Picoche for his help on this occasion.

Registry No. 4, 140438-20-6; **4a**, 140438-22-8; **4b**, 140438-21-7; **4c**, 140438-27-3; **5a**, 140438-30-8; **5b**, 134359-20-9; *exo*-**5**, 136266-08-5; *endo*-**5**, 134359-22-1; **6a**, 140438-31-9; **6b**, 140438-29-5; *endo*-**6**, 140438-28-4; **7a**, 140438-23-9; **7b**, 140438-25-1; **8a**, 140438-24-0; **8b**, 140438-26-2; *exo*-**11**, 108384-32-3; *endo*-**11**, 108384-28-7; **13**, 111740-30-8; **15**, 140438-34-2; **16**, 140438-32-0; **17**, 140438-33-1; BHT, 128-37-0; $CCl_3^{\bullet}$, 3170-80-7; CCl_3^-, 14478-07-0; CCl_4, 56-23-5; $H_2C{=}CHCH_2Br$, 106-95-6; $HO(CH_2)_2SO_2Ph$, 20611-21-6.

Antenna-Initiated Photochemistry of Distal Groups in Polyfunctional Steroids. Intramolecular Singlet and Triplet Energy Transfer in 3α-(Dimethylphenylsiloxy)-5α-androstan-17-one and 3α-(Dimethylphenylsiloxy)-5α-androstane-11,17-dione[1,2]

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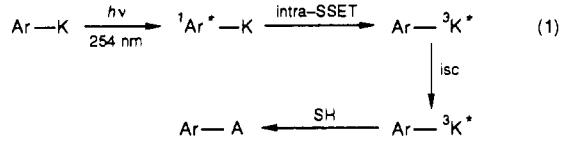
Abstract: Photolysis of 3α-(dimethylphenylsiloxy)-5α-androstane-11,17-dione (**1**) in acetonitrile with triethylamine, using 266-nm light absorbed by the dimethylphenylsiloxy (DPS) chromophore, leads to reduction of the C17 keto group as the principal photoreaction. This contrasts with the direct photolysis of the ketone moieties with 308-nm light, wherein epimerization of ring D is the major consequence and reduction is minimal. Triplet quenching studies with *cis*-1,3-pentadiene confirm that the reduction is derived from the C17 keto triplet state, while the epimerization originates with the C17 excited singlet state. Photolysis of 3α-(dimethylphenylsiloxy)-5α-androstan-17-one (**3**) under similar conditions gives qualitatively similar results but with a higher fraction of its epimer using 266-nm light and complete absence of reduction upon direct ketone excitation. Intramolecular singlet/singlet energy transfer (intra-SSET) from the DPS antenna to the carbonyl groups is demonstrable in both substrates by the reduced fluorescence quantum efficiencies and singlet lifetimes of the DPS group in these steroids. The rates of energy migration are ca. 2×10^8 and 29×10^8 s^{-1} for **3** and **1**, respectively, reflecting the greater efficiency of transfer to the more proximal C11 keto group. Intramolecular triplet/triplet energy transfer (intra-TTET) is also evidenced in **3**, for example, by the triplet-derived reduction chemistry at C17 which is uniquely characteristic of the antenna excitation; a through-bond exchange mechanism is proposed. Additional triplet chemistry observed at C17 in the diketone, **1**, is rationalized by a conversion from the singlet to the triplet manifold at the C11 ketone (i.e., C11 acts as a singlet/triplet switch) followed by triplet energy migration from C11 to C17.

As part of our general interest in the photochemistry of polyfunctional molecules and mechanisms for delocalizing and transmitting electronic excitation, we have been exploring the use of antenna chromophores to "harvest" photon energy which can then be utilized to selectively activate functioinalities distal to the site of initial excitation.[3] Our prototypical system has been the aryl/ketone functional group pair, where we have demonstrated aryl-initiated photoreduction of the carbonyl group via intramolecular singlet/singlet energy transfer (intra-SSET);[4,5] cf. eq 1 wherein Ar---K and Ar---A are the aryl ketone and product aryl alcohol, respectively.



(1)

The mechanism by which intra-SSET occurs in aryl ketones has been a subject of considerable recent interest.[6-11] There is evidence that through-bond interactions (TBI) involving bridging C–C σ bonds play a role in energy migration,[6b,8,9,11] and examples involving naphthalene/ketone pairs separated by extended, rigid C–C bridges, wherein the rates of intra-SSET are strongly dependent on the length and configuration of the C–C bridges, are taken as indicative of TBI intra-SSET primarily through an exchange mechanism.[6b,11]

Superimposed on the photophysical interest is the synthetic potential represented by the possibility of selectively activating one of two or more possible ketone targets by taking advantage of the distance between the donor and acceptor groups and/or their stereoelectronic relationship. In the study we describe below, we employ one aryl antenna group and two target ketone functionalities. The antenna, A, is a dimethylphenylsiloxy group (DPS), which we show to be an efficient singlet energy donor which can be readily attached to and detached from the molecule.[5] For the spacer which separates the aryl and ketone groups we utilize the rigid, chemically inert, steroidal androstane skeleton, which has been used by others to study intra-SSET[12,13] intra-

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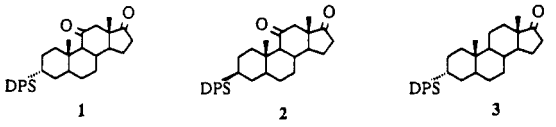
molecular triplet/triplet energy transfer (intra-TTET)[14] and intramolecular electron transfer.[15] The sequence of functionalities in our trifunctional substrates has allowed us to probe two issues: how selectively one can achieve transfer of electronic excitation to one of the two distal target ketone groups and to what extent a second energy-transfer step (i.e., energy hopping) then occurs between the proximate K_1 and K_2 moieties. The rates for both phenomena can be expected to depend on interchromophore distance and orientation. In fact, there are two reports of distance and/or stereoelectronic effects on intramolecular interactions between two ketone chromophores.[16,17] In one case, there is convincing evidence for a TBI between steroidal 11- and 17-keto groups but not for a corresponding pair of ketones at the 3 and 17 positions.[16] The second study gives evidence for a significant rate of singlet/singlet energy hopping in a rigid 1,5-dione having the two ketone groups separated by four C–C σ bonds ($k_{\text{intra-SSET}} \geq 1 \times 10^{10}$ s^{-1}), but a considerably decreased rate for a 1,7-dione in which the carbonyl groups are separated by six C–C σ bonds ($k_{\text{intra-SSET}} \leq 1 \times 10^{7}$ s^{-1}).[17]

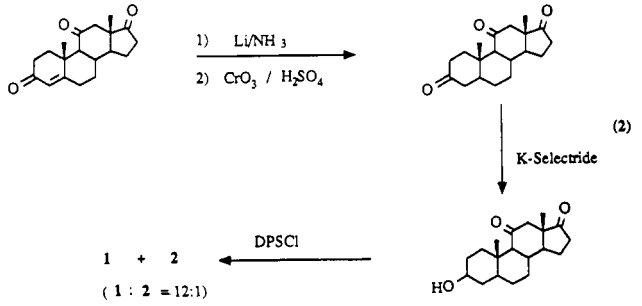
One may classify the functional group relationship embodied in the primary substrate described within this paper, 3α-(dimethylphenylsiloxy)-5α-androstane-11,17-dione (3α-DPS-5α-androstane-11,17-dione), as A----K_1--K_2 with K_1 and K_2 separated by three C–C σ bonds. Such an arrangement is but one of several interesting possible modes of distribution of these functionalities, and additional polyfunctional molecules which illustrate A--K_1----K_2 (with a five σ bond K/K separation) and K_1--A----K_2 (with an eight σ bond K/K separation and an interposed antenna A) will be the subject of future reports.

Results

Synthesis of DPS-Substituted Steroidal Ketones. The DPS-substituted steroidal ketones, e.g., 3α-DPS-5α-androstane-11,17-dione (**1**), 3β-DPS-5α-androstane-11,17-dione (**2**), and 3α-DPS-5α-androstan-17-one (**3**), were prepared by silylation of the parent steroidal alcohols with chlorodimethylphenylsilane (DPSCl).[18] The alcohol precursors of **1** and **2** (the 3α and 3β



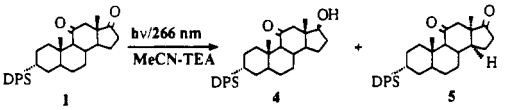
isomers of 3-hydroxy-5α-androstane-11,17-dione) were prepared by regiospecific reduction of the trione using K-Selectride[19] in THF at −78 °C (see eq 2), with the trione itself synthesized from



(2)

adrenosterone by a literature procedure.[20] The precursor to **3** is commercially available. The photochemistry of **1** and **3** is described below. The amount of purified **2** was insufficient for a photochemical study, but the photophysical data obtained are presented below.

Photoproduct Studies. Photolysis of 1 with Triethylamine (TEA) in Acetonitrile (MeCN). Photolysis of **1** (15 mM) in MeCN in the presence of TEA (43 mM) with 266-nm laser light leads to the monoreduced product, 3α-DPS-17β-hydroxy-5α-androstan-11-one (**4**), and an epimer of the starting material, 3α-DPS-5α,13α-androstane-11,17-dione (**5**), in a ratio of 2.8:1.0 (cf. eq 3). At [TEA] = 59 mM the epimer formation is completely quenched and one only observes reduction.



