Steroids as Molecular Photonic Wires. $Z \rightarrow E$ Olefin Photoisomerization by Intramolecular Triplet−Triplet Energy Transfer with and without Intervening Olefinic Gates[1]

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Received March 16, 1998

Abstract: The steroids 3β-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5α-androstane (**1**), 3β-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5-androstene (**2**), 3β-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-6-methylene-5α-androstane (**3a**), and 3α-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-6-methylene-5α-androstane (**3b**) have been prepared. The triplet−triplet excited-state energy transfer (TTET) that occurs from the C3 aryl "donor" group to the C17 ethylidene "acceptor" has been studied in detail at 10 mM steroid concentration. Irradiation with 266 nm light results in $Z \rightarrow E$ olefin isomerization of the C17 ethylidene group, a consequence of both intra- and interTTET. $\Phi_{Z \rightarrow E} = 0.037$, 0.018, 0.028, and 0.004 for **1**, **2**, **3a**, and **3b**, respectively. Detailed kinetic analyses of these compounds and appropriate models, with and without added olefin quenchers, provide a complete set of rate constants which are determined relative to an assumed energy transfer rate constant to piperylene of 7.0×10^9 M^{-1} s^{-1}. In particular, $k_{\text{intraTTET}}$ for **1** = [1.7 (±0.7)] $\times 10^6$ s^{-1}. Isomerization at C17 in **2**, due to intraTTET, is reduced (83% vs **1)** but not completely eliminated by the endocyclic alkene in ring B, which functions as a "triplet gate". The exocyclic methylene group in **3b** is more efficient in gating the intraTTET than it is in **3a** ($\Phi_{\text{TTET}} = 0.08$ vs 0.71, respectively). This higher level of gating that occurs in **3b** is attributed to a much shorter lifetime of the axial DPSO triplet, caused by an efficient through-space intraTTET from the axial DPSO group to the C6 exocyclic olefin.

Introduction

The study of molecular dimension "photonic wires" has continued to receive significant attention.[2] As part of our ongoing efforts in exploring the photoinitiated activation of functional groups distal from "antenna" chormophores, we have been elaborating the capability of the steroid framework to act as a photonic wire through which excitation energy can migrate.[3] We have used the 5α-androstane[4] and 5β-androstane[5] skeletons to mount various functionalities that fulfill specific electronic functions, with the intent of developing an understanding of how different stereoelectronic and functional group modifications affect the energy transfer process. These groups include an *antenna* to absorb incident radiation, multiplicity *switches* that convert singlet energy to triplet energy, *gates* and *relays* that impede or facilitate energy migration, and an *acceptor* which is the ultimate site of chemical reaction. The energy transmission in these systems occurs, at least in part, by a through-bond interaction (TBI) and, hence, the steroid framework serves as a "photonic wire". Others have used steroids in a similar way. Recent examples include a series of studies of long-distance energy transfer to a norbornadiene acceptor via a TBI exchange mechanism in several steroids.[6] With androst-5-ene as the spacer and the benzophenone and norbornadiene moieties attached to C17 and C3, respectively, the authors observed photoisomerization of the norbornadiene group upon excitation of the remote benzophenone chromophore with a rate constant for triplet−triplet energy transfer of 1.5×10^5 s^{-1} and a quantum efficiency of 22%.[6b,7]

In our laboratories, we have used the (dimethylphenylsilyl)-oxy (DPSO) group as the antenna, due to its favorable properties which, as outlined earlier,[8a] include a relatively short (ca. 1 ns) excited-state singlet lifetime to minimize intermolecular

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(7) Other frameworks have also been shown to be capable of energy transfer via TBI. Some of these include bicyclo[2.2.1]heptanes, bicyclo-[2.2.2]octanes, oligo[1.1.1]propellanes, polyenes, polyynes, polyphenylenes, oligothiophenes, polypeptides, polyethers, and block polymers. See citation 5 in ref 3a.

