Antenna-Initiated Photochemistry in Polyfunctional Steroids. Intramolecular Singlet and Triplet Energy Transfer between Aryl, Ketone, and Alkene Groups in 6*β*-(Dimethylphenylsiloxy)-5*β*-androstanes[1]

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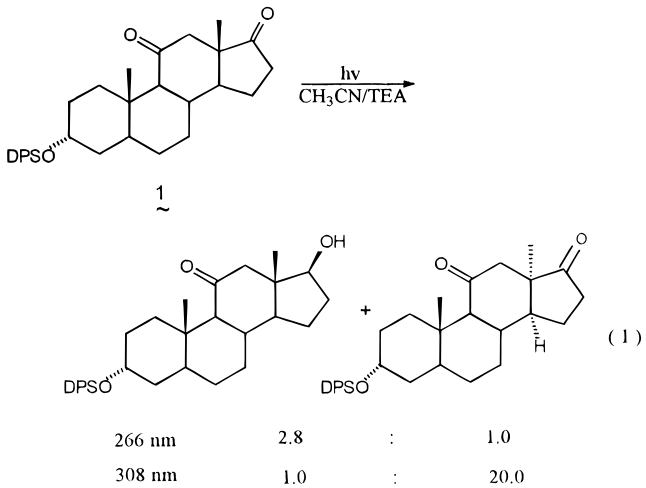
Steroids have been prepared that bear a dimethylphenylsiloxy (DPSO) group and additional C3 and/or C17 ketone functionalities. The DPSO group has been used to harvest 266 nm photons and then activate the ketone functionalities through intramolecular singlet−singlet energy transfer (intra-SSET). Thus, the monoketones 3,3-(ethylenedioxy)-6*β*-(DPSO)-5*β*-androstan-17-one (**6**) and 6*β*-(DPSO)-5*β*-androstan-3-one (**8**) both exhibit DPSO-initiated photochemistry at the carbonyl groups. Irradiation of the diketone, 6*β*-(DPSO)-5*β*-androstane-3,17−dione (**5**), gives two ring D-derived photoproducts, an epimer (**19**) and an enal (**18**), both coming from the C17 ketone excited singlet state. Here $\Phi_{intra-SSET}$ from the aryl antenna to the carbonyl groups is ca. 88% efficients and occurs with a rate of ca. 6.5×10^9 s^{-1}, with the chemistry indicative of facile intra-SSET between the C3 and C17 ketones. The alkylidene group at C3 (i.e., as in 6*β*-(DPSO)-3(*E*)-ethylidene-5*β*-androstan-17-one (**33**) and its *Z* isomer (**34**)) has no effect on the rate or efficiency of aryl activation of the C17 ketone.

Introduction

There has been extensive recent interest in the intramolecular transmission of electrons and excited state energy in polyfunctional molecules. A number of these efforts are directed toward the preparation of molecular electronic and photonic wires.[2] In our laboratory we have been studying photochemistry resulting from intramolecular electronic energy transfer among functionalities in polyfunctional steroids.[3] In this program we have utilized an antenna group (e.g., a dimethylphenylsiloxy (DPSO) functionality) to harvest photon energy and have explored the efficiency and selectivity by which this energy can be redistributed so as to activate distal functionalities. In particular, we have been employing multiple arrangements of antenna and acceptor groups in order to understand the consequences of intramolecular energy migration by both through-bond and through-space interactions (TBI and TSI, respectively). The distances between, and relative orientations of, the donor (DPSO) and the acceptor (typically, ketone or olefin) groups, as well as the positional relationships of the acceptor chromophores, have been varied in order to elucidate the dependence of internal energy migration on these factors.

Structures **1**−**4** depict functionality relationships we have reported on to date.[3] They are classified according to the spatial relationships of donor (D) and acceptor groups (A) (Chart 1). The "terminal" C17 carbonyl group in **1** and **2** has proven diagnostically useful because its singlet and triplet chemistry are easily differentiable and the ketone itself does not undergo significant intersystem crossing.[3] This has allowed us to use this ketone as a "reporter" group to distinguish between singlet (i.e., intramolecular singlet−singlet; intra-SSET) and triplet (intramolecular triplet-triplet; intra-TTET) energy-transfer processes. The alkene at C17 in **3** and **4** has served a similar function in that it is exclusively activated by intra-TTET. For example, in **1** and **3** there is efficient intra-SSET from the DPSO group to C11, intersystem crossing into the triplet manifold, and a transfer of triplet energy to C17 via intra-TTET. The result is exemplified by the chemistry shown in eq 1, where one may note the



(1)

266 nm	2.8	:	1.0
308 nm	1.0	:	20.0

difference in chemistry observed when **1** is excited into the antenna (266 nm) or the ketone groups (308 nm) in the presence of reductant, triethylamine (TEA).[3c] The localization of triplet energy at C17, which results in the reduction of the ring D ketone, is likewise manifested as *Z*/*E* isomerization of the C17 alkene in **3** and **4**.[3a,b] In all three cases the C11 and C6 ketones may be thought

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(1) Organic Photochemistry. 112. Part 111: Post, A. J.; Morrison, H. *J. Org. Chem.* **1996**, *61*, 1560−1561. Presented, in part, at the 209th National Meeting of the American Chemical Society, 1995, Anaheim, CA. Abstracted from the Doctoral Dissertation of S. A. Jiang, Purdue University, Aug 1995.

(2) Wagner, R. A.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759−9760 and references therein.

(3) (a) Agyin, J. F; Morrison, H. *J. Am. Chem. Soc.*, in press. (b) Morrison, H.; Agyin, K.; Jiang A.; Xiao, C. *Pure Appl. Chem.* **1995**, *67*, 111−116. (c) Wu, Z.-Z.; Nash, J.; Morrison, H. *J. Am. Chem. Soc.* **1992**, *114*, 6640−6648. (d) Wu, Z.-Z.; Morrison, H. *J. Am. Chem. Soc.* **1992**, *114*, 4119−4128. (e) Wu, Z.-Z.; Morrison, H. *Photochem. Photobiol.* **1989**, *50*, 525−530.

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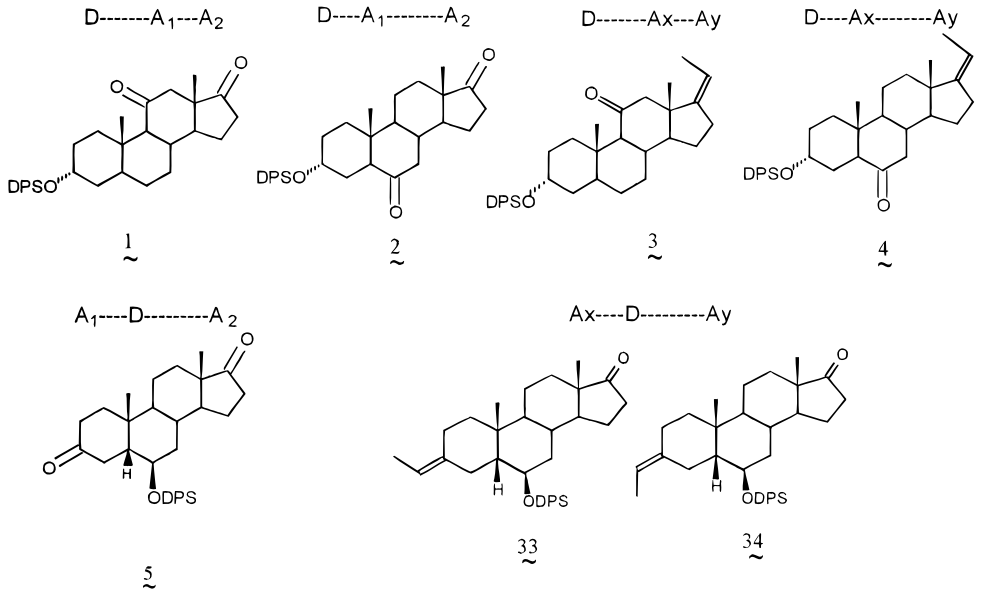
Chart 1



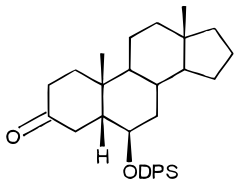
of as functioning as "singlet−triplet switches" within the steroid photonic wire. Though it appears that the C11 ketone is only able to transfer triplet energy to C17, the C6 ketone can transfer singlet energy to C17 when an appropriate (i.e., carbonyl) acceptor is present.[3d]

In the present study we describe the results of three structural modifications in the steroid "wire" that are of mechanistic interest (cf. **5**, **33**, **34**): we have employed ring A/B cis-fused 5β-androstanes as the molecular scaffold, we have inserted the DPSO antenna at C6 *between* the potential 3 and 17 ketone acceptor groups (the latter thus being at the *maximum separation* allowed by the steroid framework; cf. **5**), and we have inserted a triplet "gate" at C3 that could be expected to efficiently intercept C6 DPSO triplets (**33**, **34**). We expect the concept of multiplicity "gates" to prove quite useful in developing the properties of such photonic wires.

We also report on several monoketonic models that help us to elucidate the energy migration pathways in these trifunctional substrates.

Results

Synthesis of Compounds 5, 6, 8, 33 and 34. 6β-(DPSO)-5β-androstane-3,17-dione (**5**) was prepared in five steps as shown in Scheme 1. Compound **10** was prepared in ca. 55% yield by oxidation of the alcohol **9** and purified by chromatography. After protection of the carbonyl groups to give a mixture of **12**, **13**, and **14** (8:2:1), hydroboration and oxidation of **12** afforded 3,3;17,-17-bis(ethylenedioxy)-6β-hydroxy-5β-androstane (**15**) as the major isomer. The stereochemical assignment for **15** was based on the characteristic ^{1}H NMR chemical shift and splitting pattern for *H*C-6β-OH at 3,74−3.72 δ.[4,5] The addition from the β face is consistent with reports that hydrogenation of the 5/6 double bond in steroids bearing substituents at C3 preferentially affords 5β-products.[6−8] Treatment with acetone and a catalytic amount of $PdCl_2(CH_3CN)_2$ for 2−3 days[9] effected cleavage of the diketal to give a 4:1 mixture of **16** and the derivatized monoketone **17** in ca. 60% yield. Silylation of these products with chlorodimethylphenylsilane (DPSCl) gave **5** and **6** in 80% yield.[3] NMR analysis of **5** using 2D NOESY showed two crosspeaks corresponding to the correlation of both the 19-CH_3 at δ 1.2 and the 18-CH_3 at δ 0.85 with the DPSO methyl groups at δ 0.35 and 0.39. This confirmed the axial orientation of the DPSO group in the assignment of **5** as a 5β-androstane. Compound **8** was prepared by first removing the 17-C=O group in **9** using NH_2NH_2 in diethylene glycol and then proceeding as in Scheme 1.

