Antenna-Initiated Photochemistry in Polyfunctional Steroids. Photoepimerization of 3α-(Dimethylphenylsiloxy)-5α-androstane-6,17-dione and Its 3β Isomer by Through-Bond Exchange Energy Transfer[1]

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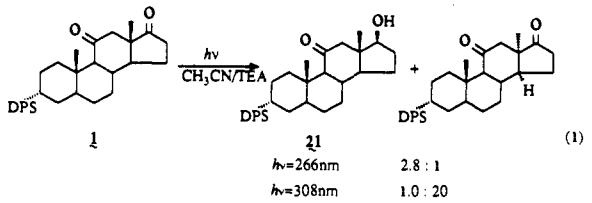
Abstract: We have previously reported that photolysis of 3α-(dimethylphenylsiloxy-5α-androstane-11,17-dione, in the presence of triethylamine (TEA) and with 266-nm light so as to selectively excite the dimethylphenylsiloxy (DPS) "antenna", primarily gives rise to triplet-derived reduction at C17. We now report on an analogous set of steroids, with a DPS antenna α or β at C3 and carbonyl groups at C6 and C17 (the title compounds, **3** and **4**). In these compounds, intramolecular singlet/singlet energy transfer (intra-SSET) from the DPS group to C6 is rapid ($k_{intra\text{-}SSET}$ = ca. 3×10^9 s^{-1}) and efficient ($\phi_{intra\text{-}SSET}$ ca. 76%), but this energy transfer is followed by a ca. 85% efficient intra-SSET from C6 to C17. The result is exclusively singlet chemistry (e.g., chemistry resulting from α cleavage) at C17 (with 60 mM TEA: **3**, ϕ = 0.23; **4**, ϕ = 0.098; eqs 3 and 4). The lower efficiency for the β isomer reflects a more than 2-fold less efficient intra-SSET relative to 3α-DPS. There is also a modest amount of triplet-derived reduction at C6 (ϕ_{red} = 0.046 at 60 mM TEA) with a 3α-DPS antenna, but no such reduction is observed when the DPS group is β. Through-bond-mediated exchange energy transfer is proposed for both the DPS → C6 and the C6 → C17 intra-SSET.

We have been interested in aryl-ketone-ketone trichromophoric steroids as models for the study of intramolecular through-space and through-bond energy migration in polyfunctional molecules, with a particular emphasis on the photochemistry elicited by such energy migration following excitation of an "antenna" functionality.[2a] One goal of this research is to utilize the potential variety of interchromophoric distances between the aryl antenna and target ketone groups, as well as between the ketone groups themselves, in order to probe the selectivity for excitation transfer to (and thus photochemistry at) a specific acceptor carbonyl group. Thus, we found that for 3α-(dimethylphenylsiloxy)-5α-androstane-11,17-dione (**1**) excitation of the dimethylphenylsiloxy (DPS) group leads to selective reduction at the 17-keto group (cf. eq 1). Of particular



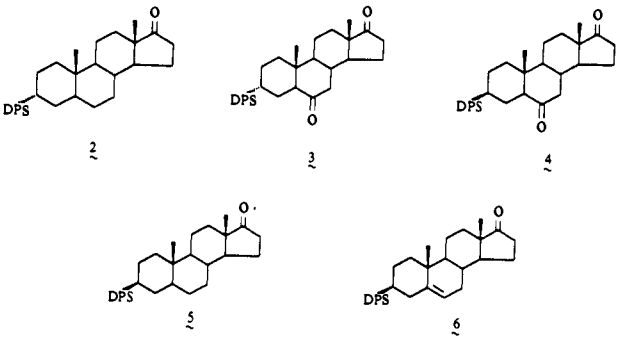
1 → 21 (1)

hν=266nm 2.8 : 1

hν=308nm 1.0 : 20

note were the following: (1) such reduction derives from the 17-keto triplet state; (2) by contrast, direct photolysis of the carbonyl groups in this steroid primarily leads to singlet-derived epimerization in ring D (eq 1); (3) energy migration modes in this molecule include facile intramolecular singlet/singlet energy transfer (intra-SSET) from C3 to C11, triplet energy hopping from C11 to C17, and intramolecular triplet/triplet energy transfer (intra-TTET) from C3 to C17 via a through-bond exchange mechanism (TBI). A concomitant study of 3α-DPS-5α-androstan-17-one (**2**) confirmed the existence of both intra-SSET and intra-TTET from C3 to C17 via a TBI mechanism.[2a]

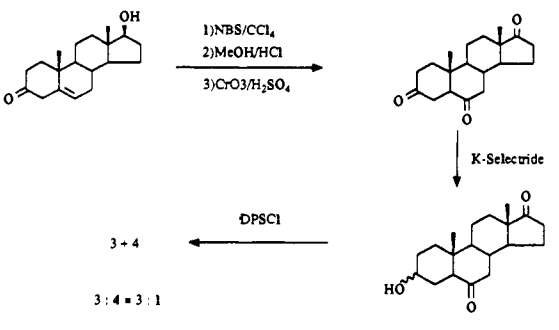
It is clear that the photophysical and photochemical properties of **1** reflect, in part, the relatively small separation between C11 and C17, i.e., three C-C σ bonds. We have classified such a system as A----K_1--K_2.[2a] We therefore decided to explore the isomeric DPS-substituted steroidal diones, 3α-DPS-5α-androstane-6,17-dione (**3**) and 3β-DPS-5α-androstane-6,17-dione (**4**), in which the two carbonyl groups are now separated by five C-C σ bonds, which brings K_1 closer to the antenna (i.e., A--K_1----K_2). Specifically, the distance between the two ketone chromophores in **3** and **4** (as calculated from MNDO-optimized structures and measured from keto carbon to keto carbon) is ca. 6.3 Å, compared with ca. 4.0 Å for **1**. We have also studied several monoketone models: 3β-DPS-5α-androstan-17-one (**5**), 3β-DPS-androst-5-en-17-one (**6**), and compound **2** (see above).[2b]



2 3 4 5 6

Results

Synthesis of the DPS-Derivatized Steroids, 2-6. The DPS-derivatized diones, **3** and **4**, were prepared by silylation of their alcohol precursors with chlorodimethylphenylsilane (DPSCl).[2a] The alcohols, 3α- and 3β-hydroxy-5α-androstane-6,17-dione, were prepared as a mixture of isomers by a literature procedure (cf. eq 2).[3] The derivatized monoketones, **2**, **5**, and **6**, were prepared in like fashion from their commercially available parent alcohols.



(2)

(1) Organic Photochemistry. 97. Part 96: Mohammad, T.; Morrison, H., *Photochem. Photobiol.* **1992**, 631-638.

(2) (a) Wu, Z. Z.; Morrison, H. *J. Am. Chem. Soc.* **1992**, *114*, 4119-4128. (b) For a preliminary communication, see: Wu, Z.-Z.; Morrison, H. *Tetrahedron Lett.* **1990**, 5865-5868.

(3) Fried, J. H.; Nutile, A. N.; Arth, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 5704-5707.

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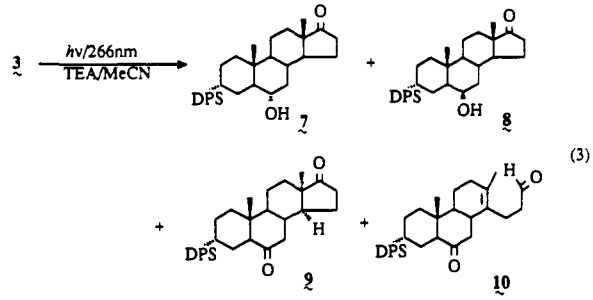
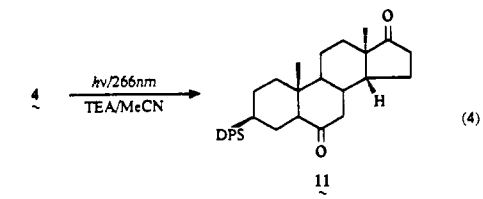
Photoproduct Studies. Photolysis of 3α-DPS-5α-androstane-6,17-dione (3) with Triethylamine (TEA) in Acetonitrile (MeCN). Irradiation of **3** (13.7 mM) in MeCN in the presence of 32.4 mM TEA with 266-nm laser light[4] leads to the formation of four primary photoproducts, two isomeric alcohols generated from reduction of the 6-keto group (3α-DPS-6α-hydroxy-5α-androstan-17-one (**7**) and 3α-DPS-6β-hydroxy-5α-androstan-17-one (**8**)) plus two products resulting from α cleavage in ring D, an epimer (3α-DPS-5α,13α-androstane-6,17-dione (**9**)), and an aldehyde (3α-DPS-6-oxo-13,17-seco-5α-androst-13-en-17-al (**10**)) in a ratio of 1.0:5.8:1.7 for (**7** + **8**):**9**:**10**, respectively (cf. eq 3). Thus, the α cleavage products constitute 88% of the overall reaction. Since **7** and **8** have identical GLC retention times, their ratio (**7**:**8**) was determined by ^{1}H NMR spectroscopy and found to be 1:1.



The products were isolated from a preparative photolysis of **3** (14 mM) with TEA (65 mM) in acetonitrile using 254-nm light. The structural assignments of the epimer **9** and aldehyde **10** are based on their NMR data. The cis fusion of the C and D rings in **9** is evidenced by the upfield shift of the 19-CH_3 group to δ 0.55 by comparison with δ 0.72 for **3**. This upfield shift is characteristic of a change to the cis ring fusion and reflects the placement of the 19-CH_3 group within the shielding cone of the 17-keto group.[6] The retention of both the 6- and 17-keto functionalities in **9** is supported by the ^{13}C NMR resonances at δ 212.1 and 221.3, respectively.[7] The assignment of the aldehyde **10** is based on the characteristic 17-C*H*=O and allylic 18-CH_3 group resonances at δ 9.75 and 1.66, respectively.[8]

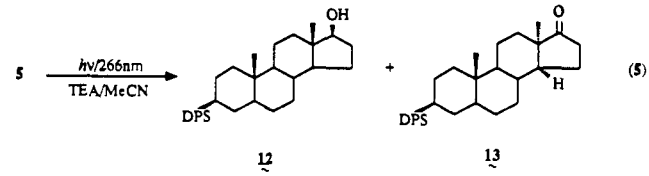
The structures of the alcohols, **7** and **8**, are assigned on the basis of their NMR and IR spectral data. The latter clearly gives evidence for the presence of an alcohol group in each case. Both products show the retention of the 17-keto group by the presence of carbonyl bands at 1730 and 1726 cm^{-1}, respectively,[9] and a sufficient amount of **8** was isolated to allow for a ^{13}C NMR spectrum, which shows the 17-keto carbonyl resonance at δ 221.4.[7] The alcohol functions are therefore at C6, and the stereochemistry in each isomer follows from the 6-C*H*OH resonances, i.e., the signal for 6-C*H*-αOH is expected to appear upfield of the 6-C*H*-βOH resonance.[10] Thus, **7** (6-C*H*-αOH) has its resonance at δ 3.30 (dt, J_d = 4.5 Hz, J_t = 10.5 Hz), while the corresponding resonance for **8** (6C*H*-βOH) comes at δ 3.67. The alcohol, **8**, was also generated by thermal reduction of **3** with K-Selectride.

