutions remained unchanged for long periods of time. The absence of dark reactions was demonstrated by recovery of only starting materials from acid solutions stored for a long time.

The UV spectrum of a freshly prepared solution of **9** in concentrated sulfuric acid (97%), showed a maximum at 270 nm, corresponding to the hydroxy carbocation **9H** (Scheme III). When the spectrum was recorded a few hours later, the change in absorption, shifting to a new maximum at 305 nm, suggested the formation of at least one new compound, as confirmed by TLC and GC analysis (See Table I, Experimental Section). A preparative scale operation afforded 1-methyl-5α,10α-estr-1-en-3-one (**12**) with a 33% yield (GC–MS analysis indicates the presence of the possible C-10 epimer). The structure of **12** was established on the basis of its analytical and spectral data. Confirmatory evidence came from the X-ray structure analysis (data available as supplementary material). Traces of the saturated compound **13** were also detected

Scheme IV

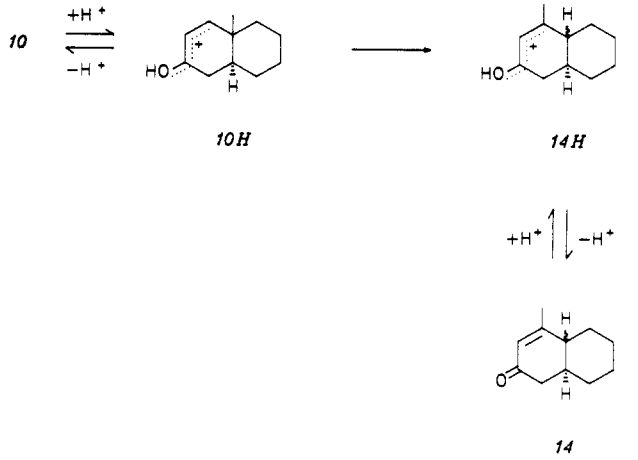


Table II. Product Distribution on Treatment of 10 with Sulfuric Acid

conditions	time, h	yield, % 10	14	*a*
H_2SO_4 (97%), 20 °C *c* 18 mg/6 mL	144	69.7	23.6	4.1
H_2SO_4 (97%), 45 °C, *c* 18 mg/6 mL	2	75.8	19.4	2.6
	4	63.1	29.6	4.5
	22	15.4	70.8	10.7

[a] Unidentified compound.

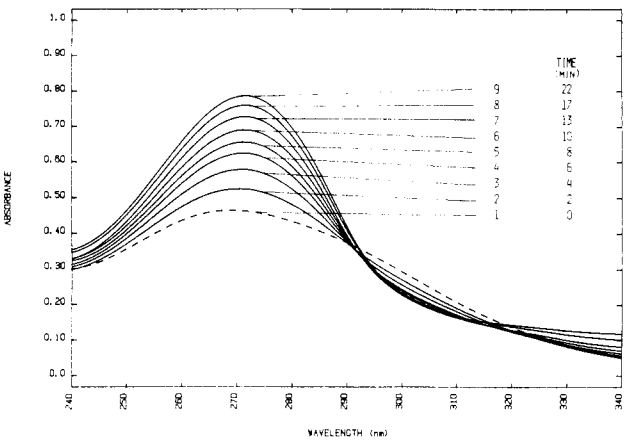


Figure 1. Change in the UV spectrum of a 6 × 10^{-5} M solution of **9** in sulfuric acid, when irradiated with a medium-pressure Hg lamp.

(GC–MS) when 80% sulfuric acid was used.

Similarly, the UV spectrum of a freshly prepared solution of **10** in 97% sulfuric acid showed a maximum at 277 nm, corresponding to the hydroxy carbocation **10H** (Scheme IV), which shifted to 290 nm when recording the spectrum a few hours later, GC analysis showed the presence of two new compounds, whose formation was temperature dependent (see Table II, Experimental Section). Preparative treatment yielded an oil (86%) mixture of two components (GC), which could not be separated by preparative SiO_2 chromatography. Structure **14** was assigned on the basis of its spectral data.