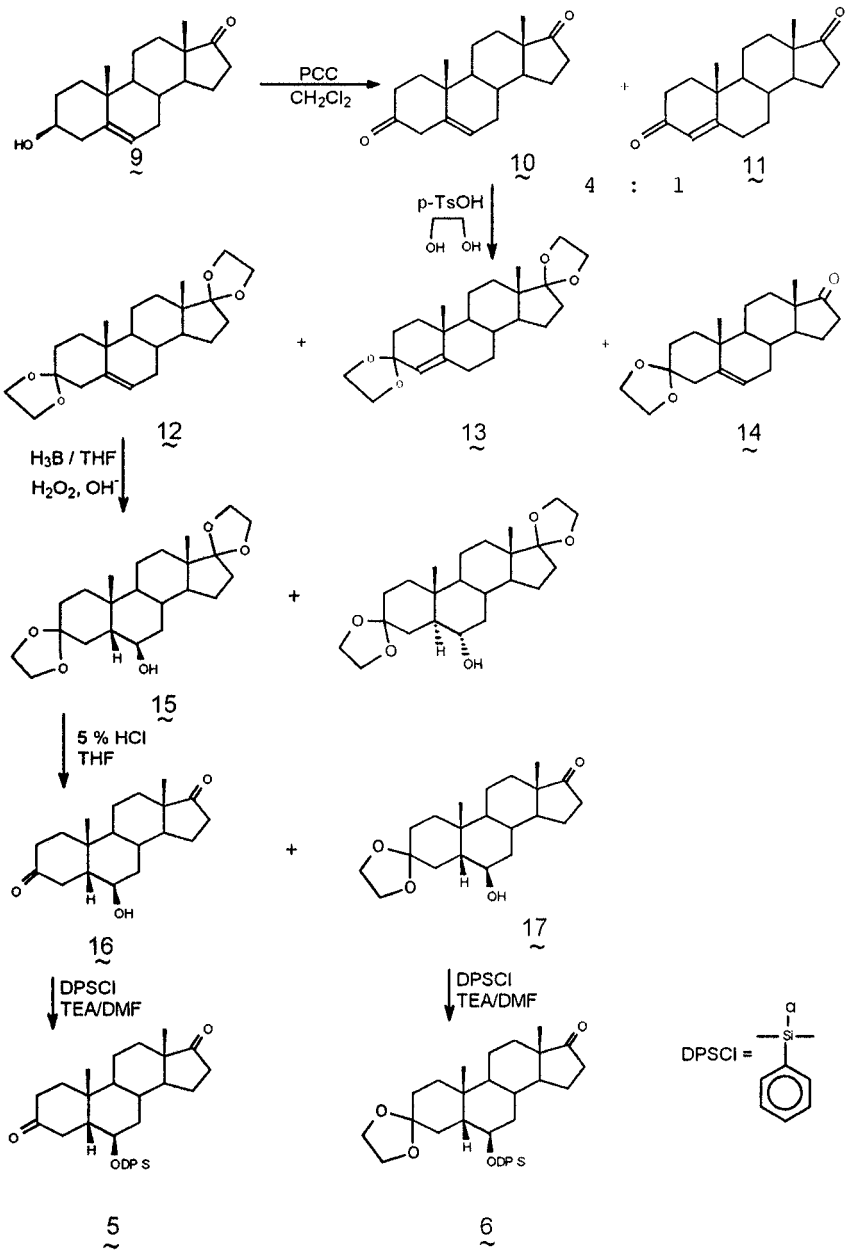


8

6β-(DPSO)-3(*E*)-ethylidene-5β-androstan-17-one (**33**) and its *Z*-isomer (**34**) were prepared by a modification of Scheme 1; i.e., the diketo alcohol, **16**, was treated with ethyltriphenylphosphonium bromide to give a mixture of *E* and *Z* isomers (**32**) in a ratio of 1.6:1. Dimethylphenylsilylation of this gave a mixture of **33** and **34** that was purified by flash and Chromatotron chromatography and then separated by HPLC. The assignment of the major isomer as having the *E* configuration was established from 1-D ^{1}H and 2-D COSY, NOESY, and HMQC NMR spectroscopy. For this isomer, the H-2 protons at δ 1.68−1.61 and the H-4 proton at 1.01−0.92 are coupled to the

(4) Bridgeman, J. E.; Cherry, P. C.; Clegg, A. S.; Evans, J. M.; Jones, E. R. H.; Kumar, V.; Meakins, G. D.; Morisawa, Y.; Richards, E. E.; Woodgate, P. D. *J. Chem. Soc. C* **1970**, 250−257.
(5) Pouchert, C. J.; Behuke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*; Aldrich: Milwaukee, 1993.
(6) Lewis, J. R.; Shoppee, C. W. *J. Chem. Soc.* **1955**, 1365−1370.
(7) Shoppee, C. W.; Pierce, J. H.; Stephenson, R. J.; Summers, G. H. R. *J. Chem. Soc.* **1955**, 694−703.
(8) Schmitt, J.; Panhouse, J. J.; Hallot, A.; Cornu, P.; Pluchet, H. *Bull. Soc. Chim. Fr.* **1963**, 807.
(9) Lipshutz, B. H.; Pollart, D.; Monforte, J.; Kotsuki, H. *Tetrahedron Lett.* **1985**, *26*, 705−708.

Scheme 1



methyl group on the olefin at δ 1.59−1.58 but not to the vinyl proton. This is consistent with placement of C2 as cis to the methyl group and trans to the vinyl proton. Support is provided by the existence of a very clear crosspeak for an H-4 resonance at δ 1.75−1.68 with the vinyl proton resonance at δ 5.33−5.28. Thus, we conclude that the major isomer (**33**) has the *E* configuration.[10]

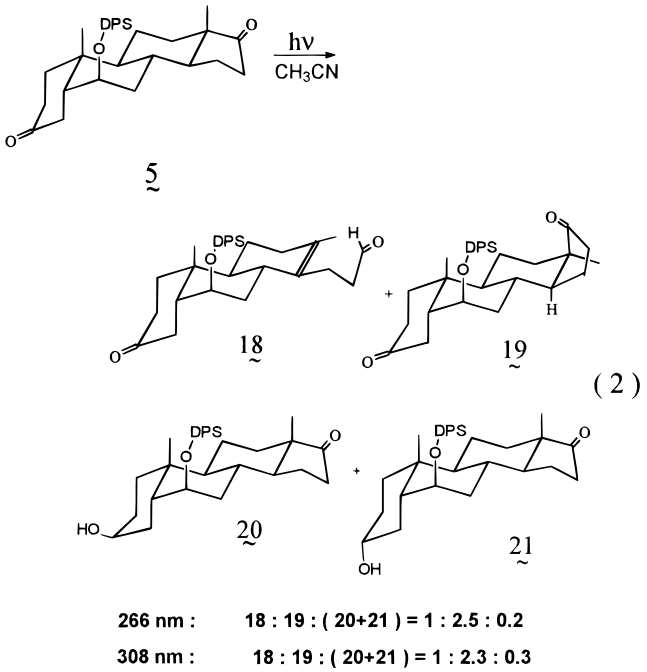
Photochemistry. Photolysis of 5 in MeCN at 266 nm. Irradiation of **5** (11.4 mM) in MeCN with 266 nm laser light (6 mJ/pulse) for 7 min resulted in the formation of two primary photoproducts generated from α cleavage in ring D: the enal, 6β-(DPSO)-3-oxo-13,17-*seco*-5β-androst-13-en-17-al (**18**) and the epimer of **5**, 6β-(DPSO)-5β,13α-androstane-3,17-dione (**19**). Also detected was a mixture of the alcohols, 6β-(DPSO)-3β-hydroxy-5β-androstan-17-one (**20**) and its 3α isomer (**21**), which are generated by reduction of the 3-carbonyl group in **5**. These products were formed in a ratio of **18**:**19**:(**20** + **21**) = 1:2.5:0.2 (eq 2).

The structural assignments for these products are based on their ^{1}H and ^{13}C NMR and mass spectral data. Both **18** and **19** are isomeric with **5**. Compound **18** has characteristic 17-C*H*=O and allylic 18-CH_3 singlet resonances at δ 9.70 and 1.65, respectively, in good agreement with literature data and our previous observations.[3c,d,11] The ^{13}C NMR spectrum shows resonances at δ 202 and 212 corresponding to the 17-*C*H=O and a *C*=O in a six-membered cyclic ketone (the resonance at δ 221 corresponding to the 17-*C*=O in **5** is absent).[5,12] For **19** the C/D cis ring fusion is supported by the characteristic upfield shift of the 19-CH_3 group to δ 1.04 from 1.24 in **5**, as observed[3c,d] for the epimeric photoproducts of **1** and **2** (e.g., the resonances for the 19-CH_3 group in **1** and its epimer appear at δ 0.99 and 0.81, respectively; the upfield

(10) Interestingly, a second, downfield H-4 resonance is also coupled with the vinyl methyl resonance.

(11) Iriarte, V. J.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1964**, *47*, 1255−1264.

(12) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR Spektroskopie*; George Thieme Verlag: Stuttgart, 1984; pp 173, 245.



(2)

266 nm : **18 : 19 : (20+21) = 1 : 2.5 : 0.2**

308 nm : **18 : 19 : (20+21) = 1 : 2.3 : 0.3**

shift is due to the placement of the 19-CH_3 group within the shielding cone of the 17-keto group when there is a cis C/D ring fusion). There is a slight (i.e., δ 0.09) downfield shift of the 18-C*H*$_3$ resonance, which is also consistent with our previous results and attributable to a change of this methyl from an axial configuration in **5** to an equatorial configuration in the epimer.[13] The retention of both the 3- and the 17-keto groups is evidenced by their ^{13}C NMR resonances at δ 212 and 222, respectively.

The two isomeric alcohols, **20** and **21**, formed in a ratio of 1:2.5, could not be separated and their structure assignments are based on IR and NMR spectral data obtained on the mixture. The OH function is evident in the IR spectrum by a sharp peak at ca. 3650 cm^{-1}. That reduction has occurred at the C3 position is evidenced by the ^{13}C NMR spectrum in which the resonances for the 3-*C*-β-OH and 3-*C*-α-OH are found at δ 71.3 and 73.3, respectively, a good fit to the data for authentic compounds containing a 3-*C*-OH group; i.e., the corresponding resonances in (+)-dihydrocholesterol and (+)-dehydroandrosterone occur at δ 71.3 and 71.4, respectively.[5] The resonance for a 17-*C*-OH normally occurs further downfield—typically δ 80−85.[5] As expected, one observes the characteristic resonance for the 17-*C* cyclopentanone at 222.4 δ. Finally, the ^{1}H NMR chemical shifts and splitting patterns at 3.54 and 4.02 δ match that expected for *H*C-3α-OH and *H*C-3β-OH, respectively, with the 3α-OH as the major isomer.[4]

Photolysis of 5 in MeCN with TEA at 266 nm. Irradiation of **5** (10.25 mM) in MeCN with TEA (28.7 mM) using 266 nm laser light (5 mJ/pulse) again gave the enal **18**, the epimer **19**, and the alcohols **20** and **21**. The products were formed in a ratio of 1:3.5:0.3. A photolysis of **5** (14.80 mM; TEA 89.4 mM) was monitored as a function of time and gave the ratios of products shown in Table 1. The relative insensitivity of the chemistry at C17 to the presence of TEA (and consequent C3 chemistry) is noteworthy; quantum efficiency studies

(13) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1991; p 175.