(3)

4:5=2.8:1.0

Compound **4** was readily isolated in 51% yield from a preparative photolysis of **1** (15 mM) with TEA (36 mM) in MeCN with 254-nm light.[21-23] Larger quantities of the epimer, **5**, were prepared by photolysis of **1** in cyclohexane (without TEA), also using 254-nm light.[24] The reaction site and stereochemical assignments of the photoproducts follow from well-established spectral precedents.[22a-c] These include characteristic chemical shifts for the 18-Me, 19-Me, and C*H*OH protons in steroidal ketones and alcohols[22a] (IR bands of ca. 1700 and ca. 1740 cm^{-1} for the six- and five-ring cyclic ketones, respectively)[22c] and the higher field (ca. δ 210) ^{13}C NMR resonance of a carbonyl group in a six-membered-ring cycloalkanone relative to a five-membered-ring cycloalkanone (ca. δ 220).[22b] Thus, both the ^{13}C NMR signal at δ 218 and the IR band at 1740 cm^{-1} of the 17-keto group in **1** are absent in **4**. The survival of the 11-keto group is manifested by the ^{13}C resonance at δ 210.8 (this signal appears at δ 209.6 in **1**) and an IR band at 1702 cm^{-1} (1708 cm^{-1} in **1**). As regards the assignment of stereochemistry to the 17C-OH, **4** has characteristic proton NMR resonances at δ 3.84 (17C-αH, t, J = 8.0 Hz), δ 0.68 (18-CH_3), and δ 0.97 (19-CH_3), all virtually

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(21) An isomer of **4**, i.e., 3α-DPS-17α-hydroxyandrostan-11-one, was also isolated from the 254-nm photolysis in 11% yield. Its IR spectrum clearly shows the presence of a strong band at 1694 cm^{-1} attributable to the 11-keto group and the absence of the characteristic 17-keto band at 1740 cm^{-1}. The 17C-αOH is evidenced by the proton NMR resonance at δ 3.74 (m, 17C-βH).[22a] The resonances of the 18- and 19-CH_3 groups were calculated on the basis of known substituent effects[22a] to be δ 0.61 and 0.98, respectively, which were in good agreement with measured values δ 0.63 and 0.99. Finally, the structural assignment was confirmed by the thermal reduction of **1** with $NaBH_4$, thus generating 3α-DPS-17α-hydroxyandrostan-11-one in an isolated yield of 5%.
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(23) The laser line was generally employed for reactions utilizing TEA because we have found that the direct excitation of TEA in MeCN at 254 nm gives rise to reduction of the C17 carbonyl group in 3α-hydroxy-5α-androstan-17-one (without epimerization).[1] There is thus a contribution of this chemistry to the photolyses of both **1** and **3** at 254 nm in acetonitrile (TEA and the DPS antenna have extinction coefficients of ϵ_{254} = 47 and 280 M^{-1} cm^{-1}, respectively). This contribution substantially diminishes when excitation occurs at 266 nm (TEA and the DPS groups have ϵ_{266} = 6 and 210 M^{-1} cm^{-1}, respectively; 43 mM TEA in the presence of 15 mM steroid absorbs 7.6% of the incident light).
(24) For photoepimerization at 13-C for 17-keto steroids, see: Wehrli, A.; Schaffner, K. *Helv. Chim. Acta* **1962**, *45*, 385–389. Schaffner, K.; Jeger, O. *Tetrahedron* **1974**, *30*, 1891–1902 and references therein.

Table I. Quantum Efficiencies for Photolysis of Compounds **1** and **3** in Acetonitrile with TEA[a]

[TEA] (mM)	$\phi_{al}(4)^b$	$\phi_{ep}(5)^b$	$\phi_{al}(6)^c$	$\phi_{ep}(7)^c$
32.3	0.011	0.0059	0.0078	0.035
43.1	0.013	0.0046	0.011	0.038
59.2	0.018	0	0.013	0.032
75.4	0.022	0	0.015	0.027
91.5	0.023	0	0.018	0.027

	Stern–Volmer plots	
	$1/\phi_{al}(4)$ vs 1/[TEA]	$1/\phi_{al}(6)$ vs 1/[TEA]
slope	2.5	3.4
intercept	10.4	18.6
ϕ_{lim}	0.07	0.05
corr coeff	0.99	0.99

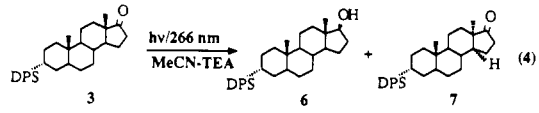
[a] All experiments with 266-nm light from an Nd:YAG laser (6.5 mJ/pulse); the data have been corrected for absorption of 266-nm radiation by TEA, which led to both a filter effect and some chemical reduction of the steroid (see Discussion). [b] $[1]_0$ = 15 mM; loss of **1** was 25–38%. [c] $[3]_0$ = 17 mM; loss of **3** was 25–30%.

identical to those of the desilylated parent alcohol, 3α,17β-dihydroxy-5α-androstan-11-one.[25] The resonances of the 18- and 19-CH_3 groups are calculated on the basis of known substituent effects[22a] to be δ 0.70 and 1.00, respectively, which are in good agreement with our measured values (δ 0.68 and 0.97). Finally, the structural assignment was confirmed by the thermal reduction of **1** with $NaBH_4$, thus generating **4** in an isolated yield of 61%.[26]

As regards the structure of **5**, its assignment as the epimer is supported by mass spectral, IR, and ^1H NMR data. Particularly noteworthy are the shifts of the 18-CH_3 resonance from δ 0.82 for **1** to δ 1.07 for **5** and the 19-CH_3 resonance from δ 0.99 (**1**) to δ 0.81 (**5**). The latter change, in particular, reflects cis ring fusion of rings C and D, which places the 19-CH_3 group in the shielding cone of the 17-keto group.

Photolysis of 1 in Cyclohexane. Photolysis of **1** (10.5 mM) in cyclohexane at room temperature for 1.5 h provided **5** as the major product in an isolated yield of 44%.

Photolysis of 3 in MeCN (±TEA). Irradiation of an MeCN solution containing **3** (17 mM) and TEA (43 mM) with 266-nm laser light at room temperature resulted in formation of the alcohol (**6**) and epimer (**7**) in a ratio of 0.29:1.0 (cf. eq 4). Preparative

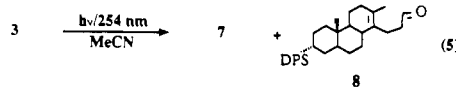


3 6 7 (4)

6:7=0.29:1.0

quantities were prepared by photolyses with 254-nm light in MeCN in the presence and absence of TEA, respectively. The assignment of the 17C-βOH configuration to **6** is supported by a ^1H NMR resonance of the 17C-αH at 3.67 (t, J = 8.4 Hz), a ^{13}C NMR resonance at δ 82.3, and an IR band at 3380 cm^{-1}. The assignment was confirmed by reduction of **3** with $NaBH_4$ in ethanol to generate **6** in 79% yield.

Photolysis of **3** (14.5 mM) in MeCN at 254 nm in the absence of TEA gave the epimer **7** and an aldehyde **8** (none of the reduction product **6** was detected) in a ratio of 3.5:1.0 (cf. eq 5).



3 7 8 (5)

7:8=3.5:1.0

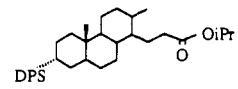
The retention of the 17-keto group in **7** is evident from an IR band at 1738 cm^{-1} and a ^{13}C resonance at δ 222.7. A C/D cis ring fusion is manifested by the downfield shift of the 18-CH_3 ^1H NMR resonance (δ 0.97 vs δ 0.82 for **3**) and the upfield shift of the 19-CH_3 resonance (δ 0.57 vs δ 0.91 for **3**). The structural assignment for **8** rests on the characteristic aldehyde proton resonance at δ 9.76 and the resonance of the allylic 18-CH_3 group at δ 1.55.[27]

Table II. Effect of *cis*-1,3-Pentadiene in the Photolysis of **1** and **3** in Acetonitrile with TEA[a]

[diene] (mM)	$\phi_{al}(4)/\phi_{al}^{\circ}(4)$	$\phi_{ep}(5)/\phi_{ep}^{\circ}(5)$	$\phi_{al}(6)/\phi_{al}^{\circ}(6)$	$\phi_{ep}(7)/\phi_{ep}^{\circ}(7)$
59.0	0.19	0.93	0	0.95
119	0	0.86	0	0.88

[a] All experiments with 266-nm light from an Nd:YAG laser (6.5 mJ/pulse); concentrations were $[1]_0$ and $[3]_0$ = 17 mM, $[TEA]_0$ = 32.3 and 59.2 mM for **1** and **3**, respectively.

Photolysis of 1 and 3 in 2-Propanol (iPrOH). Irradiation of **1** (14.1 mM) in an iPrOH solution saturated with sodium bicarbonate using 254-nm light for 60 min provided the epimer **5** and the reduction product **4** in a ratio of 4.2:1.0. Irradiation of **3** (15.4 mM) under analogous conditions for 55 min gave the epimer **7**, the aldehyde **8**, and an isopropyl ester **9** (structure assignment based on GLC/MS spectral data; see the Experimental Section) in a ratio of 1.0:3.9:1.0. No reduction was detected.



9

Quantum Efficiency Determinations for Photolysis of 1 and 3 with 254-nm Excitation. Quantum efficiencies for epimerization at C17 were determined for both compounds **1** and **3** in acetonitrile in the absence of TEA using 254-nm light. Measured values were 0.0042 and 0.089 for **1** and **3**, respectively.

Quantum Efficiency Determinations for Photolysis of 1 and 3 with 266-nm Excitation. Quantum efficiencies for photoreduction (ϕ_{al}) and photoepimerization (ϕ_{ep}), for **1** and **3**, were determined as a function of [TEA] in MeCN with 266-nm light. The data are summarized in Table I.[28] As expected, both $\phi_{al}(4)$ and $\phi_{al}(6)$ increase with increasing [TEA], the limiting quantum efficiencies being 0.07 and 0.05, respectively. Photoepimerization of **1** is completely quenched at [TEA] = 59.2 mM, while the epimerization of **3** is more gradually reduced at the higher TEA concentrations.

Quantum Efficiency Determinations for 1 and 3 with 308-nm Light. Quantum efficiencies for photoreduction and photoepimerization, for **1** (26.8 mM) and **3** (55.0 mM) in MeCN with TEA (140 mM for **1** and 165 mM for **3**), were determined using a XeCl 308-nm laser (3–6 mJ/pulse). For the photolysis of **1**, the $\phi_{al}(4)$ and $\phi_{ep}(5)$ values are 0.01 and 0.20, respectively (at 37% loss of **1**). For compound **3**, the quantum efficiency of epimerization ($\phi_{ep}(7)$) is 0.31 (25% loss of **3**). (A preparative photolysis of **3** (36 mM) in MeCN with TEA (108 mM) for 9 min, using a Rayonet Photoreactor containing 300-nm lamps, gave

(25) Chambers, V. E. M.; Denny, W. A.; Evans, J. M.; Jones, E. R. H.; Kasal, A.; Meakins, G. D.; Pragnell, J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1500–1511.

(26) Borohydride reduction of the 17-ketone functionality in the androstane series is known to give 17β-alcohols; see: Norymberski, J. K.; Woods, G. F. *J. Chem. Soc.* **1955**, 3426–3430.

(27) The chemical shifts of the allylic methyl group (δ 1.55) and the aldehyde proton (δ 9.76) in **8** match well with those (δ 1.65 and 9.87, respectively) observed in an analogous α cleavage product isolated by Iriarte, v. J.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1964**, *47*, 1255–1264.