Time-Lapse Spectrometry (TLS).[8] Solutions of ions **4H**, **7H**, **8H**, and **11H** were prepared by dissolving the corresponding enones in concentrated sulfuric acid. Successive short irradiations of these solutions with a medi-

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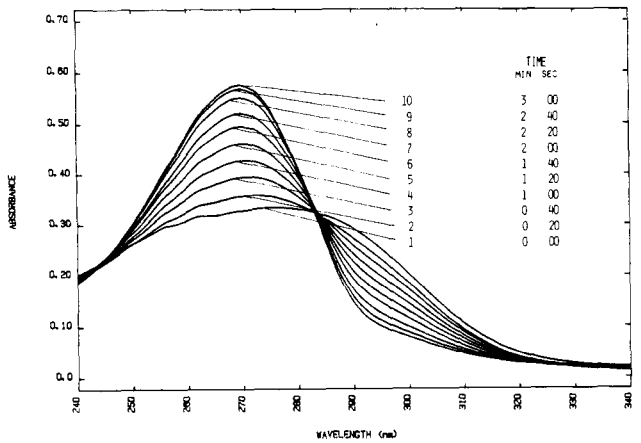


Figure 2. Change in the UV spectrum of a 5×10^{-5} M solution of **10** in sulfuric acid, when irradiated with a medium-pressure Hg lamp.

um-pressure Hg lamp did not bring about changes in their UV spectra.

Figure 1 shows the consecutive changes in the UV spectrum of a dilute solution of **9** in concentrated acid on successive short irradiations. Those changes were similar when a 300 nm or a medium-pressure Hg lamp was used and with 97% or 80% sulfuric acid. The absorption band centered at 270 nm, characteristic of **9H**, was substituted progressively during the irradiation by a new absorption band with λ_{max} = 272 nm, with greater absorptivity, the absence of a well-defined isosbestic point, suggesting side reactions.[8] It is to note that the dark rearrangement of **9H** described in the previous section is much slower than the photoreaction observed in this experiment.

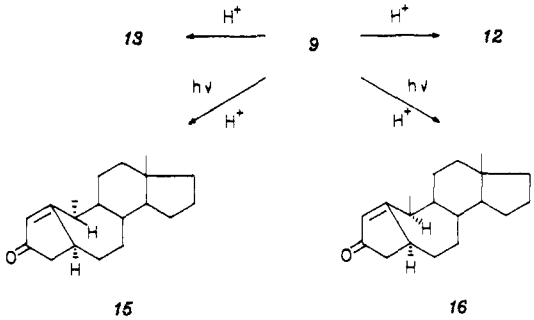
Similarly, Figure 2 shows the analogous changes in the UV spectrum for **10** after short irradiations at 300 nm. The absorption band centered at 277 nm, characteristic of **10H**, was substituted progressively during the irradiation by a new absorption band at λ_{max} = 268 nm, with stronger absorptivity. Again this process is much faster than the dark rearrangement of **10H** described above.

Finally, the behavior of ions **12H** and **14H**, arising from the dark acid-induced rearrangement of **9H** and **10H** (Schemes III and IV) was studied. Solutions of **12H** and **14H** were generated by dissolving **12** and **14** in concentrated sulfuric acid. When irradiated with UV light, no changes in the UV spectra of these solutions were observed.

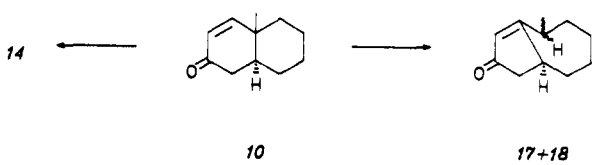
Preparative-Scale Irradiations in Sulfuric Acid. The synthesis of the starting materials (**4** and **7**–**11**) has been already described (see Experimental Section). The most suitable conditions for the preparative irradiations were established after different assays at analytical scale.

Irradiation of **4**, **7**, **8** and **11** in 97% sulfuric acid yielded back the unchanged starting materials. In the case of **9**, a 8.1×10^{-3} M solution in 80% sulfuric acid was irradiated at 300 nm in a preparative immersion unit (quartz). The progress of the photoreaction was evaluated by GC analysis of aliquots, following the procedure described in the Experimental Section. After 48 h of irradiation, a mixture of the following compounds was obtained: 5(10→1)*abeo*-5α,10α-androst-1-en-3-one (**15**) (24%),[9] 5(10→1)*abeo*-5α-androst-1-en-3-one (**16**) (29%), 5α-androstan-3-one (**13**) (18%), **12** (4%), unchanged starting material **9** (16%), and traces of impurifities (Scheme V).[10] After its chromatographic separation, their structures were established on

Scheme V



Scheme VI



the basis of its analytical and spectroscopic data. The structure of **15** and **16** was further confirmed by X-ray analysis (data available as supplementary material).