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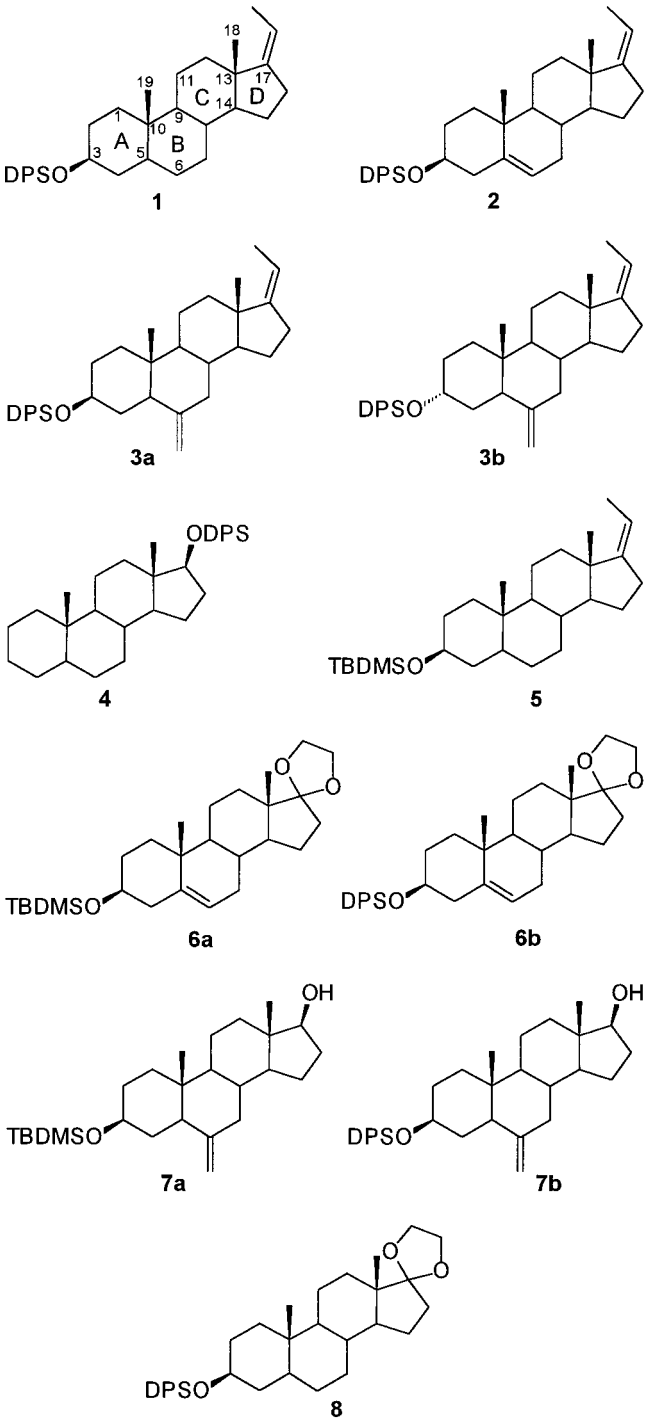
10.1021/ja9808595 CCC: $18.00
Published on Web 04/02/1999

processes.[8b] Ketones have served as the recipients of intramolecular singlet−singlet and triplet−triplet energy transfer (intraSSET and intraTTET, respectively), whereas olefins have been used to probe intraTTET exclusively.[3,4] These studies demonstrated the use of intervening ketone groups as "*singlet−triplet switches*" in the steroidal photonic wires.[3,4] Thus, we have reported that in the molecule 3α-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5α-androstane (3αDPSO/17*Z*), excitation of the DPSO antenna leads to triplet photochemistry at the distal C17 ethylidene ($Z \rightarrow E$ photoisomerization) with a quantum yield of $\Phi_{Z\rightarrow E} = 0.043$.[3a] Insertion of a ketone at C6 in 3α-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5α-androstan-6-one (3αDPSO/6/17Z) improved the quantum yield of isomerization almost 10-fold to $\Phi_{Z\rightarrow E} = 0.36$ upon DPSO excitation. It was shown that the quantum efficiency of intraSSET from 3αDPSO to the C6 ketone is ca. 90%, so that the greater efficiency of olefin isomerization requires that a significant portion (91%) of the singlet energy transferred to C6 is switched to triplet energy before ultimate transfer to C17 (82%; $k = 8.3 \times 10^8$ s^{-1}).