(28) Even at 266 nm some portion of the photoreduction is caused by TEA excitation.[23] We can estimate this fraction from quantum efficiencies obtained for the TEA-initiated chemistry. For example, we have measured the quantum efficiencies for reduction of 15 mM 3α-hydroxy-5α-androstane-11,17-dione and 17 mM 3β-hydroxy-5α-androstan-17-one (models for **1** and **3**, respectively) by photoexcitation of TEA in MeCN to be 0.05 and 0.08, respectively. At 43 mM TEA and 15 mM steroid, the amine absorbs 7.6% of the light when admixed with **1**[23] and 8.5% of the light in the presence of **3** (ϵ_{266} = 163 M^{-1} cm^{-1}). The observed quantum efficiency thus includes a contribution to the reduction of **1** = 0.05 × 0.076 = 0.0038, which has been subtracted to give the number presented in Table I. An analogous calculation for **3** shows that 38% of the uncorrected $\phi_{al}(6)$ at this TEA concentration is due to amine excitation. In fact, the true contribution may be lower than this, since aryl groups can quench the TEA excited state.[29]

(29) The rate constant of quenching of TEA* by benzene is 2.1 × 10^{10} M^{-1} s^{-1}; see: Halpern, A. M.; Wryzykowska, K. *J. Photochem.* **1981**, *15*, 147–157.

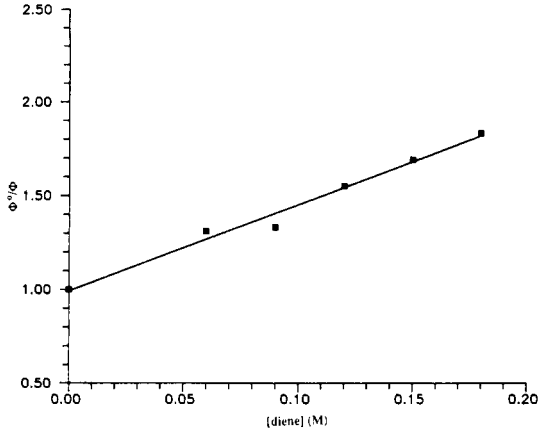


Figure 1. Stern–Volmer plot for *cis*-1,3-pentadiene quenching of the 266-nm-initiated photoepimerization of **1** in acetonitrile.

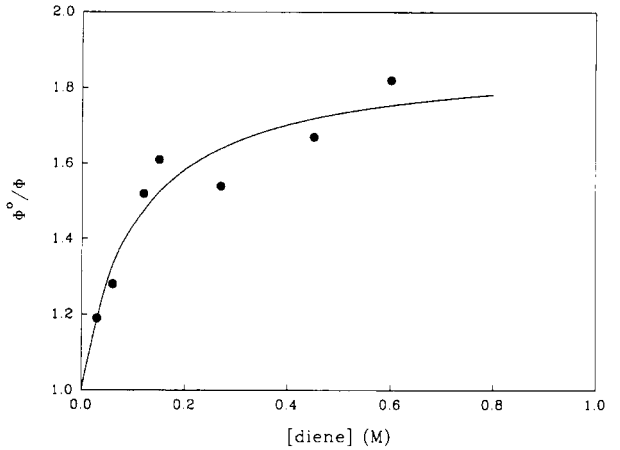


Figure 2. Stern–Volmer plot for *cis*-1,3-pentadiene quenching of the photoepimerization of **3** in acetonitrile using 254-nm light.

the epimer **7** and the aldehyde **8** in a ratio of 6.8:1.0. No reduction of **3** was observed.)

Irradiation of 4 in MeCN/TEA with 300-nm Light. The photolysis of compound **4** was studied in order to probe the photochemistry of an 11-keto group under the MeCN/TEA conditions.[30] Irradiation of a solution containing **4** (22.6 mM) and TEA (108 nM) at 300 nm for 40 min showed no change in the concentration of **4** using GLC and an internal standard.

Quenching Studies with *cis*-1,3-Pentadiene. The degree of triplet involvement in the antenna-induced photoreduction and photoepimerization reactions was probed using *cis*-1,3-pentadiene (E_T = 58.3 kcal/mol)[31] and the Nd:YAG laser line at 266 nm. The reduction reaction was studied for both **1** and **3** with the MeCN/TEA conditions; the data are given in Table II.

The effect of 0.060–0.180 M *cis*-1,3-pentadiene on the photoepimerization of **1** (16.2 mM) was explored in MeCN without TEA on excitation at 254 nm. A Stern–Volmer plot of the data is presented in Figure 1; the slope and intercept are $k_q\tau_0$ = 5.6 M^{-1} s^{-1} and 1.00, respectively (corr coeff = 0.99). A comparable plot for **3** (254-nm excitation) is presented in Figure 2 and shows curvature indicative of both quenchable and unquenchable components to the photoepimerization. The data were analyzed by a least-squares fit to the equation corresponding to a reaction derived from a quenchable triplet component ($k_q\tau_0$ = 18.4 ± 5.4 M^{-1} s^{-1}) and an unquenchable singlet component (singlet = 53 ± 3%).[32] No quenching was observed when **3** was photolyzed with 300-nm light in the presence of 0.030–0.15 M *cis*-1,3-pentadiene.

Table III. Photolysis of **3** in 2-Propanol in the Presence and Absence of Cyclohexanone[a]

[cyclohexanone] (mM)	$\phi_{ep}(7)/\phi_{ep}°(7)$	$\phi_{ald}(8)/\phi_{ald}°(8)$
10.2	0.98	0.96
15.3	0.96	1.01
20.4	0.96	0.98
25.5	0.87	0.92
30.6	0.85	0.88

[a] $[3]_o$ = 15 mM; 254-nm excitation.

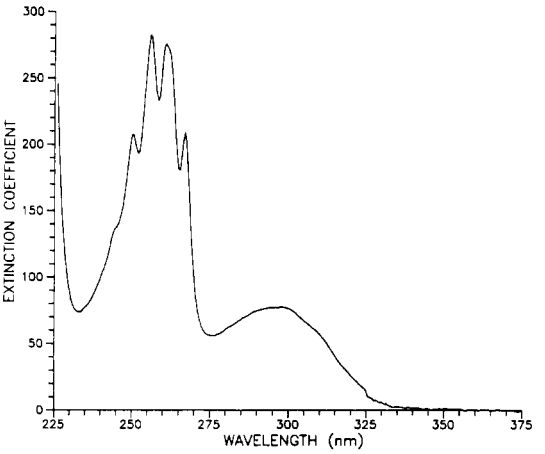


Figure 3. Absorption spectrum of 3β-DPS-androstane-11,17-dione (**2**) in MeCN.

Effect of Added Cyclohexanone on the Photochemistry of 1 or 3. The addition of cyclohexanone to such reactions has proven useful as a test of the possible contribution of intermolecular SSET to the photoreduction.[4,5] Photolysis of **1** (17 mM) in MeCN in the presence of TEA (32 mM) and cyclohexanone (17 mM) with 266-nm light gave only a 0.6% conversion of cyclohexanone into cyclohexanol at a 17% loss of **1**. Likewise, excitation of **3** under the same conditions gave rise to 2.8% reduction of the cyclohexanone at a 23% loss of **3**. A more extensive study of **3** in the presence of various concentrations of cyclohexanone was carried out in iPrOH with 254-nm light; the results are presented in Table III. Quenching of product formation from **3** was observed only when the concentration of external ketone was appreciably higher than that of the steroid. In a separate study, the photolysis of 4-(dimethylphenylsiloxy)cyclohexanol (15 mM) and cyclohexanone (6 mM) in 2-propanol with 254-nm light for 15 min gave a 1.6% conversion of cyclohexanone into the alcohol. By contrast, photolysis of 4-[(phenylacetyl)oxy]cyclohexanol and cyclohexanone under identical conditions led to 44.7% conversion of the ketone into the alcohol.

Spectroscopy. The absorption spectra of **1**, **2**, and **3** reflect the component aryl and ketone (or diketone) chormophores, with no apparent evidence of significant interaction between these. This is reflected in the extinction coefficients for the n→π* transitions of these steroids: 34, 45, 67, and 71 M^{-1} cm^{-1} for 3α-hydroxy-5α-androstan-17-one, **3**, 3α-hydroxy-5α-androstane-11,17-dione, and **1**, respectively. A typical spectrum is shown in Figure 3 for **2** in MeCN. Absorption maxima are seen at the following (λ nm; ε M^{-1} cm^{-1}): DPS chromophore, 250 (207), 256 (282), 262 (276), and 267 (209); carbonyl groups, 298 (77).

The fluorescence properties of the DPS antenna are illustrated by **6**, which shows aryl emission centered at 285 nm with $\phi_f(6)$ = 0.0053 in MeCN (cf. Figure 4) relative to toluene in cyclohexane (ϕ_f = 0.14).[33] The 0,0 transition energy for $S_0 \rightarrow S_1$ is

(30) Photocyclization involving intramolecular hydrogen abstraction by the 11-keto group has been reported for some steroids (ethanol solvent); see: (a) Wehrli, H.; Heller, M. S.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1961**, *44*, 2162–2173. (b) Iriarte, J.; Schaffner, K.; Jeger, O. *Ibid.* **1963**, *46*, 1599–1609.

(31) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; p 5.

(32) Gano, J. E. *Mol. Photochem.* **1972**, *4*, 527–533. Wagner, P. J. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II.

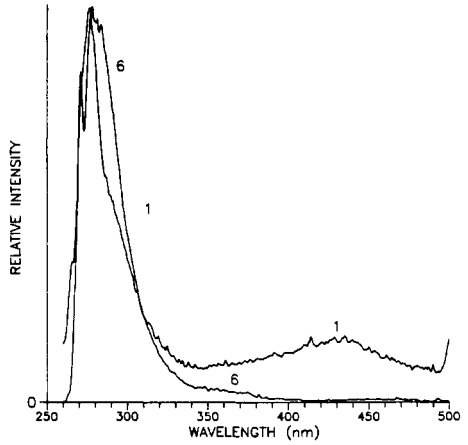


Figure 4. Normalized fluorescence spectra of **1** and **6** in MeCN.

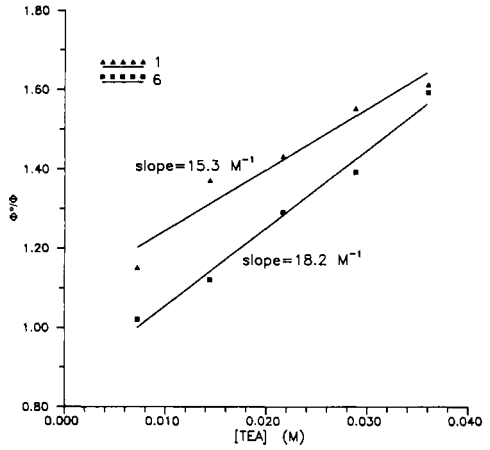


Figure 5. Quenching of fluorescence of **1** and **6** by TEA in MeCN at 25 °C.