In order to exclude its possible intermediacy in the formation of the photoproducts **15** and **16**, **12** was irradiated under the same conditions as **9**, for 12 h. No traces of **15** and **16** were detected and only starting material was recovered. This behavior is in agreement with the TLS analysis of **12H** (see above).

A 1.8×10^{-2} M solution of **10** in 97% sulfuric acid was irradiated at 300 nm in quartz tubes. The progress of the reaction was again evaluated by GC analysis of aliquots, as described in the Experimental Section. After 72 h of irradiation and chromatographic separation of the reaction mixture, three main products were obtained: 4-methyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1*H*)-one (**14**) (13%)[9] and (2*R*)- and (2*S*)-2-methyl-bicyclo[5.3.0]dec-10-en-9-one (**17** (2*R*) + **18** (2*S*)) (60%) (Scheme VI), together with two minor (<9%), less polar saturated compounds, isomers of **10**, which could not be identified. The structure of **14** was established by comparison with an independent sample prepared by acid treatment of **10**. The mixture **17** + **18** could not be separated by SiO_2 column chromatography. Structures **17** and **18** were assigned on the basis of the spectroscopic data of the mixture and its GC–MS analysis. Again **14** is not an intermediate in the formation of **17** and **18** since the former is stable under the photoreaction conditions.

Discussion

The observed behavior of **9** in concentrated acid solution in the dark can be rationalized as follows. Formation of hydroxycarbocation **12H**, precursor of **12**, can be interpreted as the result of a Wagner–Meerwein rearrangement from the carbenium ion **9H**, involving two stereospecific 1,2-shifts. Migration of the methyl group from the β face of the steroid would yield **19H**[11] and the subsequent 1,2-shift of hydride from α face of the molecule would give the carbocation **12H** (Scheme VII, path a). This dark reaction can be explained in its first step by the coplanarity of the empty p orbital of the carbenium ion and the σ orbital supporting the migrating methyl group.

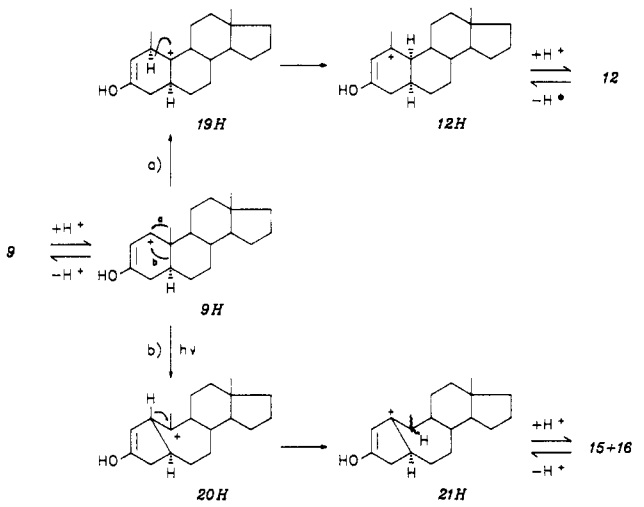
The saturated compound **13** (Scheme III) can be the result of an acid catalyzed disproportionation, a phenom-

(9) Yields calculated on GC analysis.

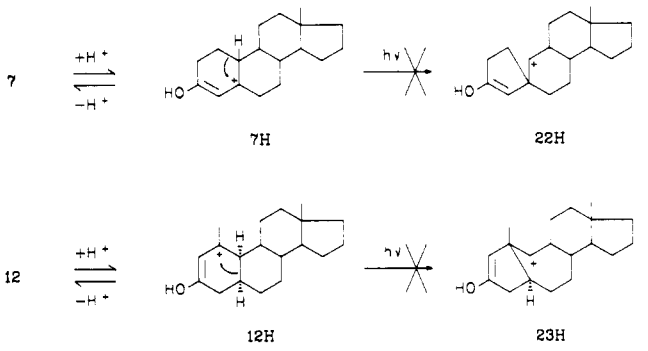
(10) For a short preliminary paper of these results, see: Lupón, P.; Ferrer, J. C.; Piniella, J. F.; Bonet, J. J., *J. Chem. Soc., Chem. Commun.* **1983**, 718.