Photolysis of 3β-DPS-5α-androstane-6,17-dione (4) with TEA in MeCN. An acetonitrile solution containing the dione **4** (13 mM) and TEA (61 mM) was irradiated with 266-nm light to give a single α cleavage product virtually exclusively, i.e., the epimer 3β-DPS-5α,13α-androstane-6,17-dione (**11**; cf. eq 4).



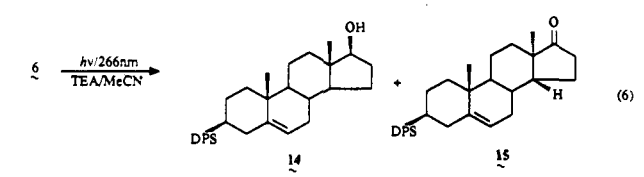
The product was isolated from the preparative photolysis of **4** (22 mM) with TEA (71 mM) in acetonitrile using 254-nm light, and its structure was assigned on the basis of its characteristic ^{1}H and ^{13}C NMR spectra. These include a proton resonance at δ 0.58, which is appreciably upfield of the resonance at δ 0.78 in **4** and characteristic of an epimeric 19-CH_3 group (see above), and ^{13}C resonances at δ 209.8 (6-C=O) and 221.0 (17-C=O) which are comparable to those (δ 212.1 and 221.3, respectively) of the 3α-DPS isomer (**9**).

Photolysis of 3β-DPS-5α-androstan-17-one (5) with TEA in MeCN. Irradiation of an acetonitrile solution containing **5** (15 mM) and TEA (61 mM) with 266-nm light resulted in formation of the alcohol 3β-DPS-5α-androstan-17β-ol (**12**) and the epimer 3β-DPS-5α,13α-androstan-17-one (**13**) in a ratio of 1.0:3.1 (cf. eq 5). This observation is analogous to that observed for the 3α



isomer, **2**.[2a] The assignment of **12** as the 17-C-βOH alcohol is supported by the ^{1}H NMR resonance at δ 3.58 (assignable to the 17-C-α*H*) and the ^{13}C NMR signal at δ 82.3 (characteristic of the 17-*C*-βOH). Both resonances match well with those of the isomeric alcohol, 3α-DPS-5α-androstan-17β-ol (δ 3.67 and 82.3, respectively).[2a] Compound **12** was also formed by reduction of **5** with $NaBH_4$ in ethanol. The C/D cis ring fusion of the epimer **13** is evidenced by the upfield position of the 19-CH_3 ^{1}H NMR signal at δ 0.62 (relative to δ 0.91 for **5**), the 18-CH_3 resonance at δ 0.95, and the 17-C=O resonance at δ 222.5, all of which are close to the values observed for the 3α-DPS isomer (δ 0.57, 0.97, and 222.7, respectively).[2a]

Photolysis of 3β-DPS-5-androsten-17-one (6) in Acetonitrile with TEA. Irradiation of an acetonitrile solution containing **6** (15 mM) and TEA (32 mM) with 266-nm light led to the formation of the alcohol (**14**) and the epimer (**15**) in a ratio of 1.0:1.3 (cf. eq 6). Assignment of **14** as the 17-C-βOH alcohol is supported by a ^{1}H NMR resonance at δ 3.63 and a ^{13}C NMR resonance at δ 82.0, characteristic of 17-C-α*H* and 17-*C*-βOH, respectively, and close to those observed for the reduced analog **11** (δ 3.58 for 17-C-α*H* and 82.3 for 17-*C*-βOH). The C/D cis ring fusion of the epimer, **15**, is indicated by the ^{1}H NMR resonances of the 19-CH_3 group at δ 0.81 vs 1.01 for this group in **6**.



Photolysis of Compounds 3–5 in Acetonitrile with TEA at 300 nm. Photolysis of **3** (28 mM) in acetonitrile with TEA (143 mM) using 300-nm light gave the epimer **9**, aldehyde **10**, and the

(4) Photolyses were conducted with 266-nm light from an Nd/YAG laser rather than with 254-nm light to minimize excitation of the TEA; cf. refs 1 and 5.

(5) Wu, Z.-Z.; Hug, G.; Morrison, H. *J. Am. Chem. Soc.* **1992**, *114*, 1812–1816.

(6) Other examples of the upfield shift at C19 upon photoepimerization at C13 in 17-keto steroids may be found in ref 1.

(7) The ^{13}C chemical shifts for five- and six-membered cycloalkanones are presented: Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1984.

(8) The resonances for the 18-CH_3 and 17-C*H*=O hydrogens in **10** match well with those (δ 1.65 and 9.87, respectively) observed in an analogous aldehyde α cleavage product isolated from the photolysis of 3β-hydroxy-5-androsten-17-one acetate: Iriarte, von J.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1964**, *47*, 1255–1264.

(9) For the characteristic carbonyl stretching frequencies of five- and six-membered cycloalkanones, see: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1981.

(10) For characteristic chemical shifts of 18-Me, 19-Me, and C*H*OH in steroidal ketones and alcohols, see: Bridgeman, J. E.; Cherry, P. C.; Clegg, A. S.; Evans, J. M.; Jones, Sir E. R. H.; Kasal, A.; Kumar, V.; Meakins, G. D.; Morisawa, Y.; Richards, E. E.; Woodgate, P. D. *J. Chem. Soc. C* **1970**, 250–257.

Table I. Quantum Efficiencies for Photolysis of 3 in Acetonitrile as a Function of TEA Concentration with 266-nm Light[a]

[TEA] (mM)	loss (%)	$\phi_{loss}(3)$	$\phi_{epi}(9)$	$\phi_{red}(7+8)$	$\phi_{ald}(10)$
32.4	34.2	0.30	0.16	0.028	0.045
43.2	17.7	0.30	0.18	0.042	0.049
60.5	30.5	0.52	0.18	0.046	0.055
75.6	25.5	0.48	0.18	0.065	0.054
92.9	23.4	0.46	0.14	0.079	0.037

[a] Monochromatic 266-nm light was generated with a fourth harmonic generating crystal from a Quanta Ray DCR-1 Nd/YAG pulsed laser operating at 10 Hz; $[3]_0$ = 13.7 mM, laser pulse energy = 1.8 mJ/pulse. The quantum efficiency data have been corrected for absorption of 266-nm light by TEA (ϵ_{266} = 6 M^{-1} cm^{-1}), which leads to both a filter effect and some chemical reduction.[4]

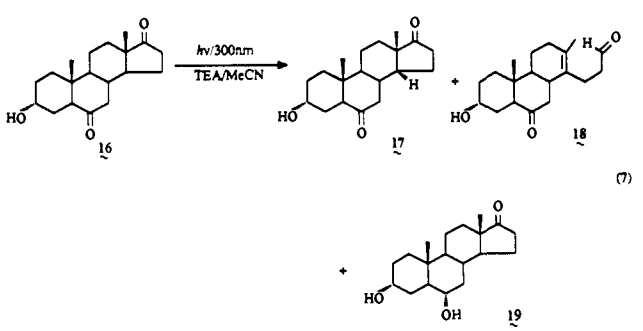
Table II. Quantum Efficiencies for Photolysis of 2, 4, and 5 in Acetonitrile with TEA with 266-nm Light[a]

compd	loss (%)	ϕ_{loss}	ϕ_{epi}	ϕ_{red}
4	16.7	0.29	0.098	b
5	22.1	0.067	0.034	0.011
2	29.9	0.070	0.033	0.011

[a] $[4]_0$ = 13.2 mM, $[5]_0$ = 15.0 mM, and $[TEA]_0$ = 60.5 mM; 266-nm laser pulse energy = 1.7 and 4.9 mJ/pulse for 4 and 5, respectively. $[2]_0$ = 14.9 mM, $[TEA]_0$ = 60.5 mM, and 266-nm laser pulse energy = 5.8 mJ/pulse. The quantum efficiency data have been corrected for absorption of 266-nm light by TEA (ϵ_{266} = 6 M^{-1} cm^{-1}), which leads to both a filter effect and some chemical reduction.[4] [b] Not detectable.

6-COH alcohols 7 and 8 as the major products in a ratio of 6.1:2.0:1.0.[11] Thus, α cleavage accounts for 89% of the overall photoreaction. Under the same conditions, the 3β isomer, 4, formed the epimer, 11, plus a second product in a ratio of 5:1. The new product is tentatively assigned to an aldehyde isomeric with 10 on the basis of the characteristic ^{1}H NMR signal at δ 9.76 for 17-C*H*=O. Photolysis of the monoketone, 5, at 300 nm produced the epimer, 13, and the alcohol, 12, in a ratio of 22.5:1.0.

Photolysis of 3α-Hydroxy-5α-androstane-6,17-dione (16) in Acetonitrile with TEA at 300 nm. An acetonitrile solution of 16 (30 mM) and TEA (140 mM) was irradiated at 300 nm to give the epimer 17, aldehyde 18, and diol 19 in a ratio of 5.7:2.0:1.0 (cf. eq 7). Though the products could not be isolated in pure form, the ^{1}H NMR spectrum of the mixture provided data comparable to those obtained for other α cleavage products. Thus, the presence of 17 is evidenced by characteristic resonances at δ 0.58 and 1.02 for the 19-CH_3 and 18-CH_3 groups, respectively (for the DPS analog 9: δ 0.54 and 1.02). The presence of 18 is indicated by a resonance at δ 9.80 for the aldehyde proton (DPS analog 10: δ 9.75). Finally, the formation of a 6-C-αOH alcohol as in 19 is confirmed by the diagnostic signal at δ 3.30 (cf. for the 6-C*H*-αOH in the DPS monoalcohol 7 δ 3.30).



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Quantum Efficiencies for Photolysis of 3–5 with 266-nm Excitation. Quantum efficiencies for the loss of dione 3, $\phi_{loss}(3)$, photoepimerization, $\phi_{epi}(9)$, photoreduction of the 6-keto group, $\phi_{red}(7+8)$, and formation of the aldehyde, $\phi_{ald}(10)$, were measured as a function of [TEA] (32.4–92.9 mM) in acetonitrile with 266-nm laser light (1.8 mJ/pulse). The data are summarized in Table I. The quantum efficiencies for product formation account for 78–90% of the loss of starting material at the lower TEA concentrations, but the mass balance drops to 54–62% at ≥60 mM TEA. No reduction at C17 was observed in these experiments.