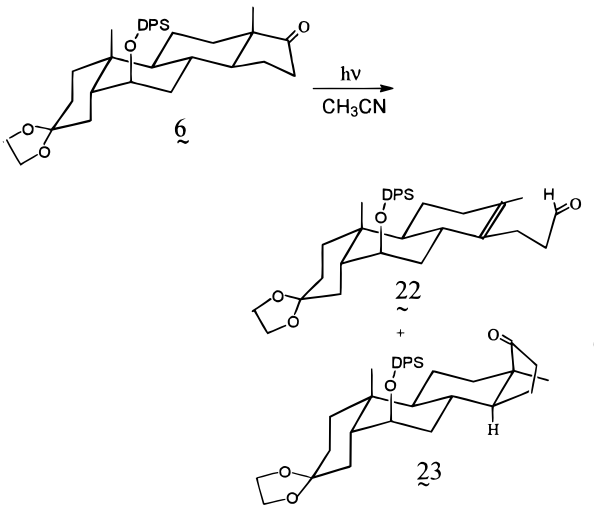
Table 1. Time Course and Product Ratios for the Photolysis of 5 with TEA

time (min)	**18**	**19**	**20** + **21**
10	1	3.0	0.4
20	1	3.3	0.6
30	1	3.2	0.8
40	1	3.3	0.8

carried out with varying concentrations of TEA confirm the fact that C17 chemistry proceeds independent of C3 reduction (see Table 1).

Photolysis of 5 in MeCN at 308 nm. An acetonitrile solution of **5** (10.56 mM) was irradiated with 308 nm laser light for 5 min and found to form compounds **18**, **19**, and (**20** + **21**) in a ratio of 1:2.3:0.3 (cf. eq 2). Photolysis for a shorter irradiation time gave only **18** and **19** (1:2.8) with **20** and **21** undetectable. Photolysis with TEA (ca. 50 mM) gave **18**, **19**, **20**, and **21** in a ratio of 1:3.8:0.5 with a shorter photolysis again yielding only **18** and **19** (1:3.5).

Photolysis of the C17 Monoketone (6) in MeCN at 266 and 308 nm. An acetonitrile solution of **6** (9.0 mM) was irradiated at 266 nm (3.8 mJ/pulse) for 1.33 min. Two primary photoproducts involving α cleavage at C17 were formed: the enal (**22**) and the epimer (**23**) (1:2.8) (eq 3). ^{1}H and ^{13}C NMR spectra were obtained



(3)

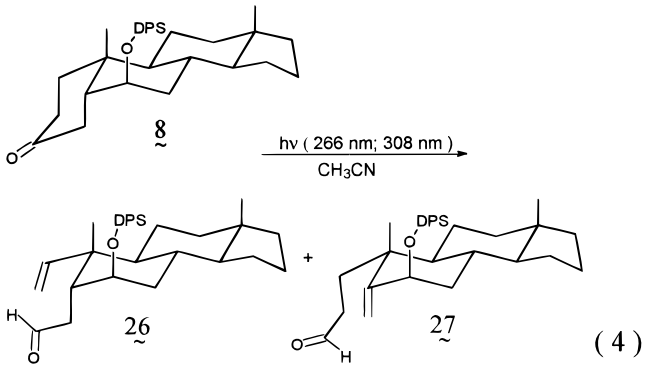
266 nm: **22 : 23 = 1 : 2.8**

308 nm: **22 : 23 = 1 : 2.5**

for samples isolated from a preparative photolysis. The structure for **22** is supported by the 17-C*H*═O and allylic 18-C*H*$_3$ resonances at δ 9.67−9.69 and 1.61(s), respectively. There is also a characteristic 17-*C*H═O resonance at δ 201.8 in the ^{13}C NMR spectrum. Compound **23** was identified by the upfield shift of the 19-C*H*$_3$ resonance to δ 0.96 (from δ 1.17 in **6**), and a corresponding downfield shift of the 18-C*H*$_3$ resonance from δ 0.85 to 0.94. The continued presence of the five-membered ring 17-*C*═O is evidenced by the ^{13}C NMR resonance at δ 222.4. The photolysis of **6** with 308 nm light gave the same two products in a similar ratio.

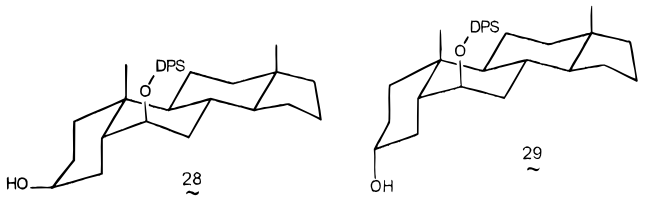
Photolysis of the C3 Monoketone, 8, at 266 and 308 nm. Photolysis of **8** (10.6 mM) in MeCN with 266 nm laser light (3.6 mJ/pulse) for 14.5 min gave two products (**26** and **27** in a ratio of 1:2.4) that were subsequently isolated as a mixture by a preparative photolysis. A ^{1}H NMR spectrum indicated that these

were enals since resonances appeared at δ 9.92, 9.43 and 5.67−5.03 (eq 4). The same enals were formed upon



(4)

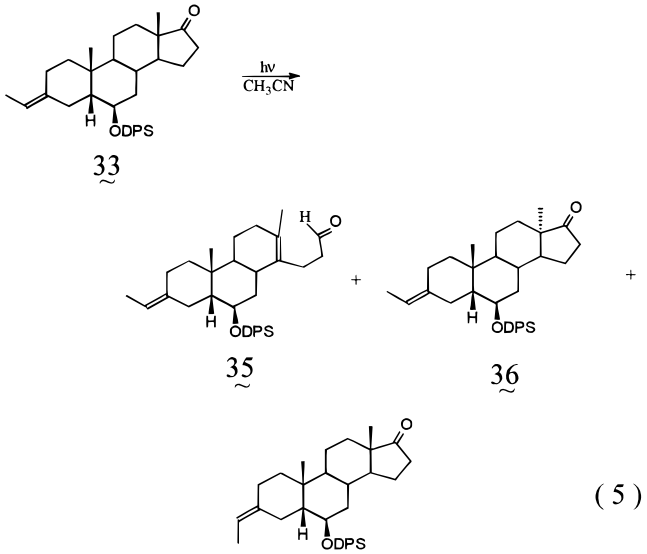
photolysis of **8** in MeCN with 308 nm laser light, but in slightly higher yield than with 266 nm irradiation. Photolysis of **8** with TEA (53.0 mM) using 266 nm light gave two isomeric alcohols in a ratio of 1:1.5. Their structures were assigned as compounds **28** and **29** on the basis of resonances in the ^{1}H NMR at δ 3.4−3.5 for the *H*C-3α-OH (**29**) and δ 3.9−4.2 for the *H*C-3β-OH (**28**). This was also the case when **8** was photolyzed in MeCN containing TEA using 308 nm light.[14]



Photolysis of 33 and 34 in MeCN at 266 nm. Irradiation of **33** (8.48 mM) or **34** (7.58 mM) in MeCN with 266-nm laser light (4 mJ/pulse) for 1 min resulted in the formation of three primary photoproducts in both cases. Compound **33** gave its *Z* isomer and the ring D cleavage products, enal **35** and epimer **36** (see eq 5). Photolysis of **34** also gave three primary photoproducts, the E isomer, and the ring D cleavage products **37** and **38** (eq 6).

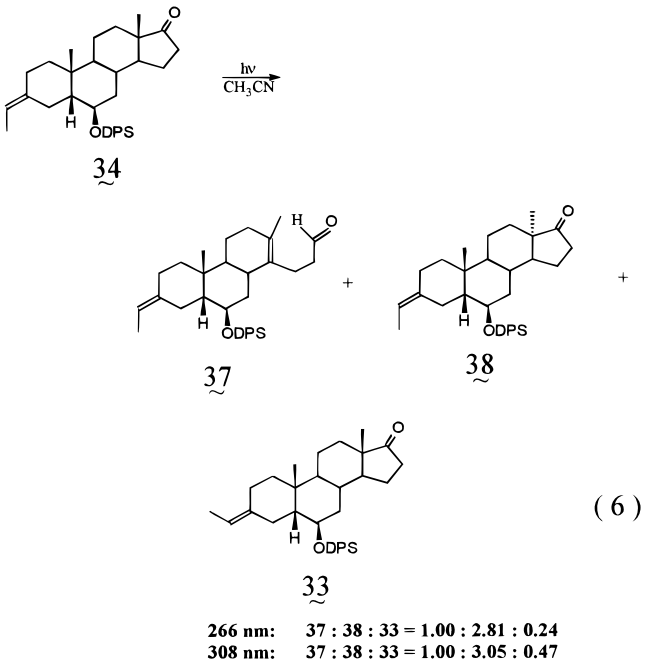
The ring D cleavage products were obtained by a preparative photolysis of a mixture of **33** and **34** (27.2 mM) in MeCN with 266-nm laser light. The three pairs of isomers were detected by GLC analysis. The structural assignments for compounds **35**−**38** follow from the ^{1}H and ^{13}C NMR spectra of the mixture. The presence of the two isomeric enals was indicated by a pair of characteristic 17-C*H*=O resonances at δ 9.75−9.73 and 9.71−9.68 and allylic 18-CH_3 singlets at ca. δ 1.62, in good agreement with literature data and our previous observations.[3c,d,11] The ^{13}C NMR spectrum shows the absence of the resonance at δ 221 corresponding to the 17-*C*=O in **33** and **34** and a new resonance at δ 202 corresponding to the 17-*C*H=O carbon.[5,12]

The C/D cis ring fusion in **36** and **38** is evidenced by the characteristic upfield shift of the 19-CH_3 resonances to δ 0.96 from δ 1.24 in **33** and **34**. The upfield shift has



(5)

266 nm: 35 : 36 : 34 = 1.00 : 1.71 : 0.09
308 nm: 35 : 36 : 34 = 1.00 : 1.77 : 0.13



(6)

266 nm: 37 : 38 : 33 = 1.00 : 2.81 : 0.24
308 nm: 37 : 38 : 33 = 1.00 : 3.05 : 0.47

been observed previously[3c,d] and is due to the placement of the 19-CH_3 group within the shielding cone of the 17-keto group when there is a cis C/D ring fusion. There is a smaller downfield shift of the 18-CH_3 resonance from δ 0.65 to 0.93 which is also consistent with our previous results and attributable to a change of this methyl from an axial configuration in **1** and **2** to an equatorial configuration in the epimer.[12] Finally, the retention of the 17-keto group is indicated by a ^{13}C NMR resonance at δ 222.