(11) Discrete species with positive charge on a specific carbon atom are used only for facilitating the comprehension of the mechanism.

Scheme VII



Scheme VIII



enon described in the literature,[12] the corresponding oxidized compound not being isolated.

The formal mechanism for the formation of the photoproducts **15** and **16** involves a photochemically induced migration of the C(5)–C(10) bond in **9H** to give **20H** and a second hydride 1,2-shift toward C(10) to yield the carbocation **21H**, protonated form of the isolated compounds **15** and **16** (Scheme VII, path b). An analogous mechanism has been postulated to explain the results after the irradiation in strong acid solution of 4,4-dimethylcyclohexenone.[13]

The fact that a mixture of stereoisomers (**15** + **16**) is obtained indicates that the process is not stereospecific, probably in its second step.

As mentioned above, **12H** is photostable and cannot be an intermediate in the formation of **15** and **16** via an alternative mechanism.

The results obtained after the irradiation of the octalone **10** in strong acid solution indicate that, in this case, there is a similarity of behavior between the bicyclic and the tetracyclic substrates, with an assumed common mechanism.

On the contrary, unlike their bicyclic analogue **1**, steroids **4** and **8** do not react when irradiated in acidic medium. This lack of reactivity must be attributed to conformational and/or electronic effects derived from the presence of steroid ring C or both rings C and D, which cannot be stated from the present experimental information.

The lack of photochemical reactivity in concentrated acid solution of **7**, which is the 19-nor analogue of **4**, can be explained according to the proposed mechanism for the rearrangement of **1**. The photochemically induced 1,2-shift **1H** → **2H** (Scheme I) implies the conversion of the hydroxy carbocation **1H** to the tertiary carbocation **2H**. In the case of **7** a 1,2-migration of this type (Scheme VIII) would involve the thermodynamically more unfavourable conversion of **7H** to the secondary carbocation **22H**, and this could prevent the initial step of the reaction. To assess this hypothesis, the octalone **11** was irradiated under the same conditions as **1**, being quantitatively recovered unchanged. This result gives support to **2H** as an intermediate in the photoisomerization of **1**.

Likewise, the photounreactivity of **12**, in contrast to **9**, can be also explained in terms of the difference in stability of the implied carbocations. The conversion **12H** → **23H** (secondary) (Scheme VIII) would be thermodynamically more unfavorable than the analogous conversion **9H** → **20H** (tertiary) (Scheme VII).

Conclusion

It has been pointed out that in many instances, there is a very marked correspondence of the photoreactions of a protonated compound and those of the carbonyl compound itself.[13] Therefore, the remarkable differences in photochemical behavior existing between the carbenium ions described in this work and the conjugated enones from which they derive by protonation, deserve to be emphasized: while 17β-acetoxy-4-androsten-3-one undergoes the type A photorearrangement[5] and 3β-acetoxycholest-5-en-7-one suffers a double bond shift[14] when UV-irradiated in neutral medium, **4H** and **8H** are unreactive, as shown (it is to be remarked that the bicyclohexanone rearrangement is not observed with 19-nortestosterone, when irradiated in *tert*-butyl alcohol or benzene).[14] Also although 1-androsten-3-ones yield only dimerization products when irradiated with UV light,[15] **9H** affords the photorearranged *abeo* steroids **15** and **16**.

The marked differences in reactivity obserbed between the carbenium ions themselves seem to indicate the existence of important conformational and/or electronic requirements for the reactions to proceed.

We feel these facts are of interest, both from the mechanistic point of view and their possible synthetic utility. Work is in progress to better determine the influence of the above mentioned factors on the outcome of the irradiation of these reactive intermediates.

Experimental Section

General Remarks. Extractions were carried out with diethyl ether. Lobar silica gel prepacked columns (Merk) were used for preparative chromatography. Infrared spectra were recorded on a Perkin-Elmer 683 or 580 instrument. Ultraviolet spectra were measured on a Hewlett-Packard 8450A spectrophotometer. ^{1}H NMR spectra were run on either a Bruker WH-270 or a Varian XL-200 spectrometer. The chemical shifts are reported in δ values relative to tetramethylsilane, which was used as internal standard. The following abbreviations are employed: (s) singlet, (d) doublet, (m) multiplet, (br) broad, (c) complex signal. Mass spectra were measured on a Hewlett-Packard 5930A or a Varian MAT CH5 instrument. Melting points are uncorrected.