Most of our previous steroid studies have involved the use of the DPSO antenna as a singlet energy donor. However, as noted above, relatively inefficient olefin isomerization was indeed observed in the nonketonic compound 3αDPSO/17*Z*. Though this chemistry must be a consequence of TTET from the DPSO group to the remote olefin, the details of the process were not examined in depth. In particular, the antenna would now be operating as a donor through its relatively long-lived triplet state, thus creating the potential for a duality of intra- and intermolecular TTET processes. We thus report a detailed study of the DPSO triplet-sensitized olefin isomerization of the 17-(*Z*)-ethylidene group in 3*β*-DPSO-17-(*Z*)-ethylidene-5α-androstane (**1**; Chart 1).

This paper also explores the efficiency through which intervening olefins may function as triplet energy *gates* to modify TBI intraTTET. To this end, we have placed both endocyclic and exocyclic olefins on the B-ring of the steroid nucleus through the synthesis of 3*β*-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5-androstene (**2**), 3*β*-((dimethylphenylsilyl)-oxy)-17-(*Z*)-ethylidene-6-methylene-5α-androstane (**3a**), and 3α-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-6-methylene-5α-androstane (**3b**). The model compounds 17*β*-((dimethylphenylsilyl)oxy)-5α-androstane (**4**), 3*β*-((*tert*-butyldimethylsilyl)oxy)-17-(*Z*)-ethylidene-5α-androstane (**5**), 3*β*-((*tert*-butyldimethylsilyl)oxy)-17-(ethylenedioxy)-5-androstene (**6a**), 3*β*-((dimethylphenylsilyl)oxy)-17-(ethylenedioxy)-5-androstene (**6b**), 3*β*-((*tert*-butyldimethylsilyl)oxy)-6-methylene-5α-androstan-17*β*-ol (**7a**), 3*β*-((dimethylphenylsilyl)oxy)-6-methylene-5α-androstane-17*β*-ol (**7b**), and 3*β*-((dimethylphenylsilyl)oxy)-17-ethylenedioxy-5α-androstane (**8**) have been prepared and will also be discussed.

Chart 1



Results

Synthesis of Target Compounds 1, 2, 3a, and 3b. The C-17 monoolefin **1** was prepared via a Wittig reaction of epiandrosterone followed by silylation with chlorodimethylphenylsilane. The material was formed predominantly as the *Z* isomer, based on literature precedent.[9] Compound **2** was prepared in like manner from dehydroisoandrosterone, giving predominantly the *Z* isomer.[10] Compound **3a** was prepared in eight steps as outlined in Scheme 1. Testosterone acetate was brominated with NBS followed by hydrolysis in HCl/methanol to produce 17*β*-hydroxy-5α-androstan-3,6-dione, as described earlier.[11] This material was treated with 2-ethyl-2-methyl-1,3-dioxolane at reflux for 5 min to selectively form the 3-ketal in 42% isolated yield.[12] The 3-(ethylenedioxy)-17*β*-hydroxy-5α-androstan-6-one was treated with the ylide of methyltriphenylphosphonium bromide in THF to form the 6-methylene compound.[13] The