Resonances for the C*H*=C and allylic CH_3 appear at δ 5.04−5.15 and 1.55−1.53, respectively. The olefinic carbons are also evidenced by several signals at δ 114.68, 114.75, 114.77, and 139.21, 139.27, 139.30 in the ^{13}C NMR spectrum.

Photolysis of 33 and 34 in MeCN at 308 nm. Acetonitrile solutions of **33** (8.48 mM) or **34** (7.58 mM) were irradiated with 308-nm laser light (4 mJ/pulse) for 1 min and each found to form the same three photoprod-

(14) Analogous results were obtained by irradiation of the analogous monoketone, 6β-(dimethylphenylsiloxy)-5β-cholestan-3-one (**7**), in cyclohexane with 266 nm and 308 nm laser light. The β (**24**) and α (**25**) alcohols were isolated in a ratio of 1:4.5. Details may be found in ref 15.

(15) Jiang, S. A. Doctoral Dissertation, Purdue University, W. Lafayette, IN, Aug 1995.

Table 2. Quantum Efficiencies for Photolysis of 5 with 266 and 308 nm Light

solvent	% loss	Φ_{-5}	Φ_{18}	Φ_{19}
		266 nm		
MeCN	18	18.1×10^{-2}	3.20×10^{-2}	10.6×10^{-2}
C_6H_{12}	25	26.7×10^{-2}	5.33×10^{-2}	12.8×10^{-2}
		308 nm		
MeCN	10	30.8×10^{-2}	6.85×10^{-2}	20.6×10^{-2}
C_6H_{12}	18	31.9×10^{-2}	7.35×10^{-2}	20.8×10^{-2}

Table 3. Quantum Efficiencies for the Photolysis of 6 in MeCN with 266 and 308 nm Light

Φ_{-6}	Φ_{22}	Φ_{23}
	266 nm	
21.2×10^{-2}	4.25×10^{-2}	9.58×10^{-2}
	308 nm	
26.3×10^{-2}	5.71×10^{-2}	16.0×10^{-2}

Table 4. Quantum Efficiencies for Photolysis of 5 in MeCN in the Presence of [TEA] Using 266 and 308 nm Light

TEA (mM)	Φ_{-5}	Φ_{18}	Φ_{19}
Φ 266			
28.7	11.7×10^{-2}	2.13×10^{-2}	6.28×10^{-2}
43.0	10.1×10^{-2}	2.02×10^{-2}	5.64×10^{-2}
57.4	13.3×10^{-2}	2.23×10^{-2}	7.13×10^{-2}
71.7	11.1×10^{-2}	1.70×10^{-2}	6.39×10^{-2}
100.4	11.4×10^{-2}	1.81×10^{-2}	6.17×10^{-2}
Φ 308			
54.7	29.7×10^{-2}	6.63×10^{-2}	17.1×10^{-2}

Table 5. Quantum Efficiencies for Photolysis of 8 in CH_3CN

% loss	Φ_{-8}	Φ_{26}	Φ_{27}
		266 nm	
12	7.78×10^{-2}	1.06×10^{-2}	4.36×10^{-2}
		308 nm	
9	10.4×10^{-2}	1.81×10^{-2}	6.60×10^{-2}

ucts as had been observed with 266-nm irradiation. The ratios of these products were similar for **33** at the two photolysis wavelengths but significantly different for the irradiation of **34** (see eqs 5 and 6).

Quantum Efficiencies for Photolysis of 5, 6, 8, 33, and 34. Quantum efficiencies for the loss of the dione **5** (Φ_{-5}), and the formation of **18** and **19** (Φ_{18} and Φ_{19}), were measured in MeCN and in cyclohexane with 266 and 308 nm laser light. The data are presented in Table 2 (no reduction at C3 was observed). Quantum efficiencies for the photolysis of **6** are shown in Table 3, and quantum efficiencies for the photolysis of **5** as a function of TEA concentration are shown in Table 4. Quantum efficiencies for the photolysis of **8**, **33**, and **34** at both 266 and 308 nm are given in Tables 5 and 6.

Quenching Studies with *cis*-1,3-Pentadiene. *cis*-1,3-Pentadiene (*cis*-piperylene) ($E_T = 58.3$ kcal/mol) is an effective quencher of ketone triplets[16] and has been used to probe the excited state origin of photochemistry occurring at C17.[3] No quenching of product formation was observed when compound **5** was irradiated in the presence of 60−500 mM pentadiene using either 266 or 308 nm light.[17] Similarly, no quenching was observed upon photolysis of **6**, either at 266 or 308 nm. However, the photoproducts from the photolysis of **8** with either 266 or 308 nm, both in the presence and absence of TEA, were completely eliminated by 152 mM pentadiene.

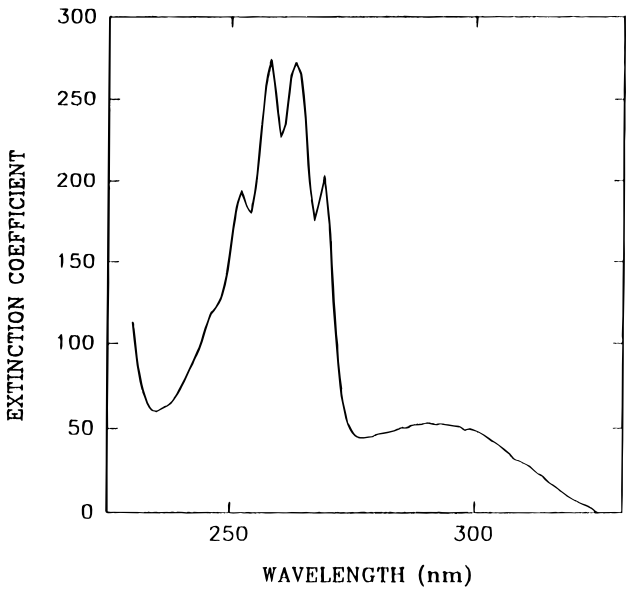


Figure 1. Absorption spectrum of compound **5** in acetonitrile.

Table 6. Quantum Efficiencies for Photolysis of 33 and 34 in MeCN

Compound **33**

Φ_{-33}	$\Phi_{E\rightarrow Z}$	Φ_{35}	Φ_{36}
	266 nm		
0.36	0.012	0.13	0.22
	308 nm		
0.82	0.035	0.26	0.46

Compound **34**

Φ_{-34}	$\Phi_{Z\rightarrow E}$	Φ_{37}	Φ_{38}
	266 nm		
0.32	0.015	0.064	0.18
	308 nm		
0.51	0.046	0.10	0.30

Effect of Added Cyclopentanone and Cyclohexanone on the Photochemistry of 5. Cyclopentanone and cyclohexanone were used to test for possible intermolecular energy transfer in **5**.[3d,e] The addition of either ketone in equimolar concentrations with **5** (ca. 11 mM) had no effect on the 266 nm photolysis; i.e., there was no change in the quantum efficiencies of product formation from **5** nor was there any loss of the added cycloalkanone.

Spectroscopy. Absorption Spectra. The aryl DPSO and the carbonyl chromophores typically show uv absorption maxima at ca. 260 nm and ca. 290 nm, respectively.[18] The absorption spectrum of **5** is a composite of these components, i.e., λ nm (ϵ M^{-1} cm^{-1}) 252 (194); 258 (257); 263 (273); 269 (203), 290 (53); cf. Figure 1. The absorption spectra of **33** and **34** are likewise composites of the individual chromophores.

Fluorescence Spectra. The fluorescence spectra for **5**, **6**, **8**, **33**, and **34** elicited by 254 nm excitation all exhibit

(16) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; pp 252, 436.

(17) In fact, some reaction enhancement was observed in the presence of piperylene. This is due to the low conversion conditions under which the quenching studies were run. We have observed that secondary photochemistry destroys the photoproducts.

(18) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry;* CRC Press: Boca Raton, FL, 1991; pp 182, 287.

(19) Birks, J. B. *Photophysics of Aromatic Molecules*; John Wiley & Sons Ltd.: New York, 1970; p 126.

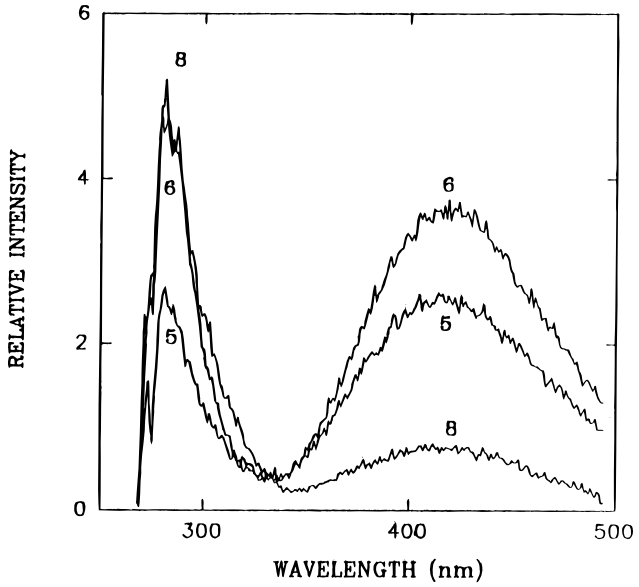


Figure 2. Normalized fluorescence spectra for compounds **5**, **6**, and **8** upon excitation at 254 nm in acetonitrile.