Table IV. Fluorescence Data for Compounds **1–4** and **6** in MeCN

steroid	ϕ_f (aryl)[a]	τ_f (ns)[b]	R^c (Å)
6	0.0053	1.20 (1.43)	
3	0.0047	0.95 (1.21)	11.6
4	0.0020	0.33	8.6
1	0.0017	0.27	8.6[d]
2		0.50	9.4[d]

[a] Using toluene in cyclohexane as a reference (ϕ_f = 0.14).[33] [b] Values in parentheses were measured in ethyl ether. [c] Defined as the distance between the phenyl carbon attached to the silicon atom and the carbon atom of the C=O group, as calculated from MNDO optimized structures. [d] Distance between the phenyl carbon and the 11-keto carbon.

estimated from the onset at 270 nm to be 107 kcal/mol. The DPS-substituted steroidal ketones show dual emission upon excitation of the phenyl chromophore at 254 nm, with aryl emission centered at 285 nm and ketone emission at ca. 400–420 nm (cf. Figure 4 for the spectrum of **1** in MeCN; the fluorescence spectra for compounds **1**, **3**, and **4** in cyclohexane have been published earlier).[2] A compilation of fluorescence data for compounds **1–4** and **6** is presented in Table IV.

Quenching of the fluorescence of **6** (4.0 mM) by TEA (7.2–36 mM) in MeCN at room temperature on excitation at 269 nm gave a linear Stern–Volmer plot with a slope of $k_q\tau_0$ = 18.2 M^{-1} (Figure 5). One can thus estimate the singlet lifetime of the DPS group by assuming that singlet quenching by the amine is diffusion-controlled (in MeCN, $k = 2.9 \times 10^{10}$ M^{-1} s^{-1}).[34] A value of 0.63 ns is so calculated, comparable to that independently obtained

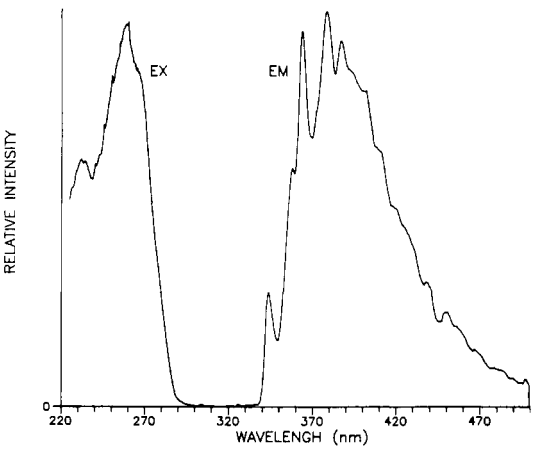


Figure 6. Phosphorescence emission and excitation of **6** in ether/methylcyclohexane at 77 K.

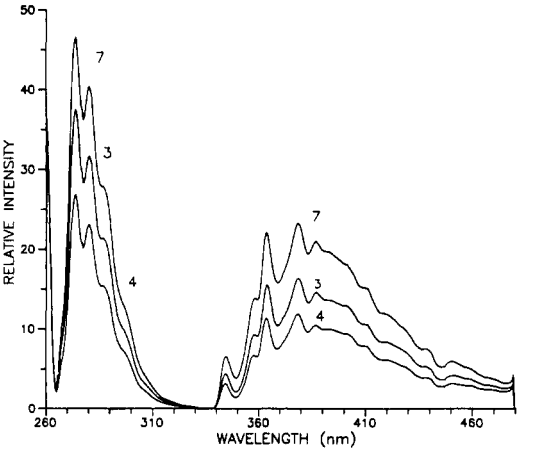


Figure 7. Total emission spectra for **3**, **4**, and **6** in an ether/methylcyclohexane glass at 77 K.

from a fluorescence lifetime measurement (τ_f = 1.2 ns; cf. Table IV). Likewise, quenching of the aryl fluorescence of **1** in the same manner gave a linear Stern–Volmer plot with a slope of $k_q\tau_0$ = 15.3 M^{-1} (Figure 5); the calculated lifetime of 0.53 ns may be compared with the measured value of 0.27 ns (Table IV).

Phosphorescence emission and excitation spectra of **6** (1.4 mM) were determined at 77 K in an ether/methylcyclohexane glass (cf. Figure 6). A triplet energy for the DPS group of ca. E_T = 84 kcal/mol was calculated on the basis of the emission onset at 340 nm. The total emission spectra of **3**, **4**, and **6** in an ether/methylcyclohexane glass at 77 K were recorded to examine the possibility of intra-TTET between the DPS and ketone groups (cf. Figure 7). Both the fluorescence and phosphorescence emissions of **3** and **4** show a diminished intensity relative to that seen in **6**, with fluorescence intensity ratios (**3**:**6** = 0.82; **4**:**6** = 0.60) comparable to the phosphorescence ratios (**3**:**6** = 0.91; **4**:**6** = 0.68). No ketonic emission was detected.

ϕ_{isc} and $E_{1/2}^{ox}$ Measurements on the DPS Antenna. The intersystem crossing efficiencies (ϕ_{isc}) of the DPS antenna were determined in polar and nonpolar media using time-resolved photoacoustic calorimetry.[35] For ethanol, 3β-DPS-5α-androstan-17β-ol was employed as a standard and gave a value of ϕ_{isc} = 0.19, while (dimethylphenylsiloxy)cyclohexane was studied in hexane and gave a value of ϕ_{isc} = 0.16. The half-wave oxidation potential ($E_{1/2}^{ox}$) of the DPS antenna was determined in acetonitrile using 3β-DPS-5α-androstan-17β-ol as the model

(33) Birks, J. B. *Photophysics of Aromatic Molecules*; John Wiley & Sons Ltd.: New York, 1970; p 126.
(34) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; p 55.

(35) Illustrative examples of the application of time-resolved photoacoustic calorimetry (PAC) to the determination of the dynamics and energetics of photoinitiated reactions may be found in the following: Rudzki, J. E.; Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849–7854. Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 2681–2683.

Table V. Spectroscopic Parameters for the DPS Antenna in MeCN

E_S (kcal/mol)	E_T (kcal/mol)	ϕ_f[a]	ϕ_{isc}[b]	τ_f (ns)	λ_f(max) (nm)	λ_p(max)[c] (nm)
107	84	0.0053	0.19 (0.16)	1.2	282	385

[a] See footnote a of Table IV. [b] The ϕ_{isc} value was measured in ethanol, and the value in parentheses, in hexane. [c] Phosphorescence was determined in an ether/methylcyclohexane glass at 77 K.

and was found to be 2.14 V vs a saturated calomel electrode (SCE).

Discussion

Photochemistry. We have noted elsewhere[3] the properties that are desirable for an antenna to initiate photochemistry at a distal position. These include facile attachment and detachment of the antenna from the molecular framework, appreciable absorption in a region of the spectrum easily accessed in the presence of the target functional group, and a short excited state lifetime to minimize secondary and/or intermolecular energy transfer. The DPS antenna meets these requirements, and its spectroscopic parameters are summarized in Table V.

As is evident from eq 3, excitation of the antenna chromophore in compound **1** does indeed lead to chemistry at C17. The reaction in acetonitrile with TEA (43 mM) is dominated by reduction to **4**, with epimerization to **5** accounting for only 26% of the products. Photolysis of the monoketone **3** under similar conditions also results in chemistry at C17 (eq 4), though epimerization now accounts for 78% of the product. We confirmed that energy transfer from the DPS group to the target carbonyl moieties proceeded through intramolecular processes by demonstrating that added cyclohexanone had a minimal effect on the α cleavage of **3** at the typical steroid concentration (15 mM) used in these studies (cf. Table III). The shorter lifetime of the DPS excited state in **1** (cf. Table IV) assures that energy transfer in this substrate is likewise primarily intramolecular.

One may anticipate that reduction and α cleavage would be, at least in part, competitive with one another (see below). This is clearly seen in the data in Table I where increasing the TEA concentration totally quenches epimerization of **1** and partially quenches α cleavage in **3**. It is not surprising that photolysis of **1** and **3** in the poorer reducing environment of iPrOH leads to diminished percentages of alcohol product, and α cleavage chemistry accounts for 81% and 100% of the product for these two substrates, respectively.[36] Likewise, α cleavage chemistry dominates the antenna-initiated photochemistry of **1** and **3** in cyclohexane and in acetonitrile lacking TEA. The preference for reduction to the equatorial alcohol (the 17C-βOH) is well precedented for a *trans*-decalin ring fusion.[4,39] The cleavage to epimer and aldehyde, as well as to an isopropyl ester when the reaction is run in 2-propanol, is consistent with earlier studies of α cleavage of the 17-keto group.[24,40]

The antenna-initiated chemistry contrasts markedly with that obtained from the direct excitation of the 17-keto group with 308-nm light, both qualitatively and quantitatively. For example, such irradiation of **1** in the presence of 140 mM TEA in acetonitrile gives primarily epimerization, with only 5% of the alcohol (**4**) being formed, whereas photolysis via the antenna at this concentration of TEA leads exclusively to reduction. Likewise, photolysis of **3** at 308 nm affords only the α-cleaved products, epimer **7** and aldehyde **8**, whereas photolysis through the antenna gives 22% reduction.

Table VI. Summary of Quantum Efficiency Data for **1** and **3**

	$^3\phi_{al}$	$^1\phi_{ep}$	$^3\phi_{ep}$
	Direct Excitation[a]		
1	0.01	0.20	
3		0.31	
	Antenna-Initiated		
1	0.07[b]		0.0042[c]
3	0.05[b]	0.047[c]	0.042[c]

[a] 308 nm; with 140–165 mM TEA. [b] 266 nm; extrapolated to infinite TEA. [c] 254 nm; no TEA.

Reaction Multiplicity. Photoreduction of cycloalkanones is generally triplet-derived,[41] while the photoepimerization of α-substituted cycloalkanones typically occurs from the singlet state (for example, 87% of the α cleavage of 8-methyl-1-hydroindanone is singlet-derived).[41d] Thus, direct excitation of the ketone moiety in **3** gives unquenchable (i.e., totally singlet-derived) epimerization. Photoreduction, generated by antenna initiation in **1** and **3** in the presence of 30–60 mM TEA in CH_3CN, is completely quenched by 119 mM pentadiene (Table II), as expected for a triplet-derived reaction. These observations, taken together with the product studies summarized above, suggest the following conclusions: (1) for these 17-keto steroids, α cleavage of the excited singlet state is more rapid than intersystem crossing (308-nm photolysis of **1** and **3** leads to minimal reduction). (2) Antenna sensitization of **1** leads to triplet chemistry at C17, which is bypassing the 17-ketone excited singlet state (there is minimal epimerization, and that which occurs is eventually eliminated by high TEA concentrations). (3) Antenna sensitization of **3** is creating a mixture of 17-ketone singlet and triplet states, again without intersystem crossing between the two manifolds (one sees reduction under these conditions but not by direct excitation of the ketone).