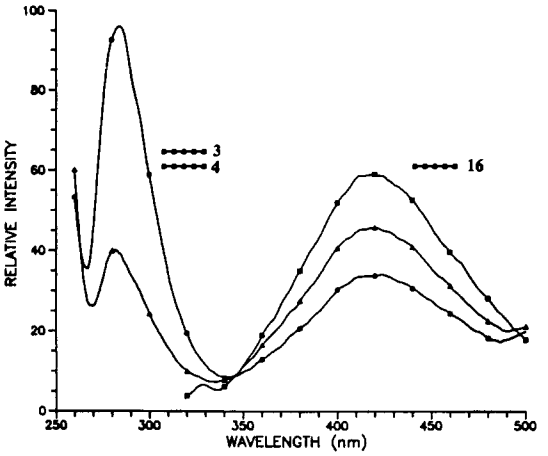


Figure 1. Corrected fluorescence spectra for compounds 3, 4, and 16 in acetonitrile at room temperature; excitation at 254 nm for 3 and 4 and at 300 nm for 16.

The quantum efficiencies for photolysis of the substrates 4 and 5 were determined at 60.5 mM TEA and are summarized in Table II. Included in the table are data for 3α-DPS-5α-androstan-17-one (2) which have been previously reported;[2a] the ϕ_{red} and ϕ_{epi} values are virtually identical to those of the 3β isomer, 5.

Quantum Efficiency of Epimerization of 5 with 308-nm Light. An acetonitrile solution of 5 (55.6 mM) and TEA (165 mM) was irradiated using a XeCl excimer laser at 308 nm (2.8 mJ/pulse) through a neutral density filter. The quantum efficiency (ϕ_{epi}) thus measured (0.36) may be compared with a value of 0.31 determined for the 3α isomer.[2a]

Effect of Added Cyclohexanone on the Photochemistry of 5. The addition of cyclohexanone has proven useful as a test of the possible contribution of intermolecular SSET to these antenna-initiated photoreactions.[2a,12,13] Compound 5 (15.2 mM) in 2-propanol was photolyzed with 254-nm light in the presence and absence of cyclohexanone (photolysis of 5 in this solvent leads exclusively to the epimer 13). At concentrations of cyclohexanone of 0, 9.0, 18.0, and 26.9 mM, 13 was formed to the extent of 4.3, 4.2, 4.0, and 3.9 mM, respectively, e.g., at the approximately equimolar concentration of external ketone (18.0 mM), there is a 7% reduction in the epimerization.

Photochemistry of 3 in Acetonitrile with TEA in the Presence of *cis*-1,3-Pentadiene. Triplet quenching by the diene was measured using the Nd:YAG laser at 266 nm (1.7 mJ/pulse) with the concentrations of 3 and [TEA] at 14.8 and 60.5 mM, respectively, and the diene concentration at 20 mM. Photoreduction was virtually eliminated while epimerization and aldehyde formation were quenched by ca. 29% and 30%, respectively. When the photolysis of 3 (29 mM) was conducted with 300-nm light using higher concentrations of both TEA (143 mM) and diene (150 mM), 14% of the epimerization and 6% of the aldehyde formation were quenched.

Spectroscopy. The absorption spectra for compounds 3–5 reflect the component aryl and diketone (or ketone) chromophores, as has been observed for 3β-DPS-5α-androstane-11,17-dione.[2a] For example, the absorption maxima and extinction coefficients for compound 3 in acetonitrile are as follows: λ_{max} nm (ϵ M^{-1} cm^{-1}) 252 (180), 258 (257), 262 (255), 269 (196), 290 (68).

The emission spectra of 3 and 4 in acetonitrile are presented in Figure 1; both compounds show dual emission, with aryl emission at ca. 285 nm and ketone emission at ca. 430 nm, though

(11) This photolysis also leads to the formation of a small quantity of 3α-DPS-17β-hydroxy-5α-androstan-6-one (ca. 3%) and 3α-DPS-5α-androstane-6,17-diol (ca. 10%).

(12) Morrison, H.; Pallmer, M.; Loeschen, R.; Pandey, B.; Muthuramu, K.; Maxwell, B. *J. Org. Chem.* **1986**, *51*, 4676–4681.

(13) Wu, Z.-Z.; Morrison, H. *Photochem. Photobiol.* **1989**, *50*, 525–530.

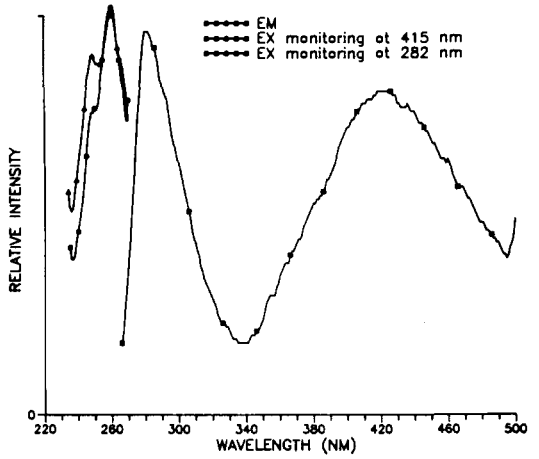


Figure 2. Corrected fluorescence emission and excitation spectra for **20** in acetonitrile at room temperature; excitation spectra for **20** in acetonitrile at room temperature; excitation at 254 nm for the emission spectrum. The excitation spectra were monitored at 282 and 415 nm.

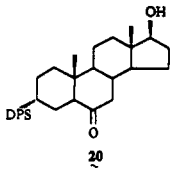
Table III. Fluorescence Efficiencies and Singlet Lifetimes in Acetonitrile[a]

compd	ϕ_f(Ar)	τ_f (ns)	compd	ϕ_f(Ar)	τ_f (ns)
3	0.00063	<0.25	**6**		0.86
4	0.0018	0.31	**20**		0.39
5	0.0047	1.04	**12**	0.0053	1.20

[a] Measured at room temperature with 254-nm excitation for ϕ_f and 266-nm excitation for τ_f. Toluene in cyclohexane served as the fluorescence standard (ϕ_f = 0.14).[14]

the diminution of aryl emission in **3** is appreciably greater than that seen for **4**. The emission spectrum of the dione **16**, i.e., the alcohol precursor of **3**, is also presented in Figure 1 for purposes of comparison.

An example of the excitation spectra in this series is presented in Figure 2 for 3α-DPS-17β-hydroxy-5α-androstan-6-one (**20**), which was prepared by silylation of the known diol 3α,17β-dihydroxy-5α-androstan-6-one. The excitation spectrum corresponds to aryl absorption whether one is monitoring at 415 or 282 nm.



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Fluorescence quantum efficiencies (ϕ_f) were determined in acetonitrile using toluene emission in cyclohexane (ϕ_f = 0.14) as a reference.[14] The data for compounds **3–5** and **12** (as a DPS reference) are given in Table III. Fluorescence lifetimes for these substrates, as well as for compounds **6** and **20**, were measured in acetonitrile at room temperature, and these data are included in Table III.

Phosphorescence emission spectra of **3–6** and **12** (1.4 mM) were determined at 77 K in an ether–methylcyclohexane glass with 254-nm excitation. All of the substrates showed toluene-like emission centered at 380 nm; no ketone phosphorescence was detectable. The spectra for **5** and **6** are superimposable, while there are small reductions in emission seen for **3** and **4** relative to **12** (ca. 27% and 18%, respectively).

Discussion

Photochemistry. As has been noted in our earlier papers,[2,15] the DPS antenna combines two properties desirable for a study of energy migration in polyfunctional molecules: a high extinction coefficient for excitation and a short singlet excited state lifetime

(14) Birks, J. B. *Photophysics of Aromatic Molecules*; John Wiley & Sons Ltd.: New York, 1970; p 126.
(15) Morrison, H. *Rev. Chem. Intermed.* **1987**, *8*, 125–145.

Table IV. Efficiencies and Rates for intra-SSET

steroid	R^a (Å)	$\phi_{\text{intra-SSET}}{}^b$	$k_{\text{intra-SSET}}{}^b$ (10^8 s^{-1})
	Monoketones		
5	13.0	0.14 (0.11)	1.4
2[c]	11.5	0.21 (0.11)	2.2
6	13.0	0.28	3.3
23[d]	12.4	0.15	1.5
24[d]	10.2	0.31	3.7
20	7.2	0.68	17
21[c]	8.6	0.73 (0.62)	22
	Diketones[e]		
3	7.2	0.79 (0.88)	32
4	7.4	0.74 (0.66)	24
1	8.6	0.78 (0.68)	29
22[c]	9.4	0.58	12

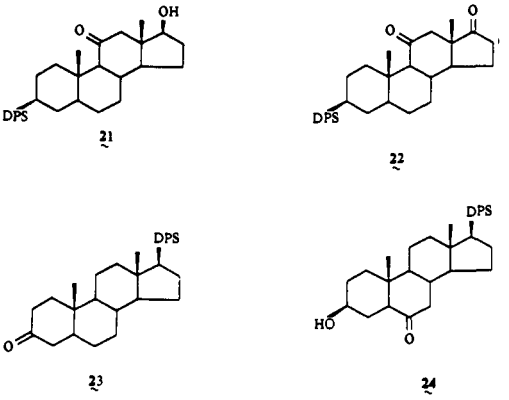
[a] Interchromophoric distance as calculated by MNDO. [b] Values calculated from fluorescence lifetimes. $\phi_{\text{intra-SSET}}$ data are in parentheses and have been calculated from fluorescence quantum efficiencies; rates derived from these are not presented because the low ϕ_f values make such rates less reliable. [c] From ref 1. [d] Unpublished results. [e] *R* represents the distance to the most proximal carbonyl group.