Table 7. Fluorescence Data for 5, 6, 8, 33, and 34 in Acetonitrile

λ_{ex} steroids	254 nm Φ_f(aryl)[a]	254 nm Φ_f(ketone)[b]	300 nm Φ_f(ketone)[c]
5	6.0×10^{-4}	3.6×10^{-3}	2.7×10^{-3}
6	9.5×10^{-4}	4.1×10^{-3}	3.1×10^{-3}
8	1.1×10^{-3}	8.4×10^{-4}	7.2×10^{-4}
33	1.1×10^{-3}	4.3×10^{-3}	4.0×10^{-3}
34	1.3×10^{-3}	4.2×10^{-3}	3.7×10^{-3}
30	5.3×10^{-3}		
31			1.2×10^{-3}

[a] Using toluene in cyclohexane as a reference ($\Phi = 0.14$).[19] [b] Using anthracene in cyclohexane as a reference ($\Phi_f = 0.36$).[19] [c] Using acetone in cyclohexane as a reference ($\Phi_f = 9.3 \times 10^{-4}$).[20]

Table 8. Singlet Lifetime Data for Compounds 5, 6, 8, 33, 34, and 30[a]

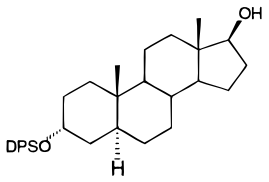
steroids	τ_f (aryl) ns	τ_f (ketone) ns
5	0.24 ± 0.01	2.27 ± 0.01; 4.50 ± 0.01
6	0.22 ± 0.01	4.92 ± 0.18
8	0.27 ± 0.04	2.44 ± 0.24
33	0.28 ± 0.02	4.6 ± 0.1
34	0.38 ± 0.01	5.1 ± 0.1
30	1.29 ± 0.08	

[a] All solutions in MeCN; excitation at 254 nm (aryl) and 300 nm (ketone).

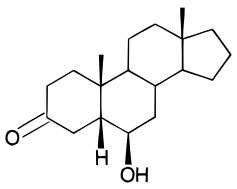
dual emission, with the aryl and ketone fluorescence centered at ca. 285 nm and 410 nm, respectively (Figure 2). Fluorescence quantum efficiencies were determined by using toluene, anthracene, and acetone as reference compounds. The data are given in Table 7, together with data for compounds **30**[3c] and **31** as DPSO and ketone standards. Fluorescence lifetimes for these substrates were measured, and these data are summarized in Table 8.

Discussion

Photochemistry. Consistent with our observations with analogous steroids such as **1** and **2** excitation of the aryl antenna in **5** at 266 nm initiates carbonyl photochemistry (cf. eq 1). Interestingly, the photochemistry (α-cleavage to **18** and **19**) primarily occurs at the C17 position rather than at the more proximal C3. However,



30



31

direct excitation of the carbonyl groups in **5** with 308 nm light gave results virtually identical to that observed with antenna excitation. There is good mass balance between the loss of starting material and the formation of identified C17 products, as evidenced by a comparison of quantum efficiencies (see Table 2), although the data are somewhat better at 308 nm (ca. 90%) than at 266 nm (68−76%). Comparable results were obtained with compounds **6** and **8** (Tables 3 and 5). Interestingly, photolysis at 308 nm gives quantum efficiency data for **5** that are essentially identical in acetonitrile and cyclohexane, whereas a somewhat less efficient reaction is observed in the more polar solvent when the antenna is irradiated at 266 nm (Table 2). We have noted in previous studies that aryldecalones exhibit a diminished efficiency of aryl to ketone intra-SSET in polar media.[21] This was attributed to the well-known blue-shift of the carbonyl n → π^* transition in polar solvents and the consequent reduction in the emission/absorption spectral overlap integral intrinsic to energy transfer. This point is discussed further below.

Experiments with added ketones, TEA, and pentadiene provide some useful mechanistic insights. Photolysis of **5** with 266 nm light in the presence of equimolar amounts of either cyclopentanone or cyclohexanone gives no evidence of quenching by the "external" ketones nor any indication of photoproducts from these reagents. This confirms that sensitization by the DPSO group is strictly intramolecular, as has been observed in previous studies.[3] Photolysis of **5** with TEA using 266 nm light increases the amount of photochemistry at C3 (i.e., reduction to **20** and **21**) without affecting either the relative amount of the two C17 products (Table 1) or the quantum efficiencies of their formation (Table 4). Both observations are consistent with C17 chemistry originating from a singlet excited state. This conclusion is reinforced by the lack of quenching of C17 chemistry in **5** by pentadiene. Chemistry at C17 is typically singlet derived, unless it is induced through specific triplet energy transfer[3d] and, not surprisingly, the C17 chemistry displayed by **6** (eq 3) is also unquenchable. By contrast, the C3 chemistry induced in **8** (eq 5) is completely quenchable by pentadiene and entirely triplet-derived.

Spectroscopy and DPSO/Ketone Intra-SSET. The 254 nm induced fluorescence spectra of three DPSO-containing steroidal ketones, **5**, **6**, and **8**, show dual emission (cf. Figure 2). The quantum efficiencies for aryl emission, and the aryl singlet lifetimes (cf. Tables 7 and 8), for these compounds are appreciably reduced relative to the nonketonic model **30**. The efficiencies of carbonyl emission elicited by DPSO excitation are comparable to those obtained by direct excitation with 300 nm light and to that of the model steroidal ketone **31**. These results confirm that there is extensive intra-SSET between the

(20) Halpern, A. M.; Ware, W. R. *J. Chem. Phys.* **1971**, *54*, 1271.
(21) Morrison, H.; Pallmer, M.; Loeschen, R.; Pandey, B.; Muthuramu, K.; Maxwell, B. *J. Org. Chem.* **1986**, *51*, 4676−4681.

Table 9. Efficiencies and Rates for Intra-SSET

steroid	$\Phi_{intra-SSET}$	$k_{intra-SSET}$ (10^9 s^{-1})
5	0.89[a] (0.81)[b]	3.2[a] (3.4)[b]
6	0.82[a] (0.83)[b]	3.7[a] (3.8)[b]
8	0.79[a] (0.79)[b]	2.9[a] (2.9)[b]
33	0.79[a] (0.78)[b]	2.8[a] (2.8)[b]
34	0.75[a] (0.71)[b]	2.0[a] (1.8)[b]

[a] Calculated from Φ_f data. [b] Calculated from $^1\tau$ data.

DPSO and carbonyl groups, the efficiencies and rates for which can be calculated using either the DPSO fluorescence quantum efficiency or lifetime data.[3c,d] The results are given in Table 9. Note the generally good agreement between the Φ_f and τ_f derived values.

The interchromophoric distances between the 6-DPSO group and C3 or C17 in these steroids are 7.7 and 8.6 Å, respectively.[22] The magnitudes of both the efficiencies and the rate constants of intra-SSET match well with our earlier observations[3c] with DPSO containing steroidal ketones in which the antenna and the carbonyl groups are separated by ca. 7−9 Å (i.e., in earlier work, efficiencies and rates of energy transfer of 70−90% and $1-3 \times 10^9$ s^{-1}, respectively). Since the earlier data were drawn from the 5α-androstane series, these results indicate that the A/B ring fusion is not, in itself, critical to energy migration within the steroid "wire".

The extensive intra-SSET is also reflected in the relative quantum efficiencies for photochemistry with 266 vs 308 nm excitation (Tables 2, 3, and 5). For compounds **6** and **8** the 266 nm/308 nm quantum efficiency ratios are 74 and 75%, respectively, in excellent agreement with the $\Phi_{intra-SSET}$ values in Table 9. Likewise, for **5** in cyclohexane there is a very good match of the quantum efficiency ratio (84%) and the $\Phi_{intra-SSET}$ data (though the latter are from photophysical data in acetonitrile). An anomaly is the match of the 266/308 nm ratio for **5** in acetonitrile (58%) vs the DPSO/ketone intra-SSET efficiency. We have noted above that, in particular, the quantum efficiency for 266 nm initiated chemistry in **5** is reduced in the polar medium. This could be caused by a reduction in the DPSO to ketone energy transfer efficiency in acetonitrile or some effect of the polar solvent on the C3/C17 communication discussed below.

Our earlier work[3] has implicated through-bond exchange energy transfer as a likely source of the DPSO to ketone activation; the data presented herein are consistent with this interpretation.

Ketone/Ketone Communication. There are several intriguing aspects of a comparison of compounds **5** and its des C3 ketone analog, **6.** Most striking are the comparable quantum efficiencies for C17 product formation in the two compounds (cf. Tables 2 and 3). This is despite the fact that there is little difference in the magnitude or rate of intra-SSET from the C6 DPSO to C3 (in **6**) and to C17 (in **8**) (Table 9). Assuming, therefore, that energy transfer from the C6 DPSO group to C3 and C17 is competitive in **5**, *there must be facile communication between the C3 and C17 excited singlet states*. We attribute the fact that the singlet carbonyl chemistry is focused entirely at C17 to the relatively large rate constant anticipated for C−C cleavage in a cyclopentanone bearing a disubstituted α carbon. The fact that quenching of the C3 triplet by TEA has no effect on C17 chemistry implies that the C3 and C17 *triplets* do *not* communicate (a conclusion supported by the studies with **33** and **34**; see below).

DPSO/Olefin and Ketone/Olefin Communication. The existence of triplet ketone chemistry at C3, upon antenna excitation in **8**, could derive either from intra-SSET and intersystem crossing of the C3 ketone singlet or by intra-TTET from the DPSO group to C3. This ambiguity is removed in **33** and **34** where only intra-TTET to C3 is possible. In fact, excitation of the aryl antenna initiates olefin isomerization of both the *E* and the *Z* isomers, confirmation of intra-TTET, and the potential of the alkene to function as a "triplet gate". The combination of the trapping of triplet energy by the C3 alkene gate, and the inefficient intersystem crossing of the DPSO antenna caused by its rapid intra-SSET to the C17 carbonyl group (Table 9), causes the primary chemistry in **33** and **34** to be the singlet-derived formation of the enal and epimer C17 α-cleavage products. The lack of DPSO intersystem crossing results in *E*/*Z* isomerization in **33** and **34**, upon 266 nm excitation, as only 3.3% and 5.7% of the product, respectively, under the conditions applied in the reactions listed in Table 6. As with **5**, one can compare the ratios of the quantum efficiencies for C17 singlet photochemistry when directly excited (308 nm) and indirectly excited (266 nm) (Table 6) to the $\Phi_{intra-SSET}$ values in Table 9. For reasons we cannot explain, the data do not match as well as for the diketone: 60 vs 75%, respectively, for **34** and 50 v. 79% for **33**. Nevertheless, our observations with these trifunctional steroids are generally consistent with the mechanisms we have outlined for the DPSO/diketone substrate, **5**.[23]

Conclusions. In summary, we have demonstrated that a DPSO antenna at C6 in the 5β androstane series can efficiently transfer singlet energy to a target group at C17 and elicit chemistry at that site. Rates and efficiencies match well with data from previously studied 5α androstanes. Energy transfer to C17 occurs in the presence of either singlet or triplet energy acceptors at C3. In fact, there is evidence that a C3 ketone can itself efficiently transfer singlet energy to C17.

Experimental Section

Complete details for the experimental portion of this paper may be found in ref 15; the salient features are summarized below.