GC analyses were performed with a Varian Aerograph 1700 instrument equipped with a flame ionization detector coupled to a Spectra Physics Autolab System I computing integrator or with a Hewlett-Packard 5790A instrument equipped with a flame ionization detector coupled to a Hewlett-Packard 3390A integrator.

(12) Kimura, A.; Harita, K. *Chem. Pharm. Bull.* **1973**, *21*, 1205. Harmon, K. M. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley Interscience: New York, 1973; Vol. 4, Chapter 29.

(13) Childs, R. F. *Rev. Chem. Intermed.* **1980**, *3*, 285.

(14) Schaffner, K. In *Organic Reactions in Steroid Chemistry*; Fried, J., Edwards, J. A., Eds.; Van Nostrand Reinhold: New York, 1972; Vol. 2; Chapter 13.

(15) Kropp, P. J. In *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1967; Vol. 1, Chapter 1.

Glass capillary columns OV 101 (length 27 m) and OV 1 (length 25 m) were used, respectively.

GC–MS analyses were carried out with an OV 1 column (length 12 m) coupled to a Hewlett-Packard GC/MS 5995A spectrometer.

Irradiations were carried out with either an immersion unit with a medium-pressure Hg lamp (Q81, Quarzlampen GmbH, Hanau), or a Rayonet RPR-208 photochemical reactor equipped with eight RUL-3000 Å lamps, at room temperature and under N_2 atmosphere.

Synthesis of the Steroidal Ketones 4, 7, 8, and 9. The oxo steroids 4, 8, and 9 were prepared from 3β-acetoxy-5-androsten-17-one and 7 from estrone, as starting materials, following the published procedures.

4-Androsten-3-one (4).[16] 3β-Acetoxy-5-androsten-17-one (24) (18.0 g, 0.055 mol) was converted to the alcohol 5-androsten-3β-ol (25) by a modified Huang-Minlon[17] reduction according to the procedure of Shapiro and Djerassi.[16] The crude solid obtained (15.0 g) was used in the next step without further purification.

The above alcohol 25 (15.0 g, 0.055 mol) was converted to the enone 4 by the Oppenauer oxidation, employing the exact conditions of Eastman and Teranishi.[18] Pure 4-androsten-3-one (4) (13.5 g, 0.050 mol, 90%) was obtained as white crystals, mp 105–106 °C (ethyl acetate) (lit.[16] mp 104–105 °C).

5-Androsten-7-one (8).[19] 5-Androsten-3β-ol (25) (3.482 g, 0.013 mol) was treated with acetic anhydride in pyridine (room temperature, 14 h) to afford the corresponding acetate 26 in quantitative yield.

Allylic oxidation of 26 (3.421 g, 0.011 mol) with CrO_3/pyridine[20] gave, after chromatographic separation (silica gel), 1.509 g (42%) of 3β-acetoxy-5-androsten-7-one (27).

Treatment of 27 (1.483 g, 4.49 mmol) with hydrochloric acid in ethanol gave 3,5-androstadien-7-one (28) in 97% yield.[21]

Finally, the enone 8 was obtained by transfer hydrogenation[22] of 28 (250 mg, 0.926 mmol) with 5% Pd/C–cyclohexene. The crude was chromatographed on silica gel to give 8 in 37% yield, mp 143.5–144 °C (ethanol) (lit.[19] mp 144.5–146 °C).

5α-Androst-1-en-3-one (9).[16] The ketone 4 (4.2 g, 0.015 mol) was subjected to lithium–liquid ammonia reduction in the same conditions as described for testosterone.[23] The crude (4.1 g), isolated as usual, was chromatographed on silica gel (cyclohexane/ethyl acetate, 9:1) to give the saturated ketone 13 (2.2 g, 0.008 mol, 52%) as the main product, mp 100–100.5 °C (ethanol/H_2O) (lit.[24] mp 104–105 °C).