(to minimize intermolecular and secondary processes). The result has been facile singlet and triplet energy transfer from the DPS group to distal ketone functionalities,[2a] and excitation of the aryl antenna in both **3** and **4** does indeed lead to carbonyl photochemistry (eqs 3 and 4). Two aspects of this photochemistry are noteworthy: the chemistry is concentrated at the more remote C17 carbonyl group, and the C17 chemistry is exclusively the consequence of α cleavage. The appearance of some reduction of the 6-keto group in **3** (ca. 16% at [TEA] = 60.5 mM; Table I) but not in **4** is also of interest. It should be noted that direct excitation of the ketone chromophores at 300 nm in **3** and **4** gives a very similar set of results, and in fact, the substrate lacking an antenna (**16**) behaves analogously, though now reduction at C17 does account for ca. 11% of the product mixture (eq 7). As in our previous studies,[2a,13] the minimal impact of external cyclohexanone assures that antenna sensitization in these substrates results from intramolecular processes. Also, as has been previously observed in related steroids,[2a] the small amount of reduction which does occur in the photolysis of **3** is totally quenchable by *cis*-1,3-pentadiene (and thus triplet-derived), whereas only modest levels of quenching of the, primarily singlet-derived, α cleavage chemistry at C17 is seen (intersystem crossing at C17 is minimally competitive with the very rapid α cleavage characteristic of this carbonyl group).[2a]

It is instructive to compare the photochemistry of these 6,17-diketones with the 11,17 series previously reported[2a] (cf. eq 1 and the introductory section). Thus, the antenna-sensitized photoreduction of the 6-keto group in **3** stands in contrast to the complete lack of observable photochemistry at C11 in **1**. This may be a consequence of the intrinsically greater reactivity of the 6-keto group vis-à-vis a ketone at C11 (the latter being quite sterically encumbered)[2a] or the greater separation of K_1 and K_2 in the C6/C17 series vs the C11/C17 series (see introduction and further discussion below). More striking is the fact that the 17-keto groups in **3** and **4** show a very high preference for α cleavage, whereas the 17-keto group in **1** is primarily reduced when internally sensitized. Rephrased, *the antenna-initiated chemistry at C17 primarily originates from the singlet manifold in the 6,17-diketones but derives from the triplet manifold in the 11,17 series.*

Energy Migration in Compounds 3 and 4—Intramolecular Singlet/Singlet Energy Transfer (intra-SSET). It is clear from the spectra in Figure 1 that there is appreciable singlet energy migration from the DPS group to the carbonyl functionalities in both **3** and **4**. The diminished fluorescence efficiencies and reduced singlet lifetimes for **3** and **4**, when compared with data for the monofunctional DPS model, **12** (cf. Table III), also give evidence for such energy transfer. The intra-SSET quantum efficiencies ($\phi_{\text{intra-SSET}}$(i)) from the DPS antenna to a ketone group in a substrate i can be readily evaluated from either the ϕ_f or τ_f values, as can the corresponding rates ($k_{\text{intra-SSET}}$(i)), by using a mono-

functional DPS reference.[2a] Using **12** for this purpose, data have been compiled in Table IV for the DPS diketones, **3** and **4**, and the DPS monoketones, **2**, **5**, **6**, and **20**. Table IV also includes data from the previously studied[2a] 3-DPS-11-keto series, i.e., the monoketone 3α-DPS-17β-hydroxy-5α-androstan-11-one (**21**) and the diketones 3α- and 3β-DPS-5α-androstane-11,17-dione (**1** and **22**), as well as data for two 17-DPS monoketones, 17β-DPS-5α-androstan-3-one (**23**) and 17β-DPS-3β-hydroxy-5α-androstan-6-one (**24**). The interchromophore distances (*R*), also included in Table IV, are defined as the distance from the carbon atom of the phenyl ring attached to the silicon atom to the carbon atom of the carbonyl group. The *R* values for **5**, **6**, and **20** were calculated with MNDO-optimized structures; an *R* value for **5** of 12.85 Å was measured by X-ray structural analysis (see the Experimental Section) and found to be in good agreement with the calculated value of 13.0 Å.



There are no surprises in Table IV. Those steroids which contain the C3 antenna adjacent to a carbonyl group at C6 (e.g., **3**, **4**, and **20**) show high efficiencies (68–79%) and rates ((17–32) × 10^8 s^{-1}) for intra-SSET. These rates and efficiencies are comparable to those seen for the 3-DPS-11-keto substrates (**1**, **21**, and **22**). The substrates bearing the antenna at C3 and the ketone at the more remote C17 (**2**, **5**, and **6**) show a ca. 3-fold or greater reduction in efficiency and a ca. 10-fold reduction in rate for intra-SSET; similar reductions in efficiencies and rates of energy transfer are seen for compounds **23** and **24**. Compound **6** represents our first trifunctional steroid, and we find it interesting that the presence of the cycloalkene modestly facilitates intra-SSET, an observation we are currently pursuing.[16]

The singlet chemistry picture which emerges from these data and the product patterns is shown in Scheme I. Though direct energy transfer from C3 to C17 can occur (as evidenced by the data for the 3-DPS 17-ketones in Table IV), the two-step process proposed in this scheme is supported by the large increases in efficiency and rate of energy transfer to C6 vs C17 and the appreciable enhancement in ϕ_{epi} for **3** or **4** versus that observed for ketones lacking the 6-keto chromophore, e.g., **2** or **5** (e.g., at [TEA] = 60.5 mM, the ϕ_{epi} values for **3** and **4** are 0.18 and 0.098, whereas those for **2** and **5** are 0.033 and 0.034; cf. Tables I and II).

One can estimate the efficiency of the second intra-SSET step (i.e., C6 → C17) using eq 8, where ϕ_{epi}(**3**) = 0.18 (Table I), $\phi_{intra\text{-}SSET}$(C3 → C6) = 0.68 (from compound **20**, Table IV), and ϕ_{epi}(17-C=O) = 0.31 (measured by excitation of **2** at 308 nm).[1] The $\phi_{intra\text{-}SSET}$(C6 → C17) value so calculated is a remarkably high 85%.

$$\phi_{epi}(\mathbf{3}) = \phi_{intra\text{-}SSET}(C3 \rightarrow C6) \times \phi_{intra\text{-}SSET}(C6 \rightarrow C17) \times \phi_{epi}(17\text{-}C{=}O) \quad (8)$$

Because of the lack of a suitable 3β-DPS 6-ketone model analogous to **20**, we cannot directly calculate the $\phi_{intra\text{-}SSET}$(C3 → C6) value for a 3β antenna (as in, for example, **4**). However, if we assume an identical $\phi_{intra\text{-}SSET}$(C6 → C17) and use ϕ_{epi}(17-C=O) = 0.36 for **5** measured at 308 nm and ϕ_{epi}(**4**) = 0.098 (Table II), we can estimate $\phi_{intra\text{-}SSET}$(C3 → C6) for the 3β-DPS group as 32%. This is appreciably lower than the value calculated above for the efficiency of the 3α isomer C3 → C6 intra-SSET (conversely, the reduced $\phi_{intra\text{-}SSET}$ explains the large reduction in ϕ_{epi} for **4** vs **3**). A ca. 2-fold reduction in the rate of intra-SSET has likewise been observed for C3 (βDPS) → C11 relative to the 3α series.[2a]

Another interesting feature emerging from a comparison of the 3α and 3β series is the appearance of reduction at C6 in the 3α case but not with 3β (compare eqs 3 and 4). There are two options to rationalize the absence of reduction in the β series: (1) the C6 triplet is being formed in the 3α case via intra-TTET from the DPS group to the carbonyl, and no such energy transfer occurs in the β series,[17] or (2) C6 triplets are indeed forming in both the α and β substrates (by intra-TTET or via intersystem crossing of the initially generated C6 singlet), but the 3β-DPS group is functioning as an effective triplet quencher.[18,19] We have no way

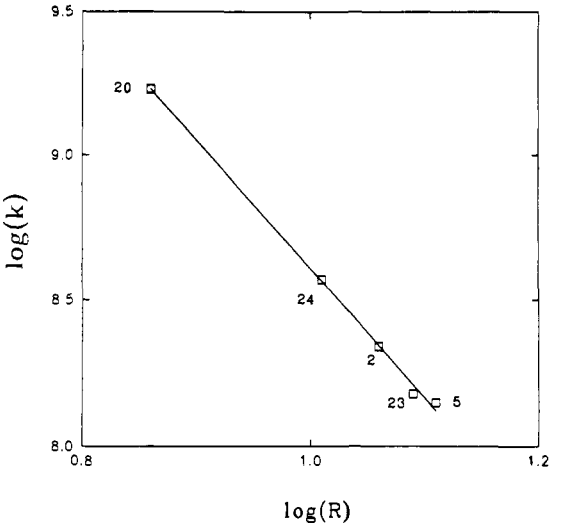
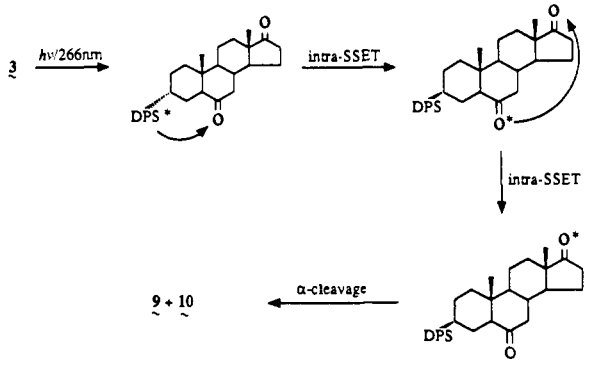


Figure 3. Double logarithmic plot of the rate of intra-SSET from the DPS singlet to the keto chromophore for steroids in acetonitrile at room temperature as a function of interchromophore distance (*R*).

Scheme I



(16) The higher fraction of alcohol generated by 266-nm photolysis of **6** may also indicate a greater efficiency of intra-TTET via a through-bond mechanism.[17] Studies to confirm this are in progress.

(17) Intra-TTET from C3 to C17 has been observed in our earlier study and attributed to a through-bond-mediated exchange process.

(18) It is certainly possible that there is (less efficient) quenching of the C6 ketone triplet by the 3α-DPS group as well.

(19) For examples of triplet energy transfer from a ketone to an aryl group, see: Whitten, D. G.; Punch, W. E. *Mol. Photochem.* **1970**, *2*, 77–80. Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E. *Mol. Photochem.* **1970**, *2*, 81–85. Wismontski-Knittel, T.; Kilp, T. *J. Phys. Chem.* **1984**, *88*, 110–115. Netto-Ferreira, J. C.; Leigh, W. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 2617–2622. Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 5487–5491. Netto-Ferreira, J. C.; Scaiano, J. C. *Tetrahedron Lett.* **1989**, *30*, 443–446. An intramolecular example: Zimmerman, H. E.; Weber, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 995–1007.

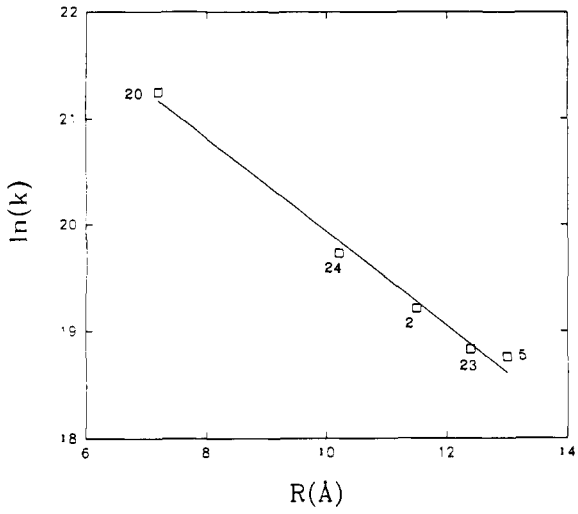
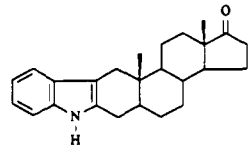


Figure 4. Exponential plot for the rate of intra-SSET from the DPS singlet to the keto chromopore for steroids in acetonitrile at room temperature as a function of interchromophore distance (R).

of differentiating these possibilities with certainty, but it should be noted that C17 reduction, and therefore intra-TTET,[17] is observed from both the α[2a] and β (eq 5) C3 DPS groups to the C17 ketone, so that the absence of C17 triplets in the presence of the C6 ketone suggests that DPS triplets are indeed being diverted to C6.