These conclusions are supported by the *cis*-1,3-pentadiene quenching studies on antenna initiation in the absence of TEA. Under these conditions, the only reaction available to the C17 triplet is α cleavage, and therefore epimerization occurring from this state should be quenchable. This is indeed observed for **1**, with the quenching of the photoepimerization reaction giving an excellent linear fit to Stern–Volmer kinetics (Figure 1).[42] One concludes that all of the antenna-initiated chemistry at C17 in **1** is triplet-derived. Since **3** gives both epimerization and reduction when excited into the antenna with TEA present, the C17 singlet and triplet should contribute to the photoepimerization reaction in the absence of TEA. One therefore expects, and indeed observes, curvature to the Stern–Volmer plot for quenching of the epimerization of **3** in the absence of the amine (Figure 2).

Quantum Efficiencies. An analysis of Figure 2 indicates that 47% of the epimerization resulting from antenna excitation is triplet-derived. Since the total quantum efficiency for antenna-initiated epimerization at C17 in **3** in the absence of TEA is 0.089, one calculates that the singlet and triplet contributions to this epimerization are 0.047 ($^1\phi_{ep}$) and 0.042 ($^3\phi_{ep}$). Both of these values are 1 order of magnitude higher than the antenna-initiated quantum efficiency for (triplet) epimerization at C17 in **1** in the absence of TEA (0.0042 ($^3\phi_{ep}$)). These $^3\phi_{ep}$ values clearly do not reflect the total yield of C17 triplets, since the limiting quantum efficiencies for reduction at C17 in **1** and **3** in acetonitrile with TEA (i.e., $^3\phi_{al}$) are 0.07 and 0.05, respectively (cf. Table I). However, the comparable $^3\phi_{al}$ values for **1** and **3** contrast with their markedly different $^3\phi_{ep}$ values and indicate that the presence

(36) An electron-transfer mechanism is commonly accepted for the photoreduction of ketone excited states by amines,[37] and the rate constant for the quenching of ketone triplets by TEA (2.3×10^9 M^{-1} s^{-1}) is some 3 orders of magnitude greater than that for 2-propanol.[38]

(37) For reviews on the photoreduction of ketones by amines, see: (a) Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141–161. (b) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1–53. (c) Karvarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 428–437.

(38) Cohen, S. G.; Litt, A. D. *Tetrahedron Lett.* **1970**, 837–840. Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048–1054.

(39) Micheau, J. C.; Paillous, N.; Lattes, A. *Tetrahedron* **1973**, *31*, 441–447 and references therein.

(40) For a review of α cleavage of alkanones, see: Weiss, D. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5.

(41) (a) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1–53. (b) Michaeu, J. C.; Paillous, N.; Lattes, A. *Tetrahedron* **1975**, *31*, 441–447. (c) Weiss, D. S. *Org. Photochem.* **1981**, *5*, 347–420. (d) Yang, N. C.; Chen, R. H.-K. *J. Am. Chem. Soc.* **1971**, *93*, 530–532.

(42) If one assumes that *cis*-1,3-pentadiene quenches the ketone triplet at a diffusion-controlled rate and that the lifetime of the 17-keto triplet is determined by its α cleavage reaction, one calculates a rate for this cleavage of 5.3×10^9 s^{-1}. This value matches well with the cleavage rate determined for 2-methylcyclopentanone (3.6×10^9 s^{-1}) and related molecules; cf. ref 40, p 352.

Table VII. Efficiencies and Rates for Intra-SSET

steroid	$\phi_{\text{intra-SSET}}$[a]	$k_{\text{intra-SSET}}$[b] (10^8 s^{-1})
3	0.21 (0.11)	2.2 (1.1)
4	0.73 (0.62)	22 (14)
1	0.78 (0.68)	29 (18)
2	0.58	12

[a] Values calculated as in eq 7; values in parentheses calculated by eq 6. [b] Values calculated by eq 8; values in parentheses calculated by eq 9.

of the 11-keto group inhibits epimerization of the 17-keto triplet. One sees a similar trend in singlet epimerization, though not so marked, since $^1\phi_{ep}$ for **1** and **3** under direct excitation conditions is 0.20 and 0.31, respectively. The quantum efficiency data are summarized in Table VI.

Energy Migration in Compounds 1 and 3—Intramolecular Singlet/Singlet Energy Transfer. Insight into the details of how energy is moving about in these trichromophoric steroids is provided by the photophysical data presented in Table IV. One notes that the existence of the keto group in **1**–**4** diminishes the fluorescence efficiency (ϕ_f) and lifetime (τ_f) for DPS emission, clearly indicative of intra-SSET. This is consistent with the dual fluorescence emission observed for **1** in Figure 4. As expected, the efficiency of intra-SSET correlates well with the interchromophore distance, as evidenced by the progressive decrease in both ϕ_f and τ_f for **3** (3α-DPS/17-keto) vs **2** (3β-DPS/11-keto) vs **1** (3α-DPS/11,17-dione) and **4** (3α-DPS/11-keto). The quantum efficiency for intra-SSET ($\phi_{\text{intra-SSET}}(i)$) from the DPS singlet to the ketone group in the substrate i (i = **1**, **2**, **3**, or **4**) can be evaluated from either the ϕ_f or τ_f values, using the fluorescence data for **6** as a reference for the intrinsic properties of the DPS group (eqs 6 and 7). The corresponding rates for intra-SSET ($k_{\text{intra-SSET}}(i)$) can then be calculated with eqs 8 and 9. The results

$$\phi_{\text{intra-SSET}}(i) = [\phi_f(\mathbf{6}) - \phi_f(i)]/\phi_f(\mathbf{6}) \quad (6)$$

$$\phi_{\text{intra-SSET}}(i) = [\tau_f(\mathbf{6}) - \tau_f(i)]/\tau_f(\mathbf{6}) \quad (7)$$

$$k_{\text{intra-SSET}}(i) = [\tau_f(\mathbf{6}) - \tau_f(i)]/[\tau_f(\mathbf{6})\tau_f(i)] \quad (8)$$

$$k_{\text{intra-SSET}}(i) = [\phi_f(\mathbf{6}) - \phi_f(i)]/[\phi_f(i)\tau_f(\mathbf{6})] \quad (9)$$

are presented in Table VII. There is good agreement between the ϕ_f and τ_f derived values, and one again notes the larger $\phi_{\text{intra-SSET}}$ and $k_{\text{intra-SSET}}$ values associated with the steroids bearing an 11-keto group. Specifically, using the ϕ_f derived data and concentrating on the 3α series, ca. 75% of the DPS singlet energy is transferred to the 11 position in the 11-keto steroids vs 21% transferred to the 17 position of the steroid lacking the 11-keto group. Likewise, the rate constants for transfer to the 11 position in **1** and **4** are 10-fold higher than for transfer to the 17 position. It is reasonable to conclude that, in a substrate having carbonyl groups at both the 11 and 17 positions, transfer to the 11 position will dominate the photophysics. This is confirmed by the absence of C17 singlet chemistry in **1** and explains the comparable ϕ_f and τ_f values for the 11-keto substrates regardless of the presence of a 17-keto group, e.g., for **4** and **1**, ϕ_f = 0.20 and 0.17 and τ_f = 0.33 and 0.27 ns, respectively. There is also a pleasing consistency between the photochemical data for **3** and the measured $\phi_{\text{intra-SSET}}$ values, i.e., multiplying the intrinsic $^1\phi_{ep}$ of 0.31 (Table VI) by the two $\phi_{\text{intra-SSET}}$ numbers provides $^1\phi_{ep}$ values for the antenna-sensitized reaction which bracket the number (0.047) experimentally observed.

Two further points are worth noting: (1) The lack of singlet chemistry in **1** also requires that none of the singlet energy being transferred to C11 in **1** is migrating to C17. (2) Though we only have preliminary data for the 3β series, there is some indication in Table VII that the rate constant for intra-SSET to the 11 position is reduced more than 2-fold by comparison with a 3α antenna.

Energy Migration in Compounds 1 and 3—Intramolecular Triplet/Triplet Energy Transfer. It has been noted above that direct excitation of the keto group(s) in both **1** and **3** leads to virtually exclusive singlet-derived epimerization of ring D, i.e., intersystem crossing of the C17 keto group is not competitive with α cleavage. Nevertheless, antenna sensitization of **3** does give C17 keto triplet chemistry, thus requiring that triplet energy transfer from the DPS group occurs in this compound. The efficiency of intersystem crossing of the DPS group in a model monochromophoric substrate is substantial (ϕ_{isc} = 0.19), and the low $\phi_{\text{intra-SSET}}$ in **3** (10–20%) should only modestly reduce it. Furthermore, triplet energy transfer between the DPS and keto groups would be exothermic since we estimate the T_1 energy of the DPS functionality to be 84 kcal/mol, while that of the 17-keto group is ca. 78 kcal/mol.[43] However, energy transfer via a through-space exchange process would be quite inefficient over the 11.6 Å separating these chromophores,[44] and *one must invoke a through-bond mechanism (TBI) to explain such energy migration.* There is precedent for intra-TTET via a TBI mechanism in systems having a rigid spacer linkage.[45] The efficiency of such triplet transfer ($\phi_{\text{intra-TTET}}$) in **3** cannot be accurately calculated because of the lack of an intrinsic quantum efficiency for reduction of the C17 keto triplet. However, assuming a ϕ_{isc} of the DPS group of 0.15–0.17 in **3** (see above) and using our measured limiting quantum efficiency for triplet chemistry at C17 of ca. 0.05 (Table VI), we may calculate a *minimum* value of ca. 30%.

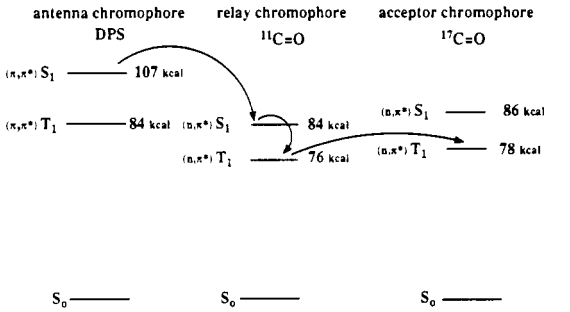


Figure 8. Mechanism for multistep intramolecular energy transfer from the DPS antenna to the C17-keto group in **1**.