A solution of 13 (1.8 g, 0.007 mol) and DDQ (1.53 g, 0.007 mol) in dioxane (55 mL) with *p*-toluenesulfonic acid (1.9 g, 0.001 mol) was left at room temperature for 4 days.[25] Following removal of the hydroquinone, the filtrate was evaporated to dryness under reduced pressure and the residue diluted with methylene chloride. After filtration through neutral alumina (methylene chloride, methylene chloride/acetone, 4:1, and methylene chloride/acetone, 1:1), the combined eluates were evaporated to dryness (1.71 g).

Chromatography of the crude on silica gel (petroleum ether/ethyl acetate, 9:1) gave first starting material 13 (60 mg, 3%) and then the pure desired enone 9 (1.030 g, 58%), mp 101–103 °C, after crystallization from acetone/petroleum ether (lit.[16] mp 102–103 °C). Two further fractions were shown to consist of the corresponding 4-en-3-one 4 (220 mg, 12%) and 1,4-dien-3-one 5 (174 mg, 10%), mp 80–81 °C (lit.[26] mp 83–84 °C).

4-Estren-3-one (7).[27] Reduction of estrone (834 mg, 3.05 mmol) following the Huang-Minlon procedure[17] afforded 3-hydroxy-1,3,5(10)-estratriene (29) in quantitative yield. Dimethyl sulfate (15 mL) was added dropwise to a solution of 29 (800 mg, 3.12 mmol) in 10% KOH (500 mL), and the solution was stirred for 3 h at room temperature. Chloroform extraction and recrystallization (acetone/petroleum ether) gave 3-methoxy-1,3,5(10)-estratriene (30) in 89.5% yield. Birch reduction of 30[28] (650 mg, 24 mmol) followed by acid hydrolysis yielded, after chromatography, 31% of the desired enone 7 together with an 11% of 5(10)-estren-3-one and 30% of 3-methoxy-2,5(10)-estradiene.

Synthesis of the Octalones 10 and 11. 4a-Methyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1*H*)-one (10).[29] This compound was prepared via $\Delta^{1,9}$-10-methyl-2-octalone (1) following the procedure of Yanagita and Yamakawa.[29] 1 was obtained by Robinson annelation of 2-methylcyclohexan-1-one and 1-(diethylamino)butan-3-one, according to the variation of Yanagita and Yamakawa[30] that uses the Mannich base instead of the methiodide, with a trace of metallic sodium. Vacuum distillation of the crude afforded 1 with 30% yield.

Lithium–liquid ammonium reduction[31] of 1, followed by bromination with bromine in acetic acid,[32] subsequent Mattox–Kendall treatment as described in the literature,[29] and finally regeneration of ketone from the corresponding (2,4-dinitrophenyl)hydrazone with pyruvic acid,[29] yielded 10. The crude product was purified by chromatography on silica gel (toluene) and subsequent vacuum distillation (12% from 1).

4,4a,5,6,7,8-Hexahydronaphthalen-2(3*H*)-one (11).[33] This compound was prepared exactly as reported by Bergman from methylvinyl ketone and cyclohexanone, by Robinson annelation.

General Procedure for the Stability Assays in Sulfuric Acid. A solution of known concentration of each product in 97% or 80% sulfuric acid was prepared. Aliquots were removed periodically. The samples were diluted with ice–water and extracted with ether, washing with water till neutral. Previous neutralization of the acidic solutions with aqueous sodium bicarbonate was found to be unnecessary. Analysis of the extracts was performed by TLC or GC. The results obtained in the case of 9 and 10 are shown in Tables I and II, respectively.

Acid-Catalyzed Rearrangement of 5α-Androst-1-en-3-one (9). The enone 9 (450 mg, 1.7 mmol) was heated at 45 °C for 53 h in 97% (by weight) aqueous sulfuric acid (200 mL). After rapid cooling and the addition of crushed ice (1000 mL), the mixture was extracted as usual, to yield an amorphous residue (402 mg) containing 14% of 9 (GC, OV 1 at 240 °C).

Chromatography on silica gel with toluene furnished 136 mg of pure 1-methyl-5α,10α-estr-1-en-3-one (12), mp 98.5–100 °C, after crystallization from diethyl ether/petroleum ether: UV (EtOH) λ_{max} 243 nm (ε 12 100); IR (KBr, cm^{-1}) 1667, 1650, 1610; ^1H NMR (270 MHz, $CDCl_3$) 0.70 (s, 3 H, 18-CH_3), 2.09 (s, 3 H, 1-CH_3), 2.20 (dd J = 18 Hz, J = 2 Hz, 1 H, 4-CH), 2.49 (dd J = 18 Hz, J = 5 Hz, 1 H, 4-CH), 2.62 (br, 1 H, 10-CH), 5.78 (br s, 1 H, 2-CH); mass spectrum, m/e (relative intensity) 272 (M^+), 122 (100).

Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.64; H, 10.56.

The structure has been confirmed by X-ray structural analysis.

Acid-Catalyzed Rearrangement of 4a-Methyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1*H*)-one (10). The octalone 10 (500 mg, 3.0 mmol) was heated at 45 °C for 3 days in 97% (by weight) aqueous sulfuric acid (170 mL). The reaction crude was worked up as above to yield 430 mg of an oil. GC analysis (OV 1 at 140 °C) indicated no 10 present, and two product peaks (t_R = 2.35 min (10%) and t_R = 2.53 min (90%)). All attempts to separate the products by chromatography on silica gel failed.

The major component was identified as 4-methyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1*H*)-one (14). Spectral Data:

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UV (EtOH) λ_{max} 237 nm; IR ($CHCl_3$, cm^{-1}) 1660–1665, 1620; ^1H NMR (270 MHz, $CDCl_3$) 1.88 (d $J \approx 1$ Hz, 3 H, CH_3), 2.07 (dd, $J = 16$ Hz, $J = 4$ Hz, 1 H, 1-CH), 2.45 (dd $J = 16$ Hz $J = 12$ Hz, 1 H, 1-CH), 5.72 (s, 1 H, 3-CH); mass spectrum, m/e (relative intensity) 164 (M^+), 122 (100).

Minor component: mass spectrum, m/e (relative intensity) 164 (M^+), 122 (100).

Time-Lapse Spectrometry. Changes in the UV spectra of a solution of known concentration [(6–7) × 10^{-5} M] of each product in 97% of 80% sulfuric acid were recorded upon successive short intervals of irradiation with light of 300-nm wavelength (RPR-3000 Å source) or a medium-pressure Hg lamp (Q 81, Quarzlampen GmbH, Hanau).

Control of the Photochemical Reactions. The irradiations were followed by TLC or GC analysis on diluted aliquots as specified for the dark reactions (see above).

Irradiation of 4, 7, 8, and 11. A solution of 100 mg, of **4** in 5 mL of 97% (by weight) aqueous sulfuric acid was irradiated for 12 h in a Pyrex vessel at room temperature, with a medium-pressure Hg lamp. After addition of crushed ice and the usual workup, removal of the solvent in vacuo yielded 96 mg of a crude which was filtered through silica gel (cyclohexane/ethyl acetate, 8:2) and identified as starting material **4**, after recrystallization from ethyl acetate (mp, TLC, and IR).

Solutions of 100 mg of **7**, **8**, and **11** in 100 mL of 97% (by weight) aqueous sulfuric acid were irradiated for 48 h as above, to yield quantitatively unchanged starting material (mp, TLC, and IR).

Irradiation of 9. A solution of 665 mg of **9** in 300 mL of 80% (by weight) aqueous sulfuric acid was irradiated for 48 h with 300-nm light without filter. After addition of crushed ice the reaction mixture was extracted with diethyl ether in the usual way to yield 609 mg of a mixture containing 20.5% of starting material **9** (GC, OV 101, at 240 °C). Chromatography on a Lobar C silica gel column (toluene/diethyl ether, 95:5) yielded first 82 mg of 5α-androstan-3-one (**13**), identical (mp, TLC, IR, MS, GC) with an independent sample prepared by the Birch reduction of **4**. A second fraction consisted of starting material **9**. The third fraction afforded an oily product identified (TLC, IR, ^1H NMR, MS, GC, UV) as **12**. Finally the last three fractions were shown to consist of 64 mg of 5(10 → 1)*abeo*-5α,10α-androst-1-en-3-one (**15**), mp 75–77.5 °C, after crystallization from methanol/water, 110 mg of a mixture of isomers **15** and **16**, and 112 mg of 5(10 → 1)*abeo*-5α-androst-1-en-3-one (**16**), mp 125–128.5 °C, after crystallization from acetone/petroleum ether.