Mechanism of DPS to Ketone Intra-SSET. There are two "nontrivial" mechanisms possible for this phenomenon: Förster dipole–dipole coupling[20] and Dexter exchange energy transfer.[21] The energy-transfer rate constants in both cases are proportional to the spectral overlap between donor emission and acceptor absorption, although the form of the expression for spectral overlap used in the Förster treatment differs from that used in the exchange treatment. The dipole–dipole interaction is a long-range energy-transfer process, with its rate of energy transfer decreasing with the inverse sixth power of R while the exchange interaction decreases exponentially with increasing R and normally is expected to become negligibly small as R increases beyond 5–10 Å.[22] There is certainly ample precedent for intra-SSET via a Förster mechanism. For example, an elegant study of compound **25**, in which the indole and 17-keto functionalities are separated by ca. 10 Å, showed that the rate of internal energy transfer varies with the solvent and is proportional to the magnitude of the Förster spectral overlap term.[23] However, we have taken the rates of



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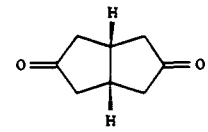
intra-SSET and the interchromophoric distances in Table IV[24] and fit these data to a double logarithmic plot (Figure 3). The slope of the least-squares-fitted line is -4.4 ± 0.12, in comparison with the value of -6 predicted by the Förster equation. In addition, we find that the Föster theory does not satisfactorily predict our observed rate constant for intra-SSET in, for example, compound **5**. When we use a value for $J_{\text{Förster}}$ calculated by numerical integration[25] of 1.67×10^{-17} cm^3 M^{-1} and an orientation factor, k^2, assumed to be $^2/_3$,[25] our calculated rate for intra-SSET is 2.6×10^6 s^{-1}, 54-fold smaller than that which has been measured (1.4×10^8 s^{-1}, Table IV). Even an assumption of k^2 at its maximum value[25] of 4 gives a rate of 4×10^7 s^{-1}, which is still far less the measured value.

On the other hand, Dexter theory may be tested through its prediction that a plot of the natural log of the measured rates of intra-SSET versus the R value should yield an effective van der Waals radius for the donor/acceptor sphere of interaction. Our data (Figure 4; slope $= -0.44 \pm 0.028$)[24] yield a value of $L = 4.5$ Å,[26] quite large in comparison with other published values of $L = 1.5$[26] and 2.3 Å,[27] especially considering that the receptor in our case is a low oscillator strength ketone. However, our observation *can* be accommodated by the assumption of through-bond interactions between the donor and acceptor, and such long-range TBI-mediated exchange energy transfer is now well precedented.[2a,26,28-30]

Mechanism of Ketone to Ketone Intra-SSET. The 6- and 17-keto chromophores are separated by five C–C σ bonds at a distance of 6.3 Å, an interchromophoric distance commonly believed to be in excess of that which could be accommodated by an exchange mechanism operating through space.[22,30] However, the efficiency of this intra-SSET is ca. 85% (vide supra) and has a rate estimated to be $\geq 4 \times 10^8$ s^{-1} (assuming a fluorescence lifetime for the 6-keto chromophore of 2 ns).[31] Such a high rate constant is inconsistent with dipole–dipole-derived transfer, because such energy transfer is strongly dependent on the oscillator strengths of the donor and the acceptor[22] and, as has been noted above, ketone chromophores have low oscillator strengths. One is left with a through-bond exchange mechanism, where rates fitting in well with our observation have been reported for other diketones, e.g., compounds **26** and **27** with $\geq 1 \times 10^{10}$ s^{-1} for the 1,5-dione separated by four C–C σ bonds and $\leq 1 \times 10^7$ s^{-1} for the 1,7-dione separated by six C–C σ bonds.[32]



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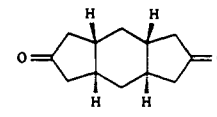

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Interestingly, there is recent photospectroscopic evidence for the coupling of ketone functionalities in the ground state of steroids, with an apparently strong dependence on the orientation of these groups on the hydrocarbon framework.[33] Our observations demonstrate that the relationship of two ketone groups on the steroid skeleton also has a profound effect on coupling in the excited state, i.e., the 11,17 steroidal diketone shows virtually no intra-SSET (thus creating antenna-initiated chemistry at C17 predominantly from the C17 *triplet*)[2a] while the 6,17-diketone

(20) Förster, T. *Fluorenzenz Organische Verbindungen*; Vandenhoech and Rprech: Gottingen, 1951.
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(22) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 9.
(23) Haugland, R. P.; Yguerabide, J.; Stryer, L. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *63*, 23–30.
(24) Compound **21** has not been included in Figure 3; its datum represents an "outlyer" somewhat above the least-squares fit to the other points.
(25) Campbell, I. D.; Dwek, R. A. *Biological Spectroscopy*; Benjamin/Cummings: Menlo Park, CA, 1984; Chapter 5, pp 113–119.
(26) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Cotsaris, E.; Hush, N. S. *Chem. Phys. Lett.* **1988**, *143*, 488–495.
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(28) Kroon, J.; Oliver, A. M.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 4868–4873.
(29) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933–3951.
(30) For contrasting views on long-range TBI-mediated exchange energy transfer, see: (a) Speiser, S.; Rubin, M. B. *Chem. Phys. Lett.* **1988**, *150*, 177–178 and (b) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Cotsaris, E.; Hush, N. S. *Chem. Phys. Lett.* **1988**, *150*, 179–180 (see also ref 28).
(31) (a) Dalton, J. C.; Turro, N. J. *Annu. Rev. Phys. Chem.* **1970**, *21*, 499–450. (b) The τ_f value of the 6-keto chromophore in **1** is likely to be less than 2 ns since it is effectively an α,α'-disubstituted cyclohexanone; our estimate of rate is therefore a minimum value.
(32) Schippers, P. H.; Dekkers, H. P. J. M. *J. Am. Chem. Soc.* **1983**, *105*, 145–146.
(33) Cvitas, Y.; Kovac, B.; Pasa-Tolic, Lj.; Ruscic, B.; Klasinc, L.; Knop, J. V.; Bhacca, N. S.; McGlynn, S. P. *Pure Appl. Chem.* **1989**, *61*, 2139–2150.

shows efficient intra-SSET and *singlet* photochemistry at C17.[34]

Conclusion. The chemistry at the 17-keto group in the C6/C17 steroidal diketones can be used to probe the nature of the intramolecular energy transfer occurring when a C3 antenna is initially excited. The dominant, singlet-derived epimerization which is observed confirms that intra-SSET from C3 → C6 → C17 is the primary pathway for energy migration. The photophysical data are best accommodated by a through-bond exchange mechanism for the intra-SSET.

Experimental Section

Instrumentation. NMR spectra were obtained with a General Electronic QE-300 or a Varian VXR-600S spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 1800 FT-IR spectrometer. Low-resolution mass spectra were determined with a Finnigan 4000 GLC–MS spectrometer (EI/CI) equipped with a DB-1 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Electron impact (EI) spectra were obtained at an ionization energy of 70 eV, and chemical ionization (CI) spectra were also obtained at 70 eV by using isobutane at a pressure of 0.30 Torr. High-resolution mass spectra were recorded on a Kratos Model MS-50 spectrometer. Absorption spectra were recorded on a Perkin-Elmer Model Lambda 3B spectrometer. Fluorescence and phosphorescence spectra were recorded on a component fluorometer[35] or a PTI Model LS-100 fluorometer. Fluorescence quantum efficiencies were measured by reference to toluene.[14] Fluorescence lifetimes were determined with a PTI Model LS-100 fluorescence lifetime spectrometer using an H_2 lamp. Fluorescence studies were conducted at room temperature with the solutions purged with argon for at least 15 min prior to use. Phosphorescence spectra were run in an ether–methylcyclohexane glass at 77 K which was degassed using a freeze–pump–thaw method at a pressure of 10^{-4} Torr for at least three cycles. Analytical GLC experiments were performed on a Hewlett-Packard Model 5710A or a Varian 3700 capillary instrument (both with flame ionization detectors) coupled to a Hewlett-Packard 3390A integrator. Product ratios represent relative peak areas and are uncorrected for detector response. The capillary columns used were the following: A, RSL-150 (Alltech, 30 m × 0.25 mm i.d., 0.25 μm film thickness), and B, DB-1 (J & W, 15 m × 0.25 mm i.d., 0.25 μm film thickness). Melting points were determined with a Fisher-Johns melting point apparatus.

Materials. 17β-Hydroxyandrost-4-en-3-one, 3β-hydroxy-5α-androstan-17-one, 3β-hydroxyandrost-5-en-17-one, K-Selectride (1 M in THF), and chlorodimethylphenylsilane (DPSCl) were purchased from Aldrich and used as received. The quencher (*cis*-1,3-pentadiene, Chemical Samples) was used as received. Tetrahydrofuran (THF, Mallinckrodt) was purified by successive distillations under nitrogen from sodium and benzophenone. Triethylamine (TEA, Mallinckrodt) was distilled from calcium hydride. *N,N*-Dimethylformamide (DMF, Fisher) was treated with 4-Å molecular sieves, followed by distillation under reduced pressure. Hexane, cyclohexane, acetonitrile, and isopropyl alcohol used in the photochemical and spectroscopic studies were of spectroquality grade from Burdick and Jackson. Toluene used as a reference for determination of fluorescence quantum efficiencies was of spectroquality grade from Fisher. Hexane, ethyl acetate, and methylene chloride used in column chromatography were bulk grade and distilled prior to use. Silica gel for chromatography was 230–400 mesh. The internal standards were 3β-DPS-5α-androstan-17-one (**5**) and its 3α isomer (**2**).