The 11-Keto Group as a Singlet/Triplet Switch. A Possible Intra-TTET Relay Pathway. In contrast to the mixture of singlet and triplet chemistry observed at C17 by antenna sensitization of **3**, we note that the antenna-initiated photochemistry of **1** derives entirely from the triplet state. One can estimate the maximum potential contribution of direct triplet transfer between the DPS and C17 keto groups in a manner identical to that used for **3** above, i.e., by calculating the ϕ_{isc} of the now much shorter lived DPS group. This value is 0.04, a number which, in contrast to what is seen for **3**, is too low to account for the limiting $^3\phi_{al}$ of 0.07 observed for **1**, even in the unlikely event that all of the DPS triplet is transferred to ring D. One must therefore turn to the DPS singlet state, and its efficient transfer by intra-SSET to C11, to account for the remaining C17 triplet chemistry. However, it is clear from the product studies that the C17 keto singlet is *not* populated by antenna sensitization, and one is forced to conclude that the excitation energy from C11 to C17 has first been converted to the triplet manifold, i.e., *the C11 keto group is acting as a singlet/triplet switch.* The complete mechanism is shown in Figure 8 and consists of three steps: DPS/11-keto intra-SSET, 11-keto intersystem crossing, and 11-keto/17-keto intra-TTET. The observable is 17-keto triplet photochemistry, i.e., reduction in the presence of TEA or epimerization in its absence.

The rate constant for the first step of this mechanism is calculated as $k_{\text{intra-SSET}} = 2.9 \times 10^9$ s^{-1} (cf. Table VII), a value

(43) This is the triplet energy for a cyclopentanone, as taken from the following: Morton, D. R.; Turro, N. J. In *Advances in Photochemistry*; Pitts, J. N., Jr., Hammond, G. S., Gollnick, K., Eds.; Wiley & Sons, Inc.: New York, 1974; Vol. 9, p 207.

(44) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; p 329.

(45) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652–2653. This is a photophysical study; to our knowledge, our observation represents the first example of photochemistry caused by such TBI intra-TTET.

comparable to that reported for other examples of intra-SSET: 2.4×10^9 s^{-1} for aryl/ketone energy transfer in 4-(benzyloxy)-cyclohexanone;[5] 2.7×10^9 s^{-1} for aryl/ketone energy transfer in *trans*-decalone;[4] $(1.3-3.0) \times 10^9$ s^{-1} for naphthyl/ketone energy transfer in bicyclooctane;[6b] and 1.2×10^9 s^{-1} for dimethoxynaphthyl/ketone energy transfer through rigid, saturated hydrocarbon bridges via four σ bonds.[8,11] The interchromophore distances in all of these molecules are in the range of ca. 6–8 Å.

The second and third steps involve intersystem crossing of the relatively photochemically inert 11-keto group[30,46] and subsequent intra-TTET. The rate constant of intersystem crossing is estimated to be $k_{isc} = (3-4) \times 10^8$ s^{-1} for the 11-keto singlet,[47] and in the absence of any singlet photochemistry, one can assume ϕ_{isc} is ~ 1. Intra-TTET is virtually isoenergetic, or perhaps slightly endothermic.[48] We have no way of measuring this rate constant or quantum efficiency. If the rate of α cleavage of the 11-keto triplet is assumed to be similar to that for 2-methylcyclohexanone, i.e., $k = 2.5 \times 10^8$ s^{-1},[50] the rate of intra-TTET must be at least competitive with this value. The rate constant for intermolecular triplet energy transfer between acetone molecules in acetonitrile has been reported to be only 10^6 s^{-1},[51] but the rate of intra-TTET in some *nonrigid* 1,4-aliphatic diketones is 3×10^8 s^{-1}.[52] As was noted in the introduction, TBI between the 11- and 17-keto groups in the rigid steroid skeleton has been demonstrated by photoelectron spectroscopy,[16] and the rate constant for intra-TTET in this system may be elevated by a TBI-mediated exchange mechanism.[8,11,16,45] As regards efficiency of C11 to C17 triplet transfer, what we can say is that it must be relatively inefficient since a comparison of the $\phi_{intra\text{-}SSET}$ of 0.78 and a limiting $^3\phi_{al}$ (corrected for the maximum possible DPS/C17 intra-TTET) of 0.03 clearly leaves a great deal of excitation unaccounted for.[53]

Conclusions

The bi- and trifunctional steroids, **3** and **1**, exhibit a rich array of photophysical and photochemical properties as a consequence of intramolecular singlet and triplet energy transfer. Of particular interest are the activation of ring D in **3** (and possibly **1**) through TBI-mediated triplet/triplet energy transfer and the ability of the 11-keto group in **1** to act as a singlet/triplet switch in transmitting excitation energy from the DPS antenna to the 17-keto group. One striking consequence of these phenomena is the unique triplet chemistry observed at C17 in **1** through antenna sensitization as opposed to the singlet chemistry at this site when directly excited.

Experimental Section

Materials. Adrenosterone, androsterone, epiandrosterone, K-Selectride (1 M in THF), and chlorodimethylphenylsilane were purchased from Aldrich and used as received. THF (Mallinckrodt) was purified by successive distillation 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 and distilled under reduced pressure. Hexane, cyclohexane, and 2-propanol used in the photochemical and spectroscopic studies were spectroquality grade from Burdick and Jackson and used as received; acetonitrile was also Burdick and Jackson spectroquality grade but was distilled from calcium hydride. Toluene used as a reference for the determination of fluorescence quantum efficiencies was spectroquality grade from Fisher. Hexane, ethyl acetate, and methylene chloride used in flash column chromatography were bulk grade and distilled prior to use. Flash column chromatography was carried out on 230–400 mesh silica gel. All reactions were run under dry nitrogen. Neutral workup in preparation of some starting materials refers to quenching the reaction with water, extracting with CH_2Cl_2, washing the organic layer with water and brine, drying, filtering, and concentrating under reduced pressure.

Instrumentation. NMR spectra were obtained with a General Electric QE-300 or a Varian VXR-600S spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 1420 ratio recording or a Model 1800 FT-IR spectrometer. Low-resolution mass spectra were determined with a Finnigan 4000 GC–MS spectrometer (EI/CI) equipped with a DB-1 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). High-resolution mass spectra were recorded on a Kratos Model MS-50 spectrometer. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Model Lambda 3B spectrometer. Fluorescence and phosphorescence spectra were recorded on a component fluorometer[56] with fluorescence quantum efficiencies measured by reference to toluene.[33] Fluorescence lifetimes were determined with a PTI Model LS-100 fluorescence lifetime spectrometer using a H_2 lamp. Fluorescence spectra were obtained at ambient temperature after degassing with argon for at least 15 min. Phosphorescence and total emission studies were run in ether/methylcyclohexane at 77 K, and the sample solutions were degassed by at least three freeze–pump–thaw cycles at a pressure of (3–4) × 10^{-5} Torr. The photoacoustic apparatus has been described elsewhere.[57] Excitation of (dimethylphenylsiloxy)cyclohexane in hexane with 266-nm light gave 88% of the photon energy back as heat. Using an estimated value of E_T = 84 kcal/mol (from the phosphorescence spectrum) gives $\phi_{isc} = 0.16$. Likewise, photolysis of 3β-DPS-androstan-17β-ol in ethanol at 266 nm gave 85% of the photon energy back as heat, thus giving $\phi_{isc} = 0.19$. Gas–liquid chromatography (GLC) analyses were performed on a Hewlett-Packard Model 5710A or a Varian Model 3700 capillary instrument (both with flame ionization detectors) coupled to a Hewlett-Packard 3390A integrator. The capillary columns used were the following: A, RSL-150 (Alltech, 30 m × 0.25 mm i.d., 0.25 μm film thickness); B, DB-1 (J & W, 15 m × 0.25 mm i.d., 0.25 μm film thickness). The internal standard was 3β-DPS-5α-androstan-17-one, unless otherwise noted. Melting points were determined with a Fisher-Johns melting point apparatus. The $E_{1/2}^{ox}$ value of 3β-DPS-5α-androstan-17β-ol (1.0 mM) in acetonitrile was measured by cyclic voltammetry on a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with platinum electrodes. The measurement was made in high-purity acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The half-wave oxidation potential was found to be 1.80 V relative to a ferrocene/ferrocinium reference, which was converted to $E_{1/2}^{ox}$ = 2.14 V vs a saturated calomel electrode.[58]

Photolyses. Photochemical studies were primarily carried out in a Rayonet photochemical reactor (New England Ultraviolet Corp.) equipped with 16 254-nm or 300-nm lamps (using quartz and Pyrex phototubes, respectively). Quantum efficiencies at 266 nm were determined using a Quanta Ray DCR-1 Nd:YAG pulse laser operating at 10 Hz (6.5 mJ/pulse) with a fourth harmonic generating crystal. The photon flux was 8.70×10^{16} photons/s as measured by a Scientech Model 362 power meter. Quantum efficiencies at 308 nm were determined using a Lambda Physik EMG 201 MSC pulse laser operating at 10 Hz (3–6 mJ/pulse). The photon flux in experiments involving **1** was measured to be 6.74×10^{16} photons/s by benzophenone/benzhydrol actinometry ($\phi = 0.74$ in benzene).[59] For compound **3**, a flux of 4.42×10^{16} photons/s was measured using a Scientech Model 361 power meter. A Vycor cuvette containing 2 mL of argon-degassed sample solution (ca. 15–17 mM) was placed in a sample holder. The solution was irradiated

(46) We cannot exclude reversible α cleavage of the 11-keto group as an undetectable photochemical reaction at this site.

(47) See: (a) Chandler, W. D.; Goodman, L. *J. Mol. Spectrosc.* **1970**, *35*, 232–243. (b) Shortridge, R. G., Jr.; Rusbult, C. F.; Lee, E. K. C. *J. Am. Chem. Soc.* **1970**, *92*, 1863–1871.

(48) We are estimating the E_T value for a cyclohexanone using ca. 84 kcal/mol as the energy of S_1 and assuming an S_1/T_1 gap of 8 kcal/mol.[49]

(49) Shortridge, R. G., Jr.; Rusbult, C. F.; Lee, E. K. C. *J. Am. Chem. Soc.* **1971**, *93*, 1863–1867.

(50) Dalton, J. C.; Dawes, K.; Turro, N. J.; Weiss, D. S.; Barltrop, J. A.; Coyle, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 7213–7221.

(51) Lechtken, P.; Turro, N. J. *Angew. Chem., Int. Ed. Engl.* **1973**, 314–315.

(52) Lissi, E. A.; Encinas, M. V.; Castaneda, F.; Olea, F. A. *J. Phys. Chem.* **1980**, *84*, 251–254.

(53) We have considered additional mechanisms for antenna activation of the C17 keto group, i.e., "trivial" emission/reabsorption and electron transfer. Trivial energy transfer should be minimal considering the low extinction coefficient of the ketone (ε ca. 30 M^{-1} cm^{-1}) and the low fluorescence efficiency of the DPS antenna ($\phi_f = 0.053$) in acetonitrile. One can estimate the free energy change for electron transfer using the Weller equation,[54] the half-wave oxidation potential of the DPS antenna ($E_{1/2}^{ox}$ = 2.14 V versus SCE in acetonitrile), the $E_{1/2}^{red}$ value of a ketone (−2.5 V versus SCE),[55] and the E_s of 107 kcal/mol for the DPS group. A positive free energy change is so calculated (ΔG = 1.2 kcal/mol). One notes also that the rate constants for intramolecular quenching of the DPS group are relatively independent of solvent polarity (2.2×10^8 an 1.3×10^8 M^{-1} s^{-1}, for acetonitrile and ether, respectively).