Instrumentation. ^{1}H and ^{13}C NMR spectra were obtained using 200, 300, and 500 MHz NMR spectrometers. Infrared spectra were recorded on a Perkin-Elmer Model 1800 FT-IR spectrometer. Low-resolution mass spectra were obtained using a gas chromatograph EI/CI mass spectrometer. High-resolution mass spectra were recorded on a Kratos Model MS-50; data from this instrument have a standard deviation of 1.98 parts per million. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Model Lambda 3B spectrophotometer. Steady state fluorescence spectra were recorded on an SLM Aminco SPF-500C spectrofluorometer with a 250 W xenon arc lamp. Quantum efficiencies were measured by

(22) Distance data were obtained by calculations using a Silicon Graphics Personal Iris 4D/35 Computer with MacroModel V3.5X Software: Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440. MM2* method: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(23) We find it striking that direct excitation of the C17 carbonyl group with 308 nm light in **33** and **34** also leads to isomerization of the C3 alkene (4.6 and 10% of the product for **33** and **34**, respectively; Table 6). Though these results imply intra-TTET from the C17 ketone triplet to C3, such an explanation would be inconsistent with the lack of ISC we have observed in a C17 ketone. Studies of substrates lacking the C6 DPSO group are in progress.

reference to toluene and anthracene or acetone. Fluorescence lifetimes were determined with an ISS K2-002 Digital MPF computer-selectable cross-correlation lifetime spectrometer with a xenon arc lamp as a light source and a WG280 cutoff filter used in the emission light path when the emission monochrometer was not used. Fluorescence lifetimes were also obtained with a PTI Model LS 100 fluorescence lifetime spectrometer using a nitrogen dye laser as the light source. All the fluorescence studies were conducted in regular 10 × 10 mm fluorescence cells and at room temperature with the solutions purged with argon for at least 15 min prior to use. Gas chromatography utilized a Varian 3700 FID capillary instrument coupled to a Hewlett-Packard 3390A integrator, with the following J & W Scientific DB-1, 0.25 μm film thickness columns: (A) 15.0 m × 0.25 mm i.d., (B) 12.5 m × 0.25 mm i.d., (C) 10.0 m × 0.25 mm i.d. The internal standard for 6β-(DPSO)-5β-androstane-3,17-dione and 3,3-(ethylenedioxy)-6β-(DPSO)-5β-androstan-17-one (**5** and **6**) was 3α-(DPSO)-5α-androstane-3,17-dione with response factors (RF) from [mass (X)/mass (I.S.)] = (RF) [area (X)/area (I.S.)] = 0.86 and 0.90, respectively. The internal standard for 6β-(DPSO)-5β-androstan-3-one (**8**) was 3α-(DPSO)-5α-androstan-17-one; R_f = 0.84. HPLC analyses and separations were conducted on a Varian Star 9000 system equipped with a variable wavelength UV−vis detector. The HPLC traces were recorded with a HP3395 integrator. The HPLC columns used were an Econosil C-18 column (Alltech) 25 cm × 4.6 mm, 10 μm, or a Microsorb-MV C-18 column (Rainin) 25 cm × 4.6 mm, 5 μm. Preparative separations were also carried out with a Chromatotron Model 7924T thin layer instrument (Harrison Research). Melting points were determined with a Fisher-Johns apparatus and are uncorrected.

Materials. The following chemicals were obtained from the Aldrich Chemical Co.; they were used as received and stored at room temperature except where mentioned: 3β-hydroxy-5-androsten-17-one ((+)-dehydroisoandrosterone); Celite; pyridinium chlorochromate (PCC); 1,2−ethanediol; chlorodimethylphenylsilane (DPSCl), stored in a desiccator; *cis*-1,3-pentadiene, stored at −20 °C; borane, 1.00 M solution in tetrahydrofuran (THF), stored at −20 °C; 5-cholesten-3β-ol (cholesterol); di(ethylene glycol); hydrazine hydrate; ethyltriphenylphosphonium bromide; potassium *tert*-butoxide, stored in a desiccator; anthracene (99.9%); cyclopentanone; cyclohexanone; Florisil; benzene-d_6 (99+% D); acetone (99.9+%); palladium(II) chloride. Flash column chromatography employed E. Merck 9285, 230−400 mesh silica gel.

The following chemicals were obtained from other suppliers. Fisher Chemical: hydrogen peroxide, 30 wt % solution in water; Cambridge Isotope Laboratory: chloroform-*d* (99.8% D). Mallinckrodt: tetrahydrofuran and diethyl ether, both distilled under nitrogen from sodium−benzophenone ketyl in a recycling still; triethylamine was distilled from calcium hydride prior to use; *N*,*N*-dimethylformamide was treated with 4-Å molecular sieves followed by distillation under reduced pressure.

Spectrograde solvents: acetonitrile (Fisher; Baxter); hexane (Fisher); cyclohexane (Fisher; Aldrich); toluene (Fisher); and acetone (Fisher) were used in the photochemical and spectroscopic studies without further purification and kept stored under dry nitrogen.

Photolyses. Laser photolyses at 266 nm utilized a Continuum NY-61 Nd:YAG laser equipped with quadropole frequency doubler. A 2× beam enlarger was used in front of the photolysis cell to avoid cell damage. Laser photolyses at 308 nm utilized a Luminics EX-700 Pulsemaster Excimer laser equipped with a Pyrex beam splitter. A 7 × 9 mm beam mask was used in the photolyses of small solution volumes. Power meters were Opher Model 3A-P-CAL-S or 30A-P. Sample solutions were placed in 10 × 10 mm vycor square cells and were purged with argon for at least 15 min prior to use. For quantum efficiency determinations argon-degassed solutions ca. 8−12 mM in substrate were irradiated with either 266- or 308-nm laser light for 1 min using the power meters for the actinometry. The photolysates were analyzed by GC using internal standards and appropriate response curves. All photochemical studies were run at room temperature.

Syntheses. 6β-(DPSO)-5β-androstane-3,17-dione (5). 3β-Hydroxy-5-androstene-3,17-dione (**10**) was prepared by the following sequence. 5-Androsten-3β-ol-17-one (2.27 g, 7.88 mmol) was dissolved in CH_2Cl_2 (40 mL) and added to a suspension of PCC (6.80 g, 31.5 mmol) and Celite (4.76 g) in CH_2Cl_2 (30 mL).[24] The mixture was stirred for 3.5 h at rt. The mixture was diluted with ether and filtered through a short column of silica gel or Florisil, which were twice washed with CH_2Cl_2 and ethyl acetate. Evaporation of the combined organic solution gave a 4:1 mixture of **10** and its Δ^3 isomer, **11**, which was purified by flash column chromatography (35% EtOAc/hexane) to give **10** as a white solid (1.20 g, 53%). IR (Nujol): 1720 (3-C=O), 1740 (17-C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.41−5.38 (d, 1 H), 3.28−2.81 (AB q, 2 H), 2.56−1.26 (m, 17 H), 1.23 (s, 3 H), 0.93 (s, 3 H). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 221.10, 210.13, 138.82, 122.08, 51.34, 49.03, 48.01, 47.30, 37.24, 36.76, 36.49, 35.53, 31.21, 31.06, 30.36, 21.53, 20.30, 18.86, 13.23.

A mixture of **10** (1.20 g, 4.20 mmol), 2 equiv 1,2-ethanediol, and 10 mg of *p*-toluenesulfonic acid monohydrate in toluene was heated at reflux overnight, using a Dean−Stark head to remove water as formed.[25] The cooled reaction mixture was diluted with an equal volume of ether and washed with 10% sodium carbonate and then with water until neutral to litmus. The washed organic layer was dried with anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure. The residue was separated by flash column chromatography (35% EtOAc/hexane) to give 3,3;17,17-bis(ethylenedioxy)-5-androstene (**12**), **13**, and **14** (8:2:1). Compounds **13** and **14** were recycled to generate **12**. Spectral data for **12**. IR (CH_2Cl_2): no absorption at 1720 (3-C=O) or 1740 (17-C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.36−5.34 (m, 1 H), 3.98−3.84 (m, 8 H), 2.54−2.09 (AB q, 2 H), 2.04−1.05 (m, 17 H), 1.03 (s, 3 H), 0.86 (s, 3 H). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 140.00, 121.81, 119.36, 109.30, 65.08, 64.49, 64.38, 64.14, 50.40, 49.36, 45.63, 41.66, 36.58, 36.15, 34.08, 32.09, 30.98, 30.89, 30.42, 22.63, 20.47, 18.67, 13.98.

A solution of 6.0 mL (6.0 mmol) of 1.00 M borane−THF complex was added dropwise to a solution of **12** (1.50 g, 4.0 mmol) in 30 mL of dry THF in an ice bath. The reaction mixture was stirred 1 h at 0 °C and then overnight at rt. Excess borane was decomposed by dropwise addition of water until hydrogen was no longer evolved. A 3 N solution of NaOH (10 mL) was then added, followed by dropwise addition of 30% H_2O_2 (10 mL). The mixture was stirred at 40−50 °C for 1 h and then brought to rt. The aqueous phase was saturated with NaCl and extracted with 3 × 25 mL of ether. The combined organic layers were washed with water, dried over $MgSO_4$, and removed at reduced pressure. The residue was purified by flash column chromatography (10% *i*-PrOH/hexane) to give a mixture of 3,3;17,17-bis(ethylenedioxy)-6β-hydroxy-5α-androstane, **15**, and its 5α,6α-isomer (4:1) (2.0 g, 5.1 mmol, 85%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 3.95−3.84 , 3.78−3.72, 2.06−1.15, 1.14, 0.86. ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 119.45, 109.33, 72.39, 65.08, 64.39, 64.10, 64.04, 50.19, 47.67, 45.92, 35.83, 34.57, 34.24, 34.02, 33.44, 30.71, 30.58, 29.54, 22.43, 20.08, 14.24.

Five mol % of $PdCl_2(CH_3CN)_2$ was added to a solution of 2.0 g (5.1 mmol) of the mixture of **15** and its 5α,6α-isomer dissolved in 40 mL of acetone.[9] After the mixture was stirred for 2 days at rt the acetone was removed under reduced pressure and the resulting residue redissolved in ether. The ether was washed with 3 × 25 mL of saturated NH_4Cl and water and dried over $MgSO_4$. The solvent was removed at reduced pressure and the residue purified by flash column chromatography (25% *i*-PrOH/hexane) to give 6β-hydroxy-5β-androstane-3,17-dione, **16** (0.50 g), and 6α-hydroxy-5α-androstane-3,17-dione **17** (0.12 g). **16**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 3.79−3.78 (d, 1 H), 2.52−1.31 (m, 20 H), 1.26 (s, 3 H), 0.93 (s, 3 H). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 221.22, 211.95, 71.24,

(24) Kurth, M. J.; O'Brien, M. J.; Hope, H.; Yanuck, M. *J. Org. Chem.* **1985**, *50*, 2626−2632. Parish, E. J.; Luo, C.; Parish, S.; Heidepriem, R. W. *Synth. Commun.* **1992**, *22*(19), 2839−2847.