Photolyses. Photochemical studies were mainly carried out in a Rayonet photochemical reactor (Model RPR-100, Southern New England Ultraviolet Co.) equipped with 254-nm or 300-nm lamps, a merry-go-round turntable, and a cooling fan. For 254-nm photolysis, a sample solution was irradiated in a quartz tube (length 12 cm × 1.2 cm o.d.); for 300 nm, a sample was irradiated in a Pyrex tube (length 10 cm × 1.2 cm o.d.). Quantum efficiencies at 266 nm were measured using a Quanta Ray DCR-1 Nd/YAG pulse laser (10 Hz, laser pulse energy 1.5–6.5 mJ/pulse) with a fourth harmonic generating crystal, using a Scientech Model 362 power meter. Quantum efficiencies at 308 nm were determined using a Lambda Physik EMG 201 MSC laser (10 Hz, 3–6 mJ/pulse) with a Scientech Model 361 power meter. All sample solutions for photolysis were purged with argon for at least 15 min prior to use.

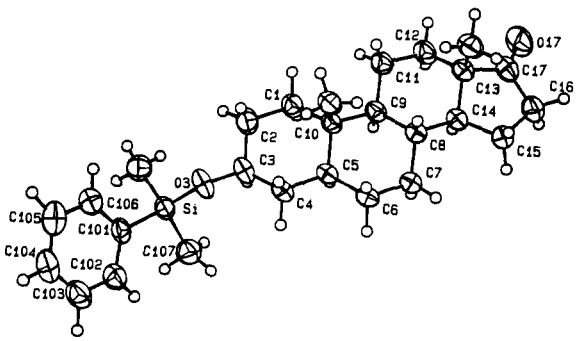

Figure 5. X-ray structure of **5**.

All photochemical studies were run at room temperature under dry nitrogen. "Neutral workup" refers to the quenching of a reaction with water, extracting with CH_2Cl_2, washing of the organic layer with water and brine, and drying, filtering, and concentrating the organic extract in vacuo.

Preparation of 17β-Hydroxy-5α-androstane-3,6-dione. The title compound was readily prepared by following the reported procedure[36] in 32% overall yield, mp 219–223 °C (lit.[36] mp 222–227 °C).

5α-Androstane-3,6,17-trione. A 100-mL three-neck flask, equipped with a stir bar, reflux condenser, and dropping funnel and containing the Jones reagent (0.90 g of CrO_3, 0.8 mL concentrated H_2SO_4, 2.0 mL of H_2O), was charged with 25 mL of an acetone solution of 17β-hydroxy-5α-androstane-3,6-dione (609 mg, 2 mmol). The Jones reagent was added dropwise into the solution at 0 °C with stirring. The reaction mixture became dark green in the first few minutes, and the reagent was added to the mixture until it became red-brown. After stirring for 10 min, the mixture was subjected to neutral workup to give a yellowish solid (493 mg, 81% yield), mp 189–192 °C (lit.[37] mp 191–194 °C).

3-Hydroxy-5α-androstane-6,17-dione. The 3-keto group of 5α-androstane-3,6,17-trione (582 mg, 1.93 mmol) in THF (16 mL) was reduced with K-Selectride (1 M in THF, 1.95 mL, 1.95 mmol) at −78 °C as previously described[2a] to give a yellowish solid (538 mg, 92% yield). GLC analysis (column A, at 250 °C) showed two peaks at t_R = 13.87 min (3α isomer) and t_R = 14.33 min (3β isomer) in a ratio of 77:23.[38] For the mixture of 3α and 3β isomers: IR (Nujol, cm^{-1}) 3420 (br, OH), 1734 (C=O), 1710 (C=O); ^1H NMR ($CDCl_3$, 300 MHz) for 3α isomer δ 0.75 (19-CH_3), 0.86 (18-CH_3), for 3β isomer δ 0.78 (19-CH_3), 0.86 (18-CH_3).[39]

3α-DPS-androstane-6,17-dione (3) and 3β-DPS-androstane-6,17-dione (4). 5α-3-Hydroxyandrostane-6,17-dione (as a mixture of the 3α and 3β isomers, 255 mg, 0.837 mmol) in DMF–TEA (4 mL:0.8 mL) was silylated with DPSCl (155 μL, 0.90 mmol) as previously described.[2a,13] A yellowish solid (432 mg) was isolated which was chromatographed with silica gel (15% EtOAc–hexane) to provide **3** (231 mg, 63% yield): prisms, mp 168–170 °C; t_R = 10.89 min by GLC analysis on column A at 280 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.34 (s, $Si(CH_3)_2$), 0.72 (s, 19-CH_3), 0.86 (s, 18-CH_3), 1.2–2.8 (m, 20 H), 4.10 (m, 3-C-βH), 7.37 (m, 3 H), 7.53 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ −1.26, −1.24, 12.45, 13.72, 20.27, 21.53, 28.16, 28.55, 31.09, 31.76, 35.57, 37.32, 41.26, 45.47, 48.03, 51.62, 51.94, 53.69, 66.08 (3-C-αOSi), 127.73, 129.43, 133.28, 138.39, 212.09 (6-C=O), 219.94 (17-C=O); IR (Nujol) 1734 (17-C=O), 1700 (6-C=O), 1296, 1248, 1166, 1116, 1062, 1042, 1018, 970, 940, 866, 832, 790, 742, 702 cm^{-1}; MS *m/e* 438 (M, 5), 423 (M − CH_3, 30), 360 (M − C_6C_6, 52), 137 ($HOSiCH_3C_6H_5$, 100); high-resolution MS (EI) *m/e* calcd 438.2590 found 438.2590; UV–vis (in MeCN) λ (nm) (ε M^{-1} cm^{-1}) 289 (68), 269 (196), 262 (255), 258 (257), 252 (180), 254 (188), 266 (168).

Chromatography also provided **4** as a white solid (76.9 mg, 21% yield): needles, mp 156–157 °C; t_R = 14.24 min by GLC analysis on column A at 280 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.37 (s, $Si(CH_3)$), 0.38 (s, $Si(CH_3)$), 0.77 (s, 19-CH_3), 0.86 (s, 18-CH_3), 1.1–2.5 (m, 20 H), 3.52 (m, 3-C-αH), 7.38 (m, 3 H), 7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ −1.13, −0.97, 13.07, 13.73, 20.67, 21.56, 29.98, 30.98, 31.11, 35.56, 36.65, 37.25, 40.77, 45.39, 48.02, 51.61, 53.92, 56.86, 71.30 (3-C-βOSi), 127.77, 129.50, 133.43, 138.17, 209.81 (6-C=O), 219.77

(34) It is potentially noteworthy that Cvitas et al. report that a 5,6 double bond appears to accentuate the coupling between the 3- and 17-keto groups. See the discussion of **6** in the text and footnote 16.

(35) Suarez, M. L.; Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1989**, *111*, 6384–6391.

(36) Fried, J. H.; Nutile, A. N.; Arth, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 5704–5707.

(37) Steroids from Steralloids Inc., Wilton, NH, 1985, p 18, Catalog No. A 2895, 5α-androstan-3,6,17-trione.

(38) K-Selectride reduction of 3-keto steroids is known to predominantly give the 3α alcohols; see: (a) Contreras, R.; Mendoza, L. *Steroids* **1979**, *34*, 121–124. (b) Gondos, G.; McGirr, L. G.; Jablonski, C. R.; Snedden, W.; Orr, J. C. *J. Org. Chem.* **1988**, *53*, 3057–3059.

(39) The chemical shifts for the 19-CH_3 and 18-CH_3 are in good agreement with those calculated on the basis of substituent effects[10] (for the 3α isomer δ 0.75 and 0.89; for the 3β isomer δ 0.78 and 0.89).

Table V. Summary of Crystal Data and Data Collection Parameters for 3β-DPS-5α-androstan-17-one (**5**)

molecular formula	$C_{27}H_{40}SiO_2$
molecular weight	424.70
space group	$P2_12_12_1$ (No. 19)
a, Å	6.6674 (9)
b, Å	18.523 (2)
c, Å	19.640 (2)
V, Å^3	2425.5 (8)
molecules per cell (*Z*)	4
d(calcd), g/cm^3	1.163
crystal dimensions, mm	0.75 × 0.63 × 0.50
temp, °C	20
radiation (wavelength)	Mo Kα (0.71073 Å)
monochromator	graphite
linear abs coeff, cm^{-1}	1.12
absorption correction applied	none
diffractometer	Enraf-Nonius CAD4
scan method	ω–2θ
h,k,l limits	0–7, 0–22, 0–23
2θ range, deg	4.00–50.00
scan width, deg	0.52 + 0.35 tan (θ)
takeoff angle, deg	2.95
programs used	Enraf-Nonius SDP
F_{000}	928.0
p-factor used in weighting	0.040
data collected	2470
unique data	2470
data with $I > 3.0\sigma(I)$	2175
number of variables	431
largest shift/esd in final cycle	0.20
R	0.032
R_w	0.042
goodness of fit	1.499

(17-C=O); IR (Nujol) 1730 (17-C=O), 1706 (6-C=O), 1316, 1252, 1200, 1116, 1074, 1010, 994, 978, 898, 872, 832, 788, 748, 728, 704 cm^{-1}; MS (EI) *m/e* 438 (M, 5), 423 (M – CH_3, 60), 360 (M – C_6C_6 58), 137 ($HOSiCH_3C_6H_5$, 100); high-resolution MS (EI) *m/e* calcd 438.2590, found 438.2581; UV-vis (in MeCN) λ (nm) (ε M^{-1} cm^{-1}) 289 (90), 269 (242), 262 (308), 258 (308), 252 (220), 254 (228), 266 (206).

3β-DPS-5α-androstan-17-one (5). Silylation of 3β-hydroxy-5α-androstan-17-one with DPSCl in DMF–TEA provided **5** as needles (73% yield): mp 109–110 °C; ^{1}H NMR ($CDCl_3$, 300 HMz) δ 0.38 (s, Si-$(CH_3)_2$), 0.81 (s, 19-CH_3), 0.84 (s, 18-CH_3), 1.0–2.4 (m, 22 H), 3.60 (m, 3-C-αH), 7.38 (m, 3 H), 7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) 221.50 (17-C=O), 138.68, 133.58, 129.53, 127.75, 72.25 (3-C-βDPS), 54.59, 51.55, 47.91, 45.03, 38.45, 37.16, 35.96, 35.72, 35.15, 31.76, 31.67, 31.02, 28.51, 21.89, 20.56, 13.92, 12.40, –0.83 (SiMe); IR (Nujol) 1736 (17-C=O), 1376, 1254, 1122, 1054, 904, 870, 824, 776, 746, 708 cm^{-1}; MS (EI) *m/e* 409 (M – CH_3, 57), 346 (M – C_6H_6, 46), 136 (100); MS (CI) *m/e* 425 (M + 1); high-resolution MS (CI) (M + 1) *m/e* calcd 425.2876, found 425.2868.