(54) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.

(55) Stackelberg, v. M.; Stracke, W. *Z. Electrochem.* **1949**, *53*, 118–125.

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

(57) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 712–714.

(58) Janz, G. J.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic Press: New York, 1973; Vol. II.

(59) Hammond, G. S.; Leermakers, P. A. *J. Phys. Chem.* **1962**, *66*, 1148–1150.

with either the 266-nm of 308-nm laser beam for 4–16 min (varying from sample to sample). All photolysis solutions were purged with argon for at least 15 min prior to irradiation. All photochemical studies were run at room temperature.

3α-(Dimethylphenylsiloxy)-5α-androstane-11,17-dione (1). 5α-Androstane-3,11,17-trione was prepared by the Birch reduction of adrenosterone followed by oxidation to the trione, which was isolated as a slightly yellow solid in an overall yield of 28%, mp 174–176 °C (lit. mp 174–176 °C).[20] The trione was reduced by K-Selectride to 3α-hydroxy-5α-androstane-11,17-dione. A 50-mL round-bottom flask with a side arm capped by a rubber septum was equipped with a magnetic stir bar and a condenser with a nitrogen inlet tube. The apparatus was flame dried under dry nitrogen. A solution of the trione (0.477 g, 1.58 mmol) in dry THF (6.5 mL) was syringed into the flask; the solution was stirred and cooled with a dry ice bath to −78 °C. A solution of K-Selectride (1.8 mL, 1 M in THF) was then added dropwise to the flask, and the yellowish mixture was stirred at −78 °C for 3 h. The mixture was warmed to room temperture, stirred for 20 min, and hydrolyzed by the addition of 5 mL of 50% ethanol in water. The organoborane was oxidized by the addition of 0.5 mL of 6 N sodium hydroxide and 1.6 mL of 30% hydrogen peroxide. The reaction mixture was saturated with anhydrous potassium carbonate, and the layers were separated. The aqueous layer was extracted with ether/THF (1:1), and the ether extract was combined with the previous organic layer. The organic layer was washed with 1 N HCl solution and a brine solution and then dried on $MgSO_4$. Evaporation afforded 385 mg of the crude alcohol, which was purified by silica gel chromatography (30% EtOAc/CH_2Cl_2 eluent) to give 3α-hydroxy-5α-androstane-11,17-dione as white crystals (223 mg, 47%) with R_f = 0.35 (TLC on silica gel/30% EtOAc/CH_2Cl_2), mp 150–151 °C (lit.[60] mp 153–155 °C).

For silylation of the dione, a 25-mL round-bottom flask with a side arm capped by a rubber septum was equipped with a magnetic stir bar and a condenser with a nitrogen inlet tube. The apparatus was flame dried under dry nitrogen and charged with anhydrous TEA (0.3 mL), anhydrous DMF (3 mL), and the dione (249 mg, 0.818 mmol). Stirring was commenced under nitrogen atmosphere, and chlorodimethylphenylsilane (155 μL, 0.94 mmol) was syringed into the reaction mixture at 0 °C. The mixture was stirred for 2 h, at which time GLC analysis (column A at 260 °C) showed the complete disappearance of the alcohol. The mixture was then diluted with benzene (10 mL) and washed successively with 2 × 3 mL of cold sodium bicarbonate (5%), 3 mL of cold 1 N HCl, and once again 3 mL of cold sodium bicarbonate (5%). The organic layer was dried ($MgSO_4$) and evaporated to give 275 mg (76%) of crude 3α-DPS-5α-androstane-11,17-dione (**1**, 92% purity by GLC analysis on column A at 260 °C), which was purified by recrystallization from acetone/hexane twice to afford prisms (175 mg), mp 170–172 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57–7.37 (m, 5 H, arom), 4.00 (s, 3β-H), 2.6–1.2 (m, 20 H), 0.99 (s, 19-CH_3), 0.82 (s, 18-CH_3), 0.35 (s, $SiCH_3$), 0.34 (s, $SiCH_3$); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 218.18 (17-C=O), 209.64 (11-C=O), 139.34, 133.71, 129.71, 128.07, 67.45, 66.51, 65.26, 51.03, 50.80, 39.18, 36.47, 36.31, 35.59, 31.76, 31.32, 29.55, 27.96, 21.90, 15.00, 11.38, −0.56, −0.78; IR (Nujol) 1740 (17-C=O), 1708 (11-C=O), 1430, 1376, 1290, 1250, 1118, 1046, 1014, 996, 964, 890, 832, 786, 752, 706 cm^{-1}; MS *m/e* 423 (M − CH_3, 5), 137 (100). Anal. Calcd for $C_{27}H_{38}O_3Si$: C, 73.92; H, 8.73; Si, 6.40. Found: C, 74.08; H, 9.03; Si, 6.31.

3β-(Dimethylphenylsiloxy)androstane-11,17-dione (2). This compound was prepared from 5α-androstane-3,11,17-trione (475 mg) as described above for the preparation of **1**, except that a mixture of 3α- and 3β-hydroxyandrostane-11,17-dione was used as the starting material for silylation. The product was purified by chromatography on silica gel with 10% ethyl acetate in hexane to give pure 3α-DPS-5α-androstane-11,17-dione (**1**) as a white solid (370 mg) and a mixture of **1** and 3β-DPS-5α-androstane-11,17-dione (**2**), which was further chromatographed with 5% ethyl acetate in hexane to give pure 3β-DPS-5α-androstane-11,17-dione (**2**, 11 mg, white solid). Recrystallization from ether/hexane gave **2** as needles (4 mg), mp 150–152 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57–7.37 (m, 5 H, arom), 3.55 (m, 3α-H), 2.6–1.2 (m, 20 H), 1.01 (s, 19-CH_3), 0.80 (s, 18-CH_3), 0.37 (s, $Si(CH_3)_2$); IR (Nujol) 1742 (17-C=O), 1706 (11-C=O), 1430, 1376, 1255, 1120, 1054, 870, 826, 776, 746, 706 cm^{-1}; MS *m/e* EI 428 (M$^+$, 5), 423 (M − CH_3, 80), 360 (M − C_6H_6, 80), 137 (100); high-resolution MS (*m/e*) calcd 438.2590, found 438.2581.

3α-(Dimethylphenylsiloxy)androstan-17-one (3). Silylation of androsterone with chlorodimethylphenylsilane by a procedure similar to that utilized for **1** afforded **3** (71%) as white crystals, mp 108–109 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64–7.43 (m, 5 H, arom), 4.07 (s, 3β-H), 2.5–1.1 (m, 22 H), 0.91 (s, 19-CH_3), 0.82 (s, 18-CH_3), 0.40 (s, 6 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 221.49 (17-C=O), 138.95, 133.33, 132.90, 129.22, 127.60, 67.21, 54.24, 51.44, 47.76, 38.86, 36.31, 36.02, 35.80, 34.98, 32.25, 31.51, 30.79, 29.40, 28.17, 21.69, 19.97, 13.75, 11.30, −1.01, −1.17; IR (Nujol) 1734 (17-C=O), 1428, 1374, 1280–1250, 1118, 1060, 1040, 1014, 970, 960, 932, 888, 868, 830, 788, 742, 726, 702 cm^{-1}; MS *m/e* EI 409 (M − CH_3, 5), 137 (100). Anal. Calcd for $C_{27}H_{40}O_2Si$: C, 76.36; H, 9.49; Si, 6.61. Found: C, 76.49; H, 9.84; Si, 6.31.

Preparative Photolysis of 1 in MeCN/TEA. A degassed solution of acetonitrile (10 mL) containing 64.8 mg (14.8 mM) of **1** and TEA (50 μL, 36 mM) was irradiated in the Rayonet reactor equipped with 16 254-nm lamps at 30 °C for 18 min. Concentration in vacuo gave 67.5 mg of a residue which was chromatographed on silica gel with 30% EtOAc/CH_2Cl_2 as eluent. Three components were isolated from silica gel with 30% EtOAc/CH_2Cl_2 and analyzed by GLC: the recovered **1** (R_f = 0.92, 23 mg); crude 3α-DPS-17α-androstan-11-one (white solid, R_f = 0.67, 6.5 mg, 11%); and 3α-DPS-17β-hydroxy-5α-androstan-11-one (**4**) (white solid, R_f = 0.50, 21.4 mg, 51%), mp 46–48 °C. 3α-DPS-17β-hydroxy-5α-androstan-11-one (**4**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60–7.40 (m, 5 H, arom), 3.99 (m, 3β-H), 3.84 (m, 17α-H), 2.3–1.0 (m, 20 H), 0.97 (s, 19-CH_3), 0.68 (s, 18-CH_3), 0.34 (s, $SiCH_3$), 0.32 (s, $SiCH_3$); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 210.80, 140.05, 133.62, 129.52, 127.90, 80.32 (17C-OH), 67.41, 64.60, 54.96, 50.65, 47.32, 39.07, 37.53, 36.21, 35.87, 32.40, 31.23, 31.04, 29.44, 27.98, 23.02, 11.93, 11.36, −0.70, −0.93; IR (Nujol) 3400 (OH), 1702 (11-C=O), 1372, 1362, 1322, 1254, 1168, 1118, 1054, 1026, 1000, 960, 908, 888, 830, 784, 734, 702 cm^{-1}; MS *m/e* EI 425 (M − CH_3, 40), 137 (100); high-resolution FAB MS (*m/e*) calcd (M + 1) 441.2825, found 441.2831.

3α-(Dimethylphenylsiloxy)-17α-hydroxyandrostan-11-one. The crude product was purified by flash chromatography on silica gel with 10% EtOAc/CH_2Cl_2 to give 3 mg of 92% pure product by GLC on column A at 270 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57–7.37 (m, 5 H, arom), 4.00 (m, 3β-H), 3.76 (m, 17β-H), 2.3–1.0 (m, ca. 20 H), 0.99 (s, 19-CH_3), 0.63 (s, 18-CH_3), 0.36 (s, $SiCH_3$), 0.35 (s, $SiCH_3$); IR (Nujol) 3474 (OH), 1694 (11-C=O), 1378, 1262, 1164, 1116, 1070, 1054, 1042, 1028, 962, 908, 892, 854, 784, 738, 702 cm^{-1}; high-resolution FAB MS (*m/e*) calcd (M + 1) 441.2825, found 441.2842.