(25) Smith, S. W.; Newman, M. S. *J. Am. Chem. Soc.* **1968**, *90*, 1249−1253.

51.25, 50.03, 47.83, 42.00, 41.88, 37.26, 36.40, 35.83, 34.80, 32.93, 31.57, 30.18, 24.53, 21.75, 20.24, 13.62. IR (CH_2Cl_2) cm^{-1}: 1712 (3-C═O), 1736 (17-C═O), 3200−3700 (O-H). MS EI *m/e*: 304 (M^+), 286 (M − H_2O). MS CI *m/e*: 305 (M + H). **17**: ^1H NMR ($CDCl_3$, 200 MHz) δ: 3.96−3.94 (s, 4 H), 3.76−3.72 (d, 1 H), 2.42−1.26 (m, 20 H), 1.19 (s, 3 H), 0.86 (s, 3 H). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 221.35, 109.11, 73.07, 64.10, 64.03.

Compound **16** (0.50 g, 1.64 mmol) was silylated with DPSCl (406 μL, 2.46 mmol) in dry DMF (3−5 mL) with anhydrous TEA (0.3 mL) at 0 °C. The reaction mixture became cloudy white immediately and then formed a light yellow precipitate. The mixture was diluted with toluene (20 mL) and washed successively with 2 × 3 mL of cold 5% $NaHCO_3$, 2 × 3 mL of cold HCl (5%), and once again with 2 × 3 mL of cold 5% $NaHCO_3$. The organic layer was dried over $MgSO_4$ and evaporated to give crude **5**, which was purified twice by the Chromatotron (20% EtOAc/hexane). Recrystallization from hexane afforded white prisms (237 mg), mp 101−103 °C. GC analysis (column A; 250 °C) showed 100.00% purity with t_R = 12.31 min. HPLC analysis using 100% CH_3CN also indicated 100% purity (t_R = 5.12 min). ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.60−7.35 (m, 5 H), 3.70−3.66 (m,1H), 2.48−1.28 (m, 20 H), 1.24 (s, 3 H, 19-Me), 0.90 (s, 3 H, 18-Me), 0.39 (s, 3 H), 0.35 (s, 3 H). ^1H NMR NOESY ($CDCl_3$, 500 MHz) showed correlations for both the 19-Me and the 18-Me groups with the DPSO methyl groups. ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 221.24, 212.03, 138.38, 133.47, 129.79, 128.02, 71.86, 51.05, 49.83, 47.74, 41.82, 41.77, 37.25, 36.35, 35.67, 34.87, 33.22, 31.47, 30.06, 24.42, 21.42, 20.06, 13.67, −1.22, −2.01. MS EI *m/e* 438 (M^+), 423 (M − Me), 361 (M − C_6H_5). MS CI *m/e*: 439 (M + H), 361 (M − C_6H_6). Anal. Calcd for $C_{27}H_{38}O_3Si$: C, 73.93; H, 8.73 found: C,73.67; H, 8.98. High resolution MS EI *m/e*: calcd 438.2590, found 438.2577.

3,3-(Ethylenedioxy)-6β-(DPSO)-5β-androstan-17-one (6). The title compound was prepared by a procedure analogous to that described for **5** above. Silylation of the alcohol **17** with DPSCl in DMF−TEA afforded crude product that was purified by the Chromatotron (20% EtOAc/hexane) and recrystallized from hexane to afford white prisms, mp 139−143 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.76−7.36 (m, 5 H), 3.91−3.89 (s, 4 H), 3.73−3.66 (m, 1 H), 2.39−1.21 (m, 20 H), 1.17 (s, 3 H), 0.86 (s, 3 H), 0.38 (s, 3 H), 0.34 (s, 3 H). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 221.30, 138.78, 133.32, 129.32, 127.70, 109.21, 72.85, 64.15, 64.04, 51.17, 47.85, 47.28, 40.37, 36.02, 35.80, 35.54, 34.67, 33.74, 31.61, 30.25, 29.68, 25.23, 21.55, 20.04, 13.81, −0.77, −1.72. High resolution MS (EI) *m/e*: calcd 483.2931, found 483.2911.

6β-(DPSO)-5β-androstan-3-one (8). The title compound was prepared in five steps by a procedure analogous to that used for the preparation of **5**. The alcohol, 5-androsten-3β-ol, was prepared by heating at reflux a mixture of 3β-hydroxy-5-androsten-17-one (2.54 g, 8.81 mmol) in di(ethylene glycol) (30 mL) with K_2CO_3 (1.0 g) and hydrazine hydrate (2.0 mL) for several hours.[26] The temperature was raised to 200 °C overnight. After cooling, a white solid appeared that was dissolved in a mixed solvent of ether and toluene. The organics were washed with 5% HCl and water before drying. The ether and toluene were removed under reduced pressure to give 5-androsten-3β-ol, which was used directly for the next step without further purification.

The alcohol was oxidized with PCC for 2.5 h to give 5-androsten-3-one, which was purified on the Chromatotron (15% EtOAc/hexane). The 3-C═O group was converted to the ketal with excess 1,2-ethanediol and *p*-toluenesulfonic acid monohydrate by refluxing in toluene overnight with ultimate purification by flash column chromatography (some migration of the olefin to the 3,4 position occurs; this material was recycled). Hydroboration and oxidation of the ketal-protected olefinic steroids produced a mixture of the 5β/6β and 5α/6α alcohols that was deketalized with $PdCl_2$. The 6β-hydroxy-5β-androstan-3-one was partially purified using the Chromatotron (30% EtOAc/hexane). Silylation of the mixture with DPSCl in DMF−TEA gave **8**, which was purified by several passes through the Chromototron to afford a white solid. ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.69−7.39 (m, 5 H), 3.70−3.69 (m, 1H), 2.52−1.31 (m, 20 H), 0.96 (s, 3 H), 0.70 (s, 3 H), 0.36 (s, 3 H), 0.33 (s, 3 H). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 211.83, 139.75, 132.95, 129.20, 127.66, 71.98, 54.00, 53.40, 52.61, 41.75, 40.72, 40.22, 39.96, 38.50, 37.80, 36.47, 34.50, 25.32, 21.24, 20.40, 17.44, 12.70, −0.92, −1.33. MS (EI) *m/e*: calcd 425.2876, found 425.2863.

6β-(DPSO)-3(*E*)-ethylidene-5β-androstan-17-one and Its *Z* Isomer (33 and 34). To a slurry of 2.9 g (7.8 mmol) of ethyltriphenylphosphonium bromide, 20 mL of dry THF, and 1.3 g (11.6 mmol) of t-BuOK under an atmosphere of nitrogen was added 2.1 g (6.8 mmol) of **16** in 10 mL of dry THF. The mixture was stirred overnight at rt. The mixture was diluted with ether and filtered through a short column of silica gel, washed with 500 mL of Et_2O, and dried over $MgSO_4$. After evaporation of the solvent the residue was purified by silica gel chromatography (35% EtOAc/hexane eluent) to give a mixture of the *E* and *Z* isomers. The starting material, **16**, was recycled.

The mixture of *E* and *Z* isomers (425 mg, 1.35 mmol) was silylated with DPSCl (330 μL, 2.46 mmol) in dry DMF (3−5 mL) with anhyd TEA (0.5 mL) for 1 h at 0 °C. The mixture was diluted with toluene (20 mL) and washed successively with 2 × 3 mL of cold 5% $NaHCO_3$, 2 × 3 mL of cold HCl (5%), and once again with 2 × 3 mL of cold 5% $NaHCO_3$. The organic layer was dried over $MgSO_4$ and evaporated to give a residue of crude **33** and **34**, which was purified twice by the Chromatotron (6% EtOAc/hexane) to afford a white solid (490 mg). GLC analysis (10.0 m column; 240 °C) indicated a ratio of *E*:*Z* of 1.6:1 (t_R = 6.2 and 5.9 min, respectively). HPLC analysis (100% CH_3CN) gave two overlapping peaks. A small amount of **33** was separated from **34** by HPLC using an analytical C-18 column with 100% CH_3CN as eluent. Spectral data for the mixture of 75% **33** and 25% **34**. ^1H NMR(C_6D_6, 500 MHz) δ: 7.62−7.18 (m, 5H) 5.36−5.32 (q, 0.25H, C*H*═C, *Z*), 5.32−5.28 (q, 0.75 H, C*H*═C, *E*), 3.79−3.77 (q, 0.25H, *H*C-6β-DPSO, *Z*), 3.76−3.73 (q, 0.75H, *HC*-6β-DPSO, *E*), 2.3−0.75 (m, incl. s at 1.24), 0.65 (s, 3 H), 0.35, 0.34 (s, 6 H). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 221.29, 139.11 and 138.88 (3-C═*C*HCH$_3$, *Z* + *E*), 133.31, 129.30, 127.69, 114.87, 73.10, and 73.05 (6β-*C*H-OH, *Z* + *E*), −0.738, −1.642. MS EI *m/e*: calcd 450.2954, found 450.2949.

Preparative Photolysis of 6β-(DPSO)-5β-androstane-3,17-dione (5) with 266 nm Light. A degassed, stirred solution of **5** (39.9 mg, 22.8 mM) in CH_3CN (4.0 mL) was irradiated at rt for 1.0 h with the 266-nm laser light (Nd:YAG, 4.0 mJ/pulse). Analysis of the irradiated solution by GC (12.5 m column; 263 °C) showed two major products at 5.64 and 5.83 min, a minor product at 13.63 min, and the starting material at 6.79 min. Analysis by HPLC (100% CH_3CN) indicated two major products with t_R = 4.64 and 4.88 min and the starting material at 5.43 min. The mixture was separated on the Chromatotron (20% EtOAc/hexane) to give the enal (6β-(DPSO)-3-oxo-13,17-seco-5β-androst-13-en-17-al, **18**) (4 mg), the epimer (6β-(DPSO)-5β,13α-androstane-3,17-dione, **19**) (7 mg), and an isomeric mixture of the alcohols, 6β-(DPSO)-3α-(β)-hydroxy-5β-androstan-17-one, **20**, **21**) (2 mg). In a second experiment, the products were isolated using an analytical C-18 HPLC column (initially 100% acetonitrile; second pass, 90 or 95% acetonitrile; 0.5 mL/min). Spectral data follow.