Crystals of **5** were prepared by recrystallization from hexane–ether. A colorless chunk having approximate dimensions of 0.75 × 0.63 × 0.50 mm was mounted on a glass fiber in a random orientation. X-ray data were collected with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator. Unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $20° < \theta < 25°$ measured by the computer-controlled diagonal slit method of centering. As a check on crystal quality, ω scans of several intense reflections were measured; the width at half-height was 0.52° with a takeoff angle of 3.0°, indicating good crystal quality. The data were collected at 20 °C using the ω–2θ scan technique. The scan rate varied from 2 to 20 deg/min (in ω). Data were collected to a maximum 2θ of 50.0°. The unit cell is an orthorhombic cell, and results are summarized in Table V and Figure 5.

3β-DPS-5-androsten-17-one (6). Silylation of 3β-hydroxyandrost-5-en-17-one with DPSCl in DMF–TEA gave **6** as prisms (67% yield): mp 113–114 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.39 (s, $Si(CH_3)_2$), 0.87 (s, 18-CH_3), 1.01 (s, 19-CH_3), 1.1–2.4 (m, 22 H), 3.51 (m, 3-C-αH), 5.27 (d, *J* = 5.1 Hz), 7.38 (m, 3 H), 7.59 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) 221.12 (17-C=O), 141.42, 138.47, 133.40, 129.45, 127.71, 120.55, 72.47 (3-C-βDPS), 51.71, 51.18, 47.50, 42.46, 37.18, 36.59, 35.80, 31.73, 31.43, 30.73, 21.82, 20.28, 19.35, 13.47, –1.07 (SiMe); IR (Nujol) 3010, 1736, 1672, 1590, 1408, 1376, 1338, 1250, 1134, 1118, 1080, 1056, 1032, 1014, 956, 884, 866, 832, 806, 786, 740, 702 (cm^{-1}); MS (EI) *m/e* 411 (M – CH_3, 13), 348 (M – C_6H_6, 11), MS (CI) *m/e* 427 (M + 1); high-resolution MS (EI) *m/e* calcd 422.2641, found 422.2638.

Preparative Photolysis of 3α-DPS-5α-androstane-6,17-dione (3) in MeCN–TEA at 254 nm. A degassed solution of acetonitrile (8 mL) containing **3** (63 mg, 18 mM) and TEA (60 μL, 54 mM) was irradiated with 16 RPR 254-nm lamps for 45 min. GLC analysis of the photolysate (on column A at 280 °C) showed six peaks at 9.36, 9.85, 10.72 (**3**), 11.34, 11.53, and 11.68 min in a peak-area ratio of 1.3:1.0:1.4:1.9:1.3:1.3 (at 90% loss of **3**). Concentration in vacuo gave 65 mg of a residue which was chromatographed on silica gel with 10% EtOAc–CH_2Cl_2 (60 mL) followed by 30% EtOAc–CH_2Cl_2 (40 mL) to give five components. The first component (a mixture, 6.6 mg) was further chromatographed with silica gel (10% EtOAc–hexane) to give 3α-DPS-5α,13α-androstane-6,17-dione (**9**, 1.6 mg). The second component (2.2 mg) was recovered **3** at t_R = 10.72 min. The third component (10 mg) was chromatographed with 30% EtOAc–hexane to give the alcohols **21** (2.1 mg) and **7** (1.5 mg).[40]

3α-DPS-6α-hydroxy-5α-androstan-17-one (7): GLC t_R = 11.34 min and R_f = 0.19 on silica gel (30% EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.35 (s, $SiCH_3$), 0.38 (s, $SiCH_3$), 0.77 (s, 19-CH_3), 0.85 (s, 18-CH_3), 1.0–2.5 (m, 22 H), 3.30 (dt, 6β-H, J_d = 4.5 Hz, J_t = 10.5 Hz), 4.10 (t, 3β-H, J_t = 2.4 Hz), 7.38 (m, 3 H), 7.59 (m, 2 H); IR (Nujol) 3504 (OH), 1730 (17-C=O), 1376, 1250, 1116, 1030, 832, 792, 726, 700, cm^{-1}; MS (EI) *m/e* 440 (M, 30), 425 (M – Me, 40), 362 (M – C_6C_6, 60), 137 ($HOSiCH_3C_6H_5$, 100); MS (CI) 441 (M + H); high-resolution MS (EI) *m/e* calcd 440.2747, found 440.2743.

3α-DPS-5α,13α-androstane-6,17-dione (9). The epimer had a GLC retention time of t_R = 9.36 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.34 (s, 6 H, $Si(CH_3)_2$), 0.54 (s, 3 H, 19-CH_3), 1.02 (s, 3 H, 18-CH_3), 1.0–2.5 (m, 20 H), 4.10 (s, 3β-H), 7.38 (m, 3 H), 7.56 (m, 2 H); ^{13}C NMR ($CDCl_3$, 150 MHz) 221.28 (17-C=O), 212.14 (6-C=O), 138.46, 133.35, 129.48, 127.77, 66.09 (3-C-α-DPS), 51.28, 51.17, 50.98, 50.39, 47.04, 41.13, 39.97, 33.46, 31.76, 31.65, 28.50, 28.10, 25.02 (18-Me), 22.35, 20.79, 12.16 (19-Me), –1.18 (SiMe), –1.23 (SiMe); IR (Nujol) 1730 (17-C=O), 1710 (11-C=O), 1380, 1250, 1080, 1060, 840, 785, 750, 715 cm^{-1}; MS (EI) *m/e* 438 (M$^+$, 5), 423 (M – Me, 20), 360 (M – C_6H_6, 40), 137 (100); high-resolution MS (EI) *m/e* calcd 438.2590, found 438.2586.

3α-DPS-17β-hydroxy-5α-androstan-6-one (21). Compound **21** had GLC t_R = 11.53 min and R_f = 0.28 on silica gel (30% EtOAc–hexane); this product was not detectable in the 266-nm photolysis: prisms, mp 163–165 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.38 (s, 6 H, $Si(CH_3)_2$), 0.75 (s, 3 H, 19-CH_3), 0.78 (s, 3 H, 18-CH_3), 1.0–2.6 (m, 22 H), 3.72 (t, 17α-H, J_t = 8.7 Hz), 4.13 (t, 3β-H, J_t = 2.4 Hz), 7.40 (m, 3 H), 7.59 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ –1.19 ($SiCH_3$), –1.16 ($SiCH_3$), 11.08, 12.52, 20.71, 23.15, 28.24, 28.65, 30.37, 31.87, 36.29, 37.97, 41.40, 43.39, 46.34, 51.42, 51.97, 53.83, 66.25 (3-C-α-DPS), 81.61 (17-C-β-OH), 127.76, 129.46, 133.35, 138.53, 212.85 (6-C=O); IR (Nujol) 3500 (OH), 1698 (6-C=O), 1378, 1310, 1258, 1116, 1024, 864, 832, 726, 700 cm^{-1}; MS (EI) *m/e* 440 (M$^+$, 5), 425 (M – Me, 25), 362 (M – C_6H_6, 100); high-resolution MS (EI) *m/e* calcd 440.2747, found 440.2738. The compound could be independently prepared by silylation of 3α,17β-dihydroxy-5α-androstan-6-one, which was itself prepared from 17β-hydroxy-5α-androstane-3,6-dione. A THF solution (10 mL) of the dione (350 mg, 1.15 mmol) was treated with K-Selectride (1.15 mL, 1 M in THF) at –78 °C to give a mixture of the C3-αOH and C3-βOH isomers in a ratio of 1.3:1.0 (by GLC analysis on column B at 230 °C). The mixture was then silylated by DPSCl in methylene chloride (25 mL) with TEA (1.5 mL) at room temperature. Chromatography on silica gel with 30% EtOAc–CH_2Cl_2 gave **21** (54 mg).

Photolysis of 3 with 300-nm Light; Isolation of 3α-DPS-6-oxo-13,17-seco-5α-androst-13-en-17-al (10). A degassed acetonitrile solution (3 mL) of **3** (31 mg, 23.5 mM) with TEA (55 mg, 182 mM) was irradiated with 15 RPR 300-nm lamps through Pyrex for 56 min. Chromatography

(40) Two other products were isolated: 3α-DPS-6-hydroxy-5α,13α-androstan-17-one (ca. 2 mg) and the diol 3α-DPS-5α-androstane-6,17β-diol (ca. 10 mg, t_R = 11.53 min) (the latter was not detected in the 266-nm photolysis). The 3α-DPS-6-hydroxy-5α,13α-androstan-17-one was a mixture of the 6α and 6β isomers having identical GLC retention times at t_R = 9.85 min: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.35 (s), 0.38 (s), 0.58 (s, 19-CH_3), 0.99 (s, 18-CH_3), 3.23 (m, 6-*CH*-αOH), 3.66 (m, 6-*CH*-βOH), 4.09 (m, 3-C-βH), 7.38 (m, 3 H), 7.60 (m, 2 H). The 3α-DPS-5α-androstane-6,17β-diol was a mixture of the 6-C-αOH and 6-C-βOH isomers in a ratio of 1.4:1.0: ^{1}H NMR ($CDCl_3$, 300 MHz) two groups of $Si(CH_3)_2$ δ 0.34/0.36 and 0.35/0.38, 3.27 (dt, 0.6 H, 6-*CH*-αOH, J_d = 4.5 Hz, J_t = 10.8 Hz), 3.62 (m, 0.4 H, 6-*CH*-βOH), 3.65 (t, 3-*CH*-αOSi, J_t = 8.1 Hz), 4.10–4.13 (m, 1 H, 17-*CH*-βOH), 7.36 (m, 3 H), 7.59 (m, 2 H).

of the photolysate on silica gel with 20% EtOAc–hexane gave **10** (1.5 mg) with GLC t_R = 8.78 min (column B at 260 °C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.34 (s, $SiCH_3$), 0.35 (s, $SiCH_3$), 0.66 (s, 19-CH_3), 1.66 (s, 18-CH_3), 4.11 (m, 3-C*H*-αOSi), 7.38 (m, 3 H), 7.56 (m, 2 H), 9.75 (17-C*H*=O).