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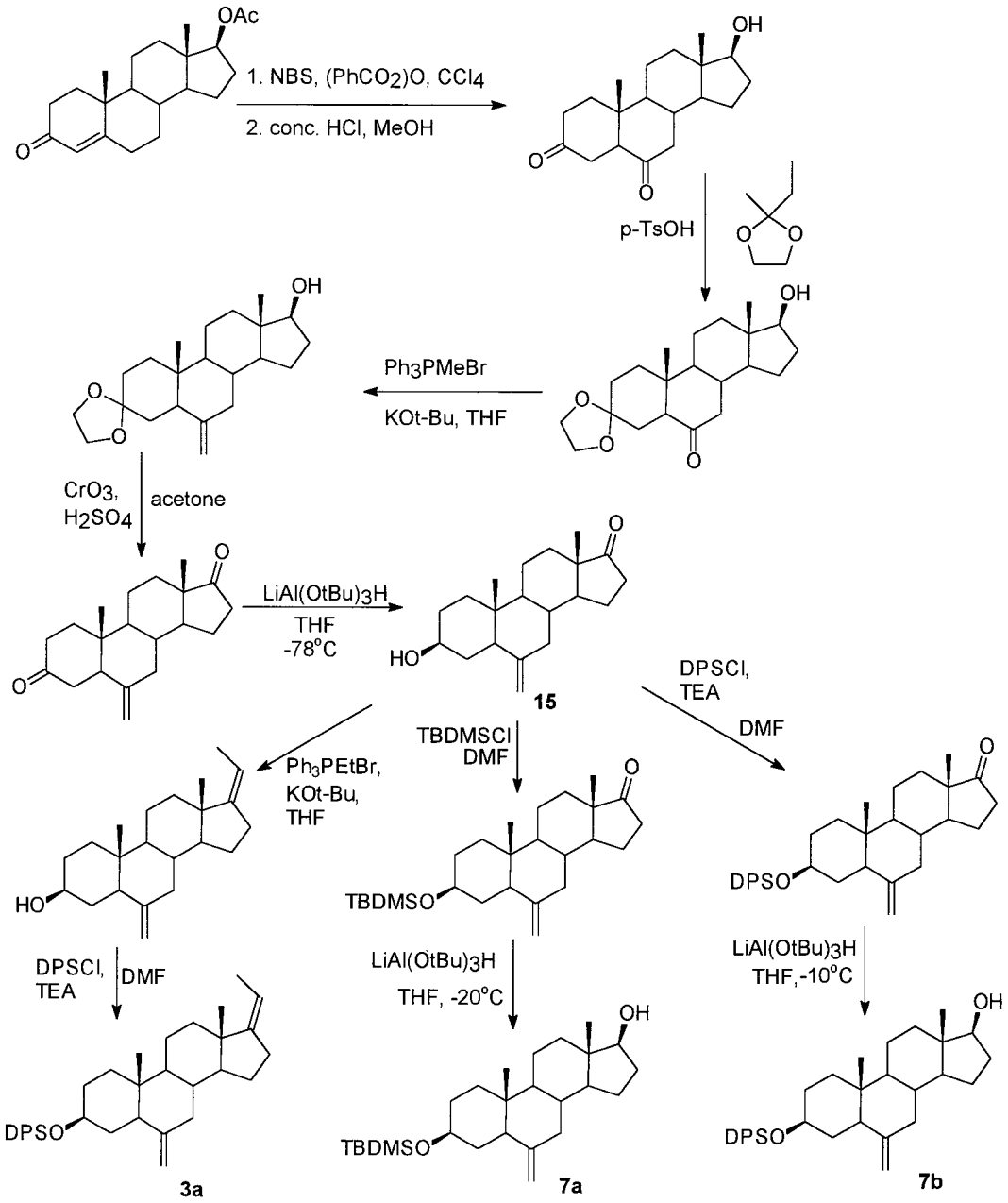
Scheme 1



3-ketal was cleaved and the 17-alcohol was oxidized to the ketone in a single step by the use of the Jones reagent.[14] This material (6-methylene-5α-androstane-3,17-dione) had properties identical with those described in the literature.[15] We found that reduction of the C17 ketone can be suppressed at low temperatures so that treatment with lithium tri-*tert*-butoxyaluminohydride at −78 °C allowed stereoselective reduction of the 3-ketone[16] to give compound **15**. A Wittig reaction of **15**, followed by reaction with chlorodimethylphenylsilane, gave the target compound **3a**.