18. IR ($CDCl_3$): 1714 (3-C═O) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ: 9.73− 9.70 (s, 1 H), 7.60−7.32 (m, 5 H), 3.73−3.68 (m, 1 H), 2.63−1.66; 1.53−1.16; 1.07−0.75 (m, 19 H), 1.65 (s, 3 H), 1.15 (s, 3 H), 0.36 (s, 3 H), 0.34 (s, 3 H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 212.12, 202.20, 162.03, 138.06, 133.29, 130.62, 127.93, 129.05, 72.42, 48.92, 42.64, 41.81, 40.10, 36.90, 36.45, 35.11, 34.02, 33.27, 32.98, 23.97, 22.02, 21.50, 19.63, −1.22, −1.76. MS (EI) *m/e*: 438 (M^+), 423 (M − CH_3), 361 (M − C_6H_5), 135 (PhSi(CH_3)$_2$). MS (CI) *m/e*: 439 (M + H), 361 (M − C_6H_6).

19. IR ($CDCl_3$): 1712 (3-C═O), 1728 (17-C═O) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.62−7.34 (m, 5 H), 3.69−3.65 (m, 1 H), 2.46−1.07 and 0.93−0.78 (m, 20 H), 1.04 (s, 3 H), 0.90 (s, 3 H), 0.35 (s, 3 H), 0.32 (s, 3 H). ^{13}C NMR ($CDCl_3$, 500

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MHz) δ: 221.92, 211.91, 138.25, 133.22, 129.66, 127.91, 72.03, 50.03, 49.30, 41.98, 39.86, 36.93, 36.52, 35.28, 35.03, 33.88, 32.73, 32.13, 25.26, 24.67, 22.47, 21.38, −1.00, −1.82). MS (EI) *m/e*: 438 (M^+), 423 (M − CH_3), 361 (M − C_6H_5), 135 (PhSi-$(CH_3)_2$). MS (CI) *m/e*: 439 (M + H), 361 (M − C_6H_6). HRMS CI *m/e*: calcd 439.2669, found 439.2678.

20,21 (2.5:1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.56−7.31 (m, 5 H), 4.14−3.26 (m, *H*C-3α(*β*)-OH, *H*C-6*β*-DPSO), 0.97 (s, 3 H), 0.93 (s, 3 H), 0.34−0.31 (s, 6 H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 222, 74.0 (*C*-6*β*-DPSO: 3*β*-OH isomer), 73.33 (C-6*β*-DPSO: 3α-OH isomer), 72.12 (*C*-3*β*-OH), 71.29 (*C*-3α-OH). MS (EI) *m/e*: 440 (M^+). MS CI *m/e*: 441 (M + H), 423 (M − H_2O).

Photolysis of 5 with TEA Using 266 nm Light. A degassed solution of **5** (30.2 mg, 22.8 mM) and TEA (28 μL, 68.5 mM) in CH_3CN (3.0 mL) was irradiated at rt for 2 h with 266-nm light (Nd:YAG, 4.0 mJ/pulse). Analysis of the irradiated solution by GC (12.5 m column; 263 °C) showed the same product mixture as was obtained without TEA. The spectra for these products were likewise identical with those described above.

Time Course Studies of the Photolysis of 5 with TEA Using 266 nm Light. A degassed solution of **5** (6.5 mg, 14.8 mM) and TEA (12 μL, 89.0 mM) in CH_3CN (1.0 mL) was irradiated at rt with 266-nm light (Nd:YAG, 4.0 mJ/pulse). The photolysis was monitored by GC (12.5 m column; 263 °C) in 10 min intervals. The results are summarized in Table 1.

Photolysis of 5 Using 308 nm Light. A degassed solution of **5** in CH_3CN (10.56 mM) was irradiated at rt with 308-nm light (YAG/dye, 3.7 mJ/pulse) for 5 min. The photolysis was analyzed by GC (12.5 m column; 250 °C). The products were the same as those formed in the 266-nm photolysis. A similar photolysis in the presence of TEA gave identical results.

Preparative Photolysis of 3,3-(Ethylenedioxy)-6*β*-(DPSO)-5*β*-androstan-17-one (6). A stirred, degassed solution of **6** (41.6 mg, 21.5 mM) in CH_3CN (4.0 mL) was irradiated at rt for 1 h with 266-nm light (Nd:YAG, 4.0 mJ/pulse). Analysis by GC (column B; 263 °C) showed two major products and the starting material (t_R = 7.04, 7.38, and 8.61 min, respectively). Identical products were formed upon photolysis with 308-nm light. The products could not be separated on the Chromatotron; spectral analysis was therefore conducted on a mixture of the enal, 3,3-(ethylenedioxy)-6*β*-(DPSO)-13,-17-*seco*-5*β*-androst-13-en-17-al (**22**), and the epimer, 3,3-(ethylenedioxy)-6*β*-(DPSO)-5*β*,13α-androstan-17-one (**23**), in a ratio of ca. 1:2.0. Spectral data for the mixture: ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.70−9.67 (s, 17-*H*C=O, enal), 7.63−7.32 (m), 3.99−3.84 (s, −OCH_2CH_2O−), 3.74−3.71 (q, *H*C-6*β*-DPSO, enal), 3.71−3.68 (q, *H*C-6*β*-DPSO, epimer) (the ratio of integrations of the two quartets is 1:2.0), 1.61 (s, 18-CH_3C=C, enal), 1.09 (s, 19-CH_3, enal), 0.97 (s, 19-CH_3, epimer), 0.94 (s, 18-CH_3, epimer), 0.38 (s, Si-CH_3, enal), 0.36 (s, Si-CH_3, epimer), 0.34 (s, SiCH_3, enal), 0.31 (s, SiCH_3, epimer). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 222.42 (17-*C*=O, epimer), 201.78 (17-H*C*=O, enal), 73.39, 73.01 (C-6*β*-DPSO, epimer, enal), 64.24, 64.08 (−O*C*H_2*C*H_2O−).

Preparative Photolysis of 6*β*-(DPSO)-5*β*-androstan-3-one (8). A stirred, degassed solution of **8** (35.6 mg, 21.0 mM) in CH_3CN (4.0 mL) was irradiated at rt for 2.0 h with 266-nm light (Nd:YAG, 4.0 mJ/pulse). Analysis of the irradiated solution by GC (column B; 253 °C) showed two major products plus starting material (t_R = 3.20, 3.53, and 5.43 min, respectively). Photolysis at 308 nm afforded the same results. The two enals, 6*β*-(DPSO)-2,3-*seco*-5*β*-androst-1-en-3-al (**26**) and 6*β*-(DPSO)-3,4-*seco*-androst-4-en-3-al (**27**), were isolated as a mixture on the Chromatotron (15% EtOAc/hexane) (2 mg) and analyzed as such. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.92 (3-*H*C=O, **26**), 9.43 (3-*H*C=O, **27**), 5.67 (H_2C=C<, **27**), 5.03−4.90 (−C*H*=CH_2, **26**).

Preparative Photolysis of a Mixture of 33 and 34 with 266 and 308 nm Light. A stirred, degassed solution of a mixture of **33** and **34** (49 mg, 27.2 mM) in CH_3CN (4.0 mL) was irradiated at rt for 50 min with 266 nm light (Nd:YAG, 4.0 mJ/pulse). Analysis by GC (column C; 240 °C) showed two pairs of major products with t_R (min) = 4.78 + 4.90 and 5.01 + 5.20 min (starting materials at 5.89 and 6.13 min). The products could not be separated on the Chromatotron and were analyzed as a mixture (see the Results).

Photolysis of 33 with 266 and 308 nm Light. A degassed solution of **33** (8.48 mM) in CH_3CN was irradiated at rt for 1 min with 266 nm laser light (Nd:YAG, 4.0 mJ/pulse). Analysis of the irradiated solution by GC (column C at 240 °C) showed three photoproducts: the enal 6*β*-(DPSO)-3(*E*)-ethylidene-13,-17-*seco*-5*β*-androst-13-en-17-al (**35**), 6*β*-(DPSO)-3(*E*)-ethylidene-5*β*,13α-androstane-17-one (**36**), and the *Z* isomer of **33** (**34**) in a ratio of 1.00:1.71:0.09. Photolysis at 308 nm gave the same products with a similar ratio (1.00:1.77:0.13).

Photolysis of 34 in CH_3CN with 266 and 308 nm Light. A degassed solution of **34** (7.58 mM) in CH_3CN was irradiated at rt for 1 min with 266 nm laser light (Nd:YAG, 4.0 mJ/pulse). Analysis of the irradiated solution by GC (column C at 240 °C) showed three photoproducts: 6*β*-(DPSO)-3(*Z*)-ethylidene-13,17-*seco*-5*β*-androst-13-en-17-al (**37**), 6*β*-(DPSO)-3(*Z*)-ethylidene-5*β*,13α-androstan-17-one (**38**), and the *E* isomer, 6*β*-(DPSO)-3(*E*)-ethylidene-5*β*,13α-androstan-17-one (**33**), in a ratio of 1.00:2.81:0.24. Photolysis at 308 nm afforded the same products in a ratio of 1.00:3.05:0.47.

Quenching Experiments for 5, 6, and 8 with *cis*-1,3-Pentadiene. Six degassed solutions of **5** (11.4 mM) in CH_3CN (1 mL) were photolyzed with the 266-nm laser (4.6 mJ/pulse) for 7 min in the presence of *cis*-1,3-pentadiene (0, 60, 100, 200, 300, 500 mM). The relative efficiencies for loss of starting material and the formation of photoproducts were obtained by GC analyses (column B; 253 °C) with 3α-(DPSO)-5α-androstane-11,17-dione as an internal standard. The data were corrected for absorption by the diene at 266 nm (ϵ_{266} = 3.5 M^{-1} cm^{-1}).[3c,d] Analogous experiments were run with 40 mM TEA.

A single point experiment was run with **6** (9.0 mM) and 100 mM *cis*-1,3-pentadiene. Analysis was as described above. Likewise, **8** (10.6 mM) was photolyzed with 152 mM *cis*-1,3-pentadiene with the 266 nm laser (3.4 mJ/pulse) and with 308 nm excimer laser (3.6 mJ/pulse) in the absence and presence of TEA. The reactions were analyzed by GC on column C at 225 °C with 17*β*-(DPSO)-5α-androstan-3-one as an internal standard.

Photolysis of 5 in the Presence of Cyclopentanone and Cyclohexanone. Degassed solutions of **5** (10.8 mM) in CH_3CN (1.0 mL) with and without cyclopentanone (10.4 mM) and cyclohexanone (10.5 mM) were irradiated at rt for 1 min. The solutions were analyzed by GC on column C at 240 °C for disappearance of the starting material and at 25 °C for loss of the ketones.

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Supporting Information Available: Proton nuclear magnetic resonance spectra are provided for compounds **5**, **6**, **18**, **19**, the mixtures **20/21** and **33/34**, and the alcohol precursor to **8** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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