3α-DPS-6β-hydroxy-5α-androstan-17-one (8). Compound **8** was prepared by the reduction of **3** with K-Selectride. A THF solution (4.5 mL) of **3** (34 mg, 0.078 mmol) was treated with K-Selectride (0.08 mL, 1 M in THF) at −78 °C for 2 h. Chromatography on silica gel (7% EtOAc–hexane) gave 18 mg of **8**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.34 (s, $SiCH_3$), 0.36 (s, $SiCH_3$), 0.89 (s, 18-CH_3), 0.99 (s, 19-CH_3), 1.0–2.4 (m, 22 H), 3.67 (m, 6-C*H*-βOH), 4.13 (m, 3-C*H*-αOSi), 7.37 (m, 3 H), 7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ −1.19 ($SiCH_3$), −1.00 ($SiCH_3$), 13.86, 14.99, 19.87, 21.77, 29.44, 30.03, 31.50, 33.55, 34.06, 35.86, 36.11, 38.36, 41.65, 47.89, 51.27, 54.18, 67.36 (3-C-αDPS), 72.01 (6-C-βOH), 127.40, 129.39, 133.37, 139.28, 221.43 (17-C=O); IR (Nujol) 3496 (OH), 1726 (17-C=O), 1376, 1250, 1116, 1028, 958, 860, 832, 794, 726, 700 cm^{-1}; MS (EI) *m/e* 440 (M, 40), 425 (M − CH_3, 30), 362 (M − C_6C_6 65), 137 ($HOSiCH_3C_6H_5$, 100); MS (CI) *m/e* 441 (M + H); high-resolution MS (EI) *m/e* calcd 440.2747, found 440.2738.

Preparative Photolysis of 3β-DPS-5-androstane-6,17-dione (4) with 254-nm Light. A degassed acetonitrile solution (10 mL) of **4** (68 mg, 15.5 mM) with TEA (50 mg, 49.5 mM) was irradiated with eight RPR 254-nm lamps for 160 min. GLC analysis on column B (at 260 °C) showed only two major peaks at 16.62 and 19.44 min (**4**) in a ratio of 1.1:1.0 with 78% loss of **4**. Chromatography on silica gel (5% EtOAc–CH_2Cl_2) gave **4** (8.4 mg) and 3β-DPS-5α,13α-androstane-6,17-dione (**11**, 7.2 mg): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.36 (s, $SiCH_3$), 0.37 (s, $SiCH_3$), 0.58 (s, 19-CH_3), 1.00 (s, 18-CH_3), 1.2–2.7 (m, 20 H), 3.51 (m, 3-C*H*-βOSi), 7.37 (m, 3 H), 7.56 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ −1.11, −0.95, 12.73, 20.82, 22.72, 24.98, 29.89, 30.88, 31.76, 33.40, 36.64, 39.84, 40.63, 46.98, 50.34, 51.22, 51.27, 56.05, 71.37, 127.80, 129.53, 133.45, 138.22, 209.75 (6-C=O), 221.00 (17-C=O); IR (Nujol) 1718 (17-C=O), 1702 (11-C=O), 1250, 1060, 840, 785, 750 cm^{-1}; MS (EI) *m/e* 438 (M, 4), 423 (M − CH_3, 100), 360 (M − C_6H_6, 68), 137 (88); MS (CI) *m/e* 439 (M + H, 90); high-resolution MS (EI) *m/e* calcd 438.2590, found 438.2581.

Preparative Photolysis of 3β-DPS-5α-androstan-17-one (5) with 254-nm Light. A degassed acetonitrile solution (13 mL) of **5** (80 mg, 14.5 mM) with TEA (45 mg, 34 mM) was irradiated with 16 RPR 254-nm lamps for 70 min. Chromatography was carried out on silica gel, eluting with 10% EtOAc–hexane (30 mL) followed by 25% EtOAc–hexane (30 mL) to give 3β-DPS-5α-androstan-17β-ol (**12**, 19 mg) and 3β-DPS-5α,13α-androstan-17-one (**13**, 10 mg). The alcohol **12** had GLC t_R = 9.76 min on column B at 260 °C: mp 106–107 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.37 (s, 6 H, $Si(CH_3)_2$), 0.71 (s, 18-CH_3), 0.79 (s, 19-CH_3), 1.0–2.5 (m, 22 H), 3.60 (m, 2 H, 3-C-αH and 17-C-αH), 7.38 (m, 3 H), 7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 138.74, 133.57, 129.53, 127.78, 82.23 (17-C-βOH), 72.39 (3-C-βDPS), 54.63, 51.14, 45.10, 43.09, 38.53, 37.26, 36.87, 35.64, 31.83, 31.73, 30.63, 28.68, 23.50, 20.89, 12.42, 11.23, −0.84, −0.80 (SiMe); IR (Nujol) 3280, 1376, 1248, 1132, 1118, 1092, 1078, 1052, 1028, 870, 826, 778, 698 (cm^{-1}); MS (EI) *m/e* 411 (M − CH_3, 13), 348 (M − C_6H_6, 11); MS (CI) *m/e* 427 (M + 1); high-resolution MS (CI) *m/e* calcd (M + 1) 427.3032, found 427.3019. 3β-DPS-5α,13α-androstan-17-one (**13**) had GLC t_R = 8.18 min (on column B at 260 °C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.36 (s, 6 H, $Si(CH_3)_2$), 0.62 (s, 19-CH_3), 0.95 (s, 18-CH_3), 1.2–2.6 (m, 22 H), 3.56 (m, 3-C-αH), 7.38 (m, 3 H), 7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) 222.47 (17-C=O), 138.55, 133.42, 129.40, 127.70, 72.19 (3-C-βDPS), 51.64, 50.75, 50.11, 44.32, 38.17, 37.72, 36.85, 35.56, 33.85, 33.03, 32.17, 31.47, 28.51, 25.27, 22.63, 21.31, 11.96, −0.93, −0.99, (SiMe); IR (Nujol) 1736 (17-C=O), 1376, 1250, 1162, 1120, 1044, 838, 818, 742, 724, 700 cm^{-1}; MS (EI) *m/e* 424 (M, 20), 409 (M − CH_3, 50), 346 (M − C_6H_6, 40); MS (CI) *m/e* 425 (M + 1); high-resolution MS (EI) *m/e* calcd 424.2798, found 424.2790.

Preparative Photolysis of 3β-DPS-androst-5-en-17-one (6) with 254-nm Light. A degassed acetonitrile solution (14 mL) of **6** (91 mg, 15.4 mM) and TEA (65 mg, 46 mM) was irradiated with 16 RPR 254-nm lamps for 55 min. Chromatography on silica gel (5% EtOAc–hexane) gave a mixture of 3β-DPS-13α-androst-5-en-17-one (**15**) and **6**, as well as 3β-DPS-androst-5-en-17β-ol (**14**, 48 mg). 3β-DPS-androst-5-en-17β-ol (14): mp 76–77 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.39 (s, 6 H, $Si(CH_3)_2$), 0.74 (s, 18-CH_3), 1.03 (s, 19-CH_3), 1.0–2.6 (m, 20 H), 3.49 (m, 3-C*H*-βOSi), 3.63 (t, 17-C*H*-βOH, J_t = 8.4 Hz), 5.25 (m, 6-C*H*=C), 7.38 (m, 3 H), 7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 141.48, 138.61, 133.56, 129.57, 127.86, 121.13, 82.00 (17-CH-βOH), 72.77 (3-C-βDPS), 51.45, 50.38, 42.83, 42.64, 37.44, 36.72, 36.69, 32.05, 31.95, 31.60, 30.63, 23.55, 20.74, 19.51, 11.06, −0.95 (SiMe), −0.87 (SiMe); IR (Nujol) 3282, 1654, 1378, 1250, 1194, 1090, 960, 888, 828, 778, 700 (cm^{-1}); MS (EI) *m/e* 424 (M, 5), 409 (M − CH_3, 4), 346 (M − C_6H_6, 37), 135 (100); MS (CI) *m/e* 425 (M + 1); high-resolution MS (EI) *m/e* calcd 424.2798, found 424.2794. The epimer **15** was inseparable from **6**; the ^{1}H NMR ($CDCl_3$, 300 MHz) data of the mixture (60% **15**) after subtraction of the NMR resonance data for **6** is as follows: δ 0.38 (6 H, $Si(CH_3)_2$), 0.81 (19-CH_3), 0.97 (18-CH_3), 0.8–2.5 (H on steroidal skeleton), 3.5 (m, 3-C-αH), 5.28 (d, J = 3.6 Hz, 6-CH=C), 7.38 (m, 3 H), 7.58 (m, 2 H).

Photolysis of 3α-Hydroxy-5α-androstane-6,17-dione (16) at 300 nm. The title compound (18.3 mg, 30 mM) was photolyzed for 40 min with TEA (ca. 40 μL, 140 mM) in acetonitrile (2 mL) in Pyrex at room temperature, using the Rayonet reactor equipped with 15 300-nm lamps. Analysis was performed with GLC on column B at 230 °C with 3β-hydroxy-5α-androstan-17-one as an internal standard.

Quantum Efficiency Determinations. A Vycor cuvette containing 1.5–2.0 mL of an argon-degassed sample solution of ca. 15–17 mM substrate, and varying TEA concentrations, was placed in a sample holder and irradiated with a 266-nm laser beam for 4–16 min (varying from sample to sample). The 308-nm quantum efficiencies utilized acetonitrile solutions (1.5 mL) of ca. 56 mM substrate and 165 mM TEA with the laser beam passed through a neutral density filter so as to reduce the laser intensity to 25%. Dark control experiments were carried out at the same temperature for each of the quantum efficiency measurements.

Photolysis of 3 with *cis*-1,3-Pentadiene. Two degassed acetonitrile solutions (1.0 mL) of **3** (7 mg, 16 mM) and TEA (28 μL, 61 mM), with and without the diene (2 μL, 20 mM) were irradiated in Vycor cuvettes at room temperature for 4.5 min using the Nd/YAG laser at 266 nm (1.7 mJ/pulse). The solutions were analyzed by GLC on column B at 270 °C with an internal standard. The loss of **3** was 25%. For the 300-nm photolysis, two degassed acetonitrile solutions (1.0 mL) of **3** (12.7 mg, 29 mM) and TEA (20 μL, 143 mM), with and without diene (15 μL, 150 mM), were irradiated in Pyrex tubes using 15 300-nm lamps in the Rayonet reactor at room temperature for 16 min. The solutions were analyzed by GLC on column A at 260 °C with an internal standard. The loss of **3** was 42%. Absorption of light by *cis*-1,3-pentadiene is negligible at both wavelengths.

Photolysis of 5 with Cyclohexanone. Degassed solutions of **5** (6.5 mg, 15.2 mM) in 2-propanol (1 mL) saturated with $NaHCO_3$ were irradiated with eight 254-nm lamps at room temperature for 6 min in the absence and presence of cyclohexanone (9.0–26.9 mM). The solutions were analyzed by GLC (column A at 270 °C) with an internal standard (3α-DPS-5α-androstan-17-one) to monitor **5**, while cyclohexanone and cyclohexanol were analyzed on the same column using a gradient temperature program starting from 50 °C.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9007569) for support of this research. The 266-nm laser experiments were performed in the NSF-sponsored Purdue Chemistry Department Multiuser Laser Laboratory or in the laboratories of Professor G. P. Kubiak. The 308-nm experiments were performed in the laboratories of Professor T. S. Zwier. We thank Dr. Phil Fanwick for his assistance in obtaining the X-ray structural data.