Compound **3b** was synthesized in three steps from 3α-hydroxy-5α-androstan-6,17-dione[4d] by first conducting a Wittig reaction with methyltriphenylphosphonium bromide at −40 °C, forming 3α-hydroxy-6-methylene-5α-androstan-17-one. This material was reacted with the ylide of ethyltriphenylphosphonium bromide as described above, and the product was silylated with chlorodimethylphenylsilane to give **3b**.

Synthesis of Model Compounds for Kinetic Studies. Compound **4** was prepared from the parent alcohol and chlorodimethylphenylsilane. **5** was prepared from 3*β*-hydroxy-17-(*Z*)-ethylidene-5α-androstane (prepared as described above) and *tert*-butyldimethylsilyl chloride (TBDMS chloride). To prepare compound **6a**, dehydroisoandrosterone was treated with 2-ethyl-2-methyl-1,3-dioxolane to form the 17-ketal,[17] followed by treatment with TBDMS chloride. Treatment of the same ketal with chlorodimethylphenylsilane gave **6b**. Compound **7a** was prepared from **15** (Scheme 1) by silylation with TBDMS chloride, followed by reduction of the C17 ketone with lithium tri-*tert*-butoxyaluminohydride at −20 °C. Compound **7b** was prepared from **15** (Scheme 1) by reaction with chlorodimethyl-

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Table 1. Fluorescence Quantum Yields and Phosphorescence Area Percentages for 1-4[a]

	ϕ_f ($\times 10^{-2}$)[b]	% phos[c]		ϕ_f ($\times 10^{-2}$)[b]	% phos[c]
1	1.2	23	**3b**	1.1	0
2	1.2	0	**4**	1.3	66
3a	1.2	0			

[a] Using 254 nm excitation in cyclohexane. [b] Measured using toluene as the reference ($\phi_f = 0.14$) in cyclohexane at room temperature.[20] Accuracy is estimated at 10%. [c] Measured in a methylcyclohexane glass at 77 K. Values are the integrated area of the phosphorescence emission relative to the area of the total emission; all data are corrected for photomultiplier response.

phenylsilane, followed by reduction of the C17 ketone with tri-*tert*-butoxyaluminohydride at −10 °C. **8** was prepared by ketalization of epiandrosterone[18] followed by reaction with chlorodimethylphenylsilane. The stereochemistry of all C3 and C17 alcohols described above is easily assigned on the basis of ^{1}H NMR analysis (see Experimental Section).[19]

Spectroscopy. Absorption Spectra. UV absorption spectra of **1**−**4** and **8** show the typical $\pi-\pi^*$ aryl transition with λ_{max} 258 nm. The presence of the unconjugated Δ^5 or 6-methylene olefins had no significant affect on the intensity or wavelength of the aryl absorption, indicating that the aryl $\pi-\pi^*$ transition is not perturbed by the olefins and that no notable ground-state interactions exist between these chromophores.

Fluorescence Quantum Yields and Singlet Lifetimes. The room-temperature fluorescence emission spectra of **1**−**4** were obtained in cyclohexane with 254-nm excitation. Each consists of a featureless band from 265 to 340 nm with λ_{max} at 280 nm. The fluorescence quantum yields are shown in Table 1 and are identical within experimental error, indicating that the olefinic groups have no affect on the DPSO singlet state. Additionally, the singlet lifetimes for **4** and a C3-DPSO model (3α-DPSO-17-(*Z*)-ethylidene-5α-androstane)[3] were determined to be 2.5 and 2.6 ns, respectively.

Fluorescence Emission of 1 with Added *cis*-2-Heptene Quencher. The fluorescence emission of a 5.7×10^{-4} M cyclohexane solution of **1** was obtained using 254 nm excitation with and without 75 mM *cis*-2-heptene. The integrated fluorescence areas were 215 and 214 area units, respectively, indicating that there is no interaction of the 2-heptene at this concentration with the DPSO singlet state.