Compound **4** and its 17α isomer were independently synthesized by thermal reduction of **1**. To a solution of 128 mg (0.29 mmol) of **1** in 15 mL of ethanol was added 11.5 mg (0.30 mmol) of $NaBH_4$ at room temperature. After the mixture was stirred for 1 h, neutral workup gave 125 mg of a white solid. Chromatography on silica gel with 25% EtOAc/hexane gave 77 mg (61%) of **4** as white crystals, mp 46–48 °C, and 6 mg (5%) of 17α isomer as a white solid. The spectral data were identical to those obtained for the photoproducts.

Preparative Photolysis of 1 in Cyclohexane. A degassed solution of 3α-DPS-5α-androstane-11,17-dione (**1**, 45.6 mg, 10.4 mM) in cyclohexane (10 mL) was irradiated at 33 °C for 1.5 h in the Rayonet reactor equipped with 16 254-nm lamps. GLC analysis showed 37% loss of **1** and only one photoproduct at 13.45 min (column A at 270 °C). Concentration in vacuo gave 47 mg of a residue which was chromatographed on silica gel with 10% EtOAc/hexane to afford 8.5 mg of recovered **1** and 7.5 mg (44%) of the epimer, 3α-DPS-5α,13α-androstane-11,17-dione (**5**) as a white solid. 3α-DPS-5α,13α-androstane-11,17-dione (**5**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57–7.37 (m, 5 H, arom), 3.99 (m, 3β-H), 2.6–1.2 (m, 20 H), 1.07 (s, 18-CH_3), 0.81 (s, 19-CH_3), 0.34 (s, $SiCH_3$), 0.33 (s, $SiCH_3$); IR (Nujol) 1736 (17-C=O), 1710 (11-C=O), 1376, 1250, 1156, 1116, 1080, 1050, 986, 964, 890, 834, 788, 750, 736, 708 cm^{-1}; MS *m/e* 423 (M − CH_3, 5), 137 (100); high-resolution FAB MS (*m/e*) calcd (M + 1) 439.2669, found 439.2674.

Preparative Photolysis of 3α-(Dimethylphenylsiloxy)androstan-17-one (3) in MeCN/TEA. A degassed solution of acetonitrile (10 mL) containing 60.0 mg (14.1 mM) of **3** and TEA (50 μL, 36 mM) was irradiated through quartz in the Rayonet reactor equipped with 16 254-nm lamps at 30 °C for 15 min. GLC analysis of the photolysate (column A at 270 °C) showed a 63% loss of **3** and two major products at 9.92 and 11.69 min, respectively (GLC peak area ratio of 1:4.2). Chromatography of the reaction mixture on silica gel with 10% EtOAc/CH_2Cl_2 gave 3α-DPS-5α-androstan-17β-ol (**6**) as a white solid (17.5 mg, 38%), mp 58–59 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62–7.41 (m, 5 H, arom), 4.04 (m, 3β-H), 3.67 (t, *J* = 8.4 Hz, 17α-H), 2.3–0.9 (m, ca. 22 H), 0.78 (s, 19-CH_3), 0.76 (s, 18-CH_3), 0.38 (s, 6 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 133.67, 133.23, 129.51, 127.93, 82.25 (17C-OH), 67.66 (3C-OSi), 54.60, 51.34, 43.24, 39.24, 37.03, 36.69, 36.28, 35.80, 32.65, 31.85, 30.76, 29.78, 28.68, 23.63, 20.62, 11.66, 11.40, −0.67, −0.82; IR (Nujol) 3376 (OH), 1374, 1338, 1280, 1250, 1164, 1118, 1046, 1026, 970, 954, 938, 916, 890, 868, 830, 784, 740, 700 cm^{-1}; MS *m/e* EI 411 (M − CH_3, 25), 137 (100); high-resolution FAB MS (*m/e*) calcd (M + 1) 427.3032, found 427.3053. The second product, epimer **7**, could not

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be isolated in sufficient quantities from this photolysis.

Compound **6** was independently synthesized by reduction of 130 mg (0.31 mmol) of **3** in ethanol with $NaBH_4$ (19 mg, 0.50 mmol) at room temperature to give 104 mg (80%) of **6** as a white solid (97% purity by GLC on column A at 270 °C). The product was purified by recrystallization from acetone/hexane to afford 71 mg of white crystals (mp 58-59 °C). Its spectroscopic data were identical with those of the photoproduct.

Preparative Photolysis of 3α-(Dimethylphenylsiloxy)androstan-17-one (3) in Acetonitrile without TEA. A degassed solution of **3** (61.5 mg, 14.5 mM) in acetonitrile (10 mL) was irradiated as described above at 33 °C for 40 min. Chromatography of the reaction mixture on silica gel with 10% EtOAc/hexane afforded the epimer, 3α-DPS-5α,13α-androstan-17-one (**7**) as a white solid (7.6 mg, 18%) and the aldehyde **8** (5.2 mg, 12%). Spectral data for 3α-DPS-5α,13α-androstan-17-one (**7**): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58-7.37 (m, 5 H, arom), 4.00 (m, 3β-H), 2.3-1.0 (m, 22 H), 0.97 (s, 18-CH_3), 0.57 (s, 19-CH_3), 0.34 (s, $SiCH_3$); ^{13}C NMR ($CDCl_3$, 151.2 MHz) δ 222.74, 139.03, 133.39, 129.26, 127.64, 67.27 (3C-OSi), 51.48, 50.86, 50.17, 38.38, 37.78, 36.24, 36.03, 33.92, 32.94, 32.22, 32.06, 29.34, 28.39, 25.32, 22.24, 21.26, 11.07, -0.95, -1.00; IR (KBr) 1738 (C=O), 1374, 1249, 1163, 1122, 1078, 1048, 1014, 987, 961, 941, 921, 877, 865, 839, 818, 784, 744, 725 cm^{-1}; MS *m/e* EI 409 (M - CH_3, 57), 137 (100); high-resolution FAB MS (*m/e*) calcd (M + 1) 425.2866, found 425.2876.

Spectral data for 3α-DPS-13,17-seco-5α-androst-13-en-17-al (**8**): ^1H NMR ($CDCl_3$, 300 MHz) δ 9.76 (s, HC=O), 7.57-7.37 (m, 5 H, arom), 4.02 (m, 3β-H), 1.55 (s, 18-CH_3), 0.68 (s, 19-CH_3), 0.34 (s, $SiCH_3$), 0.33 (s, $SiCH_3$).

A mixture of **7**, **8**, and **9** obtained from the photolysis of **3** (10 mg) in isopropyl alcohol was subjected to GLC/MS: for **7**, MS *m/e* EI M^+ = 424; for **8**, M^+ = 424; and for 2-propyl 3α-DPS-13,17-seco-5α-androstan-17-oate (**9**), M^+ = 484.

Experiments with Cyclohexanone. Degassed solutions of **3** (15 mM) in iPrOH (1 mL) saturated by $NaHCO_3$ were irradiated in the Rayonet reactor by 8 254-nm lamps at room temperature for 6 min in the absence and presence of cyclohexanone (10.2-30.6 mM). The solutions were analyzed by GLC (column A at 270 °C) with an internal standard (3β-DPS-5α-androstan-17-one) to monitor **3**, while cyclohexanone and cyclohexanol were analyzed on the same column using a gradient temperature program starting from 50 °C.

Quenching by *cis*-1,3-Pentadiene. Compounds **1** and **3** (17 mM) were photolyzed in the presence and absence of *cis*-1,3-pentadiene (59 and 119 mM) in CH_3CN with 32.3 and 59.2 mM TEA for **1** and **3**, respectively. Irradiations were with the Nd:YAG laser. The formation of **4-7** was assayed by GLC on column A at 270 °C with 3β-DPS-5α-androstan-17-one as an internal standard. In a separate experiment, **1** (16.2 mM) and the diene (0-180 mM) were irradiated in CH_3CN with the 16 254-nm lamps in the Rayonet reactor for 65 min. The reactions were analyzed by GLC on column B (245 °C) using 3α-DPS-5α-androstan-17-one as an internal standard. The data were corrected for absorption by the diene at 254 nm (ϵ_{254} = 15 M^{-1} cm^{-1}).

Quantum Efficiency Determinations. For laser studies, a Vycor cuvette containing 2 mL of argon-degassed sample solution (ca. 15-17 mM) was placed in a sample holder. The solution was irradiated with either the 266- or 308-nm laser beam for 4-16 min (varying from sample to sample). The photolysate was analyzed by GLC on column A (at 270 °C) with 3β-DPS-5α-androstan-17β-ol (prepared by silylation of epiandrosterone with DPSCl as described for the preparation of **3**) as the internal standard. The quantum efficiencies for epimerization of **1** and **3** (both 15 mM) in CH_3CN were determined by photolysis in the Rayonet reactor equipped with 16 254-nm lamps for 60 and 10 min, respectively. The formation of **5** and **7** was quantitated by GLC on colum B at 250 °C with 3β-DPS-5α-androstan-17-one as an internal standard. Actinometry was performed using the *E*/*Z* isomerization of (*E*)-1-phenyl-2-butene, for which the quantum efficiency of isomerization has been determined to be 0.20.[61] The hexane solution of (*E*)-1-phenyl-2-butene was irradiated for 4 min, and the amount of *Z* isomer was determined by GLC on column A at 80 °C. The conversion to *Z* isomer was corrected for back reaction. The quantum efficiency studies in the presence of *cis*-1,3-pentadiene were determined in analogous fashion with the data for **1** and **3** plotted in Figures 1 and 2, respectively.

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Enantioselective Complexation of Organic Ammonium Ions by Simple Tetracyclic Podand Ionophores

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Abstract: A series of enantiomerically pure, C_2-symmetric tetracyclic podands are synthesized and studied. These host molecules have methyl substitution, which allows only a few low-energy conformations, and they form well-defined complexes with chiral ammonium salts. With derivatives of α-phenethylammonium hexafluorophosphate as guests, binding enantioselectivity ranges from ~0 to 60% ee. X-ray structures of several podand/chiral ammonium perchlorate complexes are described along with a conformational analysis of the podands and their complexes.

Large rings are among the most characteristic structural features of synthetic host molecules. This is not surprising given comparisons of the binding properties of notable receptors and their acyclic analogues. In the case of pentaglyme dimethyl ether (**1**) versus 18-crown-6 (**2**), macrocyclic **2** binds *tert*-butylammonium ion 10^4 times more tightly than does **1**.[1] The case of spherand **4** is even more dramatic, with the macrocyclic **4** binding lithium and sodium 10^{12} and 10^{10} times more effectively than does **3** (Figure 1).[2] As Cram has pointed out, the function of the macrocyclic linkage is to *preorganize* the ligand to favor its binding conformation, a conformation which may be disfavored both entropically and enthalpically in the corresponding acyclic receptor or *podand*.[3]

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