15 spectral data: UV (EtOH) λ_{max} 234 nm (ε 18400); IR ($CHCl_3$, cm^{-1}) 1680, 1600; ^1H NMR (200 MHz, $CDCl_3$) 0.697 (s, 3 H, 18-CH_3), 1.232 (d $J = 7$ Hz, 3 H, 19-CH_3), 2.065 (dd $J = 18$ Hz, $J = 0.7$ Hz, 1 H, 4-CH), 2.639 (dd + m $J = 18$ Hz, $J = 6$ Hz, 1 H + 1 H, 4-CH + 10-CH), 3.00 (m, 1 H, 5-CH), 5.832 (s, 1 H, 2-CH); mass spectrum, m/e (relative intensity) 272 (M^+), 123 (100). Attempts to recrystallize **15** for elemental analysis were negative. Nevertheless a monocrystal was obtained by slow evaporation from acetone/petroleum ether, and the structure has been confirmed by X-ray structural analysis.

16 spectral data: UV (EtOH) λ_{max} 235 nm (ε 18200); IR (KBr, cm^{-1}) 1700, 1690, 1600; ^1H NMR (200 MHz, $CDCl_3$) 0.724 (s, 3 H, 18-CH_3), 1.240 (d, $J = 7$ Hz, 3 H, 19-CH_3), 2.002 (dd $J = 18$ Hz, $J = 3$ Hz, 1 H, 4-CH), 2.680 (m, $J = 1$ Hz, $J = 6$ Hz, $J = 18$ Hz, 1 H, 4-CH), 2.86 + 2.93 (2 m, 1 H + 1 H, 10-CH + 5-CH), 5.875 (br s, 1 H, 2-CH); mass spectrum, m/e (relative intensity) 272 (M^+), 123 (100).

Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.67; H, 10.67.

The structure has been confirmed by X-ray structural analysis.

Irradiation of 4a-Methyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1*H*)-one (10). A solution of 972 mg of octalone **10** in 325 mL of 97% (by weight) aqueous sulfuric acid was irradiated for 12 h with 300-nm light without filter. Dilution with crushed ice followed by the usual workup afforded 975 mg of a crude containing 7% of starting material **10** (GC, OV 101 at 150 °C). Two successive chromatographies on silica gel, the first with benzene/diethyl ether, 9:1 and 7:3, and the second with toluene, yielded 13 and 26 mg of two unidentified product, 25 mg of starting material **10** (GC, TLC), 80 mg of **14** (TLC, GC, IR, ^1H NMR, UV, and MS) and 390 mg of an oil identified as a mixture of (2*R*)- and (2*S*)-(7*S*)-2-methylbicyclo[5.3.0]dec-10-en-9-one (**17** + **18**) (GC, OV 101, at 120 °C: two product peaks, 15% and 80% intensity). Spectral data: UV (EtOH) λ_{max} 234 nm; IR ($CHCl_3$, cm^{-1}) 1685, 1600; ^1H NMR (270 MHz, $CDCl_3$) 1.14 (d, $J = 7$ Hz, 3 H, CH_3), 1.94 (dd, $J = 18$ Hz, $J = 4$ Hz, 1 H, 8-CH), 2.55 (c (dd, $J = 18$ Hz, $J = 6$ Hz, + m), 2 H, 8-CH + 2-CH), 2.92 (br, 1 H, 7-CH), 5.84 (m, 1 H, 10-CH); mass spectrum, m/e 164 (M^+).

GC/MS analysis of the mixture.

MS (15% peak), m/e (relative intensity) 164 (M^+) (66.7), 122 (81.5), 121 (70.4), 107 (88.9), 95 (81.5), 94 (100), 93 (69.1), 91 (61.7), 79 (91.4), 77 (56.8), 67 (50.6), 53 (72.8), 41 (91.4).

MS (80% peak), m/e (relative intensity) 164 (M^+) (71.2), 122 (97.5), 121 (60.7), 107 (88.3), 95 (83.4), 94 (100), 93 (78.5), 91 (65.6), 79 (100), 77 (60.1), 67 (47.2), 53 (69.3), 41 (93.3).

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Supplementary Material Available: Details of data collection, structure solution and refinement, atomic positional parameters, thermal parameters, complete tables of bond lengths and angles, and schematic drawings and stereoscopic views of molecular packings for the X-ray structure determination of **12**, **15**, and **16** (11 pages); structure factor tables for **12**, **15**, and **16** (8 pages). Ordering information is given on any current masthead page.