Fluorescence Emission of 1 with Added *cis*-Piperylene. The fluorescence emission of **1** was determined with and without 1 mM piperylene. The integrated emission areas were virtually identical, indicating that piperylene at this concentration does not interact with the DPSO singlet state.

Total Emission at 77 K in a Methylcyclohexane Glass. The total emission spectra elicited by 254 nm excitation for compounds **1**−**4** are shown in Figure 1 (see also Table 1). The DPSO phosphorescence emission is evident for compounds **1** and **4** at 345−485 nm, with that for **1** being diminished relative to the model **4**. No phosphorescence emission is visible in any of the B-ring olefin compounds. These findings are consistent with intraTTET occurring in **1**, **2**, **3a**, and **3b**. The total emission spectrum of a 3β-DPSO steroid, 3β-((dimethylphenylsilyl)oxy)-5α-androstane, was found to be identical with that for **4**.

The 0−0 transition energy for the DPSO $S_0 \rightarrow S_1$ transition is estimated from the fluorescence onset at 270 nm to be $E_S =$ 106 kcal/mol. The DPSO triplet energy, as estimated from the onset of the phosphorescence emission at 348 nm, is $E_T = 82$ kcal/mol.

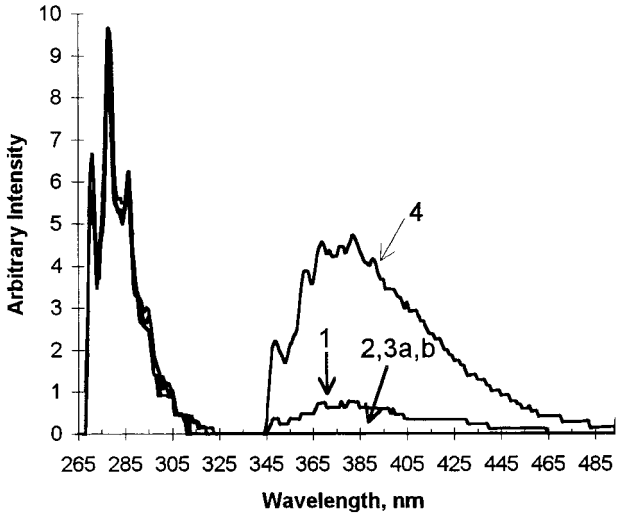
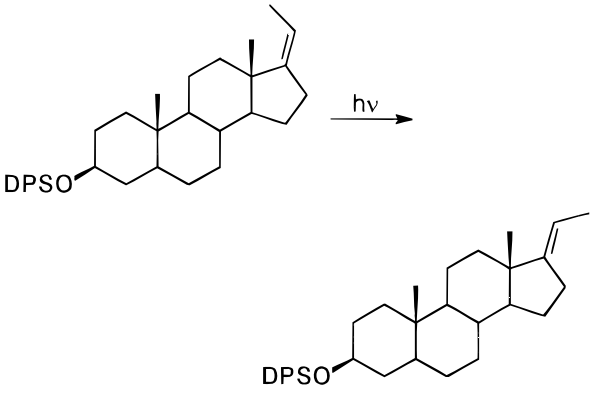


Figure 1. Total emission spectra in a methylcyclohexane glass at 77 K.

Total Emission of 4 with Added 5 Quencher. The total emission spectrum of a 1.4×10^{-3} M solution of **4** in a methylcyclohexane glass was obtained in the presence and absence of added equimolar amounts of **5**. The phosphorescence emission constituted 63% and 65% of the total emission area with and without the added steroid olefin, respectively. This supports our conclusion that energy transfer in **1**, **2**, **3a**, and **3b** is completely intramolecular in the methylcyclohexane glass at 77 K.

Photochemistry. Irradiation of 1, **2**, **3a**, and **3b.** Separate irradiations of 2.0 mL of argon-degassed 1.0×10^{-2} M cyclohexane solutions of **1**, **2**, and **3a** using the 266 nm line of a Nd:YAG laser (30 mW power) produced major photoproducts with GC retention times identical with the small amounts of *E* isomers formed during the synthesis of these substrates (eq 1).



(1)

For **3b** similar results were obtained using 2.0 mL of argon-degassed 6.1×10^{-3} cyclohexane solutions. In one case, that of compound **1**, the *E* isomer was independently synthesized by irradiation of 3β-hydroxy-17-(*Z*)-ethylidene-5α-androstane at 254 nm in cyclohexane with toluene ($E_T = 83$ kcal/mol)[20] as the sensitizer. The photolyzate was isolated and then treated with chlorodimethylphenylsilane to give a product as two separate peaks in the GC with retention times identical with those described for the irradiation of **1** directly. The identifica-

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Table 2. Irradiation of Target Molecules with Various Concentrations of *cis*-2-Heptene

	$1/\Phi^{hept}_{Z\rightarrow E}$ vs 1/[heptene] reciprocal plot data			Stern−Volmer plot of C17 isomerizn	
steroid[a]	slope (M)	intercept	R^2	$k_q\tau$ (M^{-1})	R^2
4	0.051 ± 0.005	23.4 ± 1.3	0.97		
1	0.564 ± 0.004	25.4 ± 1.2	0.99	45 ± 2	0.99
2				23 ± 1	0.99
3a				36 ± 3	0.99

[a] Steroid concentration 10 mM, ca. 3.0 mL. Irradiation times were as follows: **4**, 25 min; **1**, 15 min; **2**, 30 min; **3a**, 20 min.

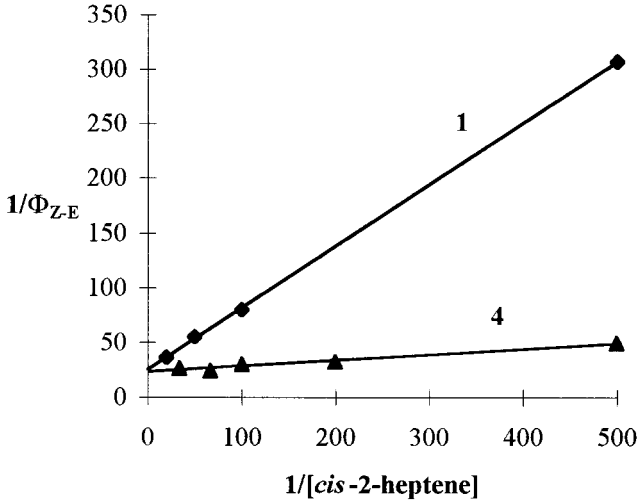

Figure 2. Reciprocal plots of isomerization of *cis*-2-heptene using **1** and **4** as sensitizers.

tion of the photoproducts of the other compounds as the *E* isomers is by analogy with the above data and with the knowledge that the characteristic reaction of the olefins with triplet donors is geometrical isomerization.[3a] For the irradiation of **1**, **2**, **3a**, and **3b**, the quantum yields of isomerization are $\Phi_{Z\rightarrow E} = 0.037 \pm 0.001$, 0.018 ± 0.002, 0.028 ± 0.002, and 0.0035 ± 0.0006, respectively.

Irradiation of 1, 2, 3a and 4 with *cis*-2-Heptene. Irradiation of 3.0 mL of a 1.0×10^{-2} M solution of **1** (argon degassed) in separate quartz tubes containing various amounts of *cis*-2-heptene was conducted in the Rayonet reactor using 4 × 254 nm lamps for 15 min. The flux was determined by using (*E*)-1-phenyl-2-butene actinometry.[21,22] The amount of *E* isomer of **1** formed was determined, and the data were analyzed by using the Stern−Volmer treatment. A plot of Φ_0/Φ vs [heptene] was linear (Table 2) with $k_q\tau = 45 \pm 2$ M^{-1}. Irradiations of **2** and **3a** were conducted in the same manner to give linear Stern−Volmer plots with the data summarized in Table 2. All results are reported with standard deviations obtained from linear regression analysis.

The amount of *trans*-2-heptene formed during the irradiation of **1** was also determined. A plot of $1/\Phi^{hept}_{Z\rightarrow E}$ *vs.* 1/[heptene] was linear, as shown in Figure 2. All reciprocal plot data are summarized in Table 2.

Five quartz tubes containing 2.7 mL of a 1.0×10^{-2} M solution of **4** (argon degassed) with various concentrations of *cis*-2-heptene (2.0×10^{-3} to 3.0×10^{-2} M) were irradiated in the Rayonet reactor using 4 × 254 nm lamps for 25 min. The flux was determined by using (*E*)-1-phenyl-2-butene actinometry.[21,22] GC analysis was used to determine the amount of *trans*-2-heptene formed, and a plot of $1/\Phi^{hept}_{Z\rightarrow E}$ vs 1/[heptene] was linear (Figure 2, Table 2).

Irradiation of 4 and 8 with *cis*-2-Heptene and Various Olefin Quenchers. Several quartz tubes containing 3.0 mL of a 1.0×10^{-2} M solution of **8** (argon degassed, cyclohexane), 5.0×10^{-3} M *cis*-2-heptene, and various concentrations of **5** as the quencher (0−15 mM) were irradiated in the Rayonet reactor using 4 × 254 nm lamps for 15 min. GC analysis was used to determine the amount of *trans*-2-heptene formed, and the data were analyzed by using the Stern−Volmer treatment. A plot of Φ_0/Φ vs [**5**] gave a straight line (Table 3) with $k_q\tau = 221 \pm 11$ M^{-1}, where k_q is actually the intermolecular rate constant for TTET from 3β-DPSO to the C17 olefin, $k_{inter17}$, and τ_{DPSO-H} is the lifetime of the 3β-DPSO group in the presence of 5 mM *cis*-2-heptene.

By similar treatment, quenching of the **4**-sensitized *cis*-2-heptene isomerization with **6a** and **7a** as quenchers gave $k_q\tau_{DPSO-H}$ values of 42 ± 4 and 47 ± 2 M^{-1}, respectively (Table 3). Here, τ_{DPSO-H} represents the lifetime of the 17β-DPSO group in the presence of 5 mM *cis*-2-heptene.

Irradiation of 6b and 7b with *cis*-2-Heptene Using 5 as the Quencher. Using the same procedure as described above, **6b** and **7b** were used as sensitizers of *cis*-2-heptene isomerization using **5** as the quencher. The slopes of the Stern−Volmer plots for **6b** and **7b** gave $k_{inter17}\tau_{DPSO-5-H} = 50 \pm 3$ M^{-1} and $k_{inter17}\tau_{DPSO-6-H} = 123 \pm 4$ M^{-1}, respectively. In these plots, $\tau_{DPSO-n-H}$ is the lifetime of the given 3β-DPSO group in the presence of either the C5 or C6 olefin, respectively (Table 3).

Irradiation of 1 with *cis*-Piperylene Quencher. Several tubes containing 3.0 mL of a 1.0×10^{-2} M solution of **1** (argon degassed, cyclohexane) with *cis*-piperylene as the quencher (1.0×10^{-4} to 2.0×10^{-3} M) were irradiated in the Rayonet reactor using 4 × 254 nm lamps for 20 min. GC analysis was used to determine the amount of steroid C17 *E* isomer formed, and the data were analyzed by using the Stern−Volmer treatment. A plot of Φ_0/Φ vs [piperylene] was linear (Figure 3) with $k_q\tau = 744 \pm 13$ M^{-1}, where k_q here is the intermolecular rate constant for TTET from DPSO to piperylene, k_{interP}, which is the fastest rate constant determined in this study.

Irradiation of 1 at Various Concentrations. Cyclohexane solutions of **1** ranging in concentration from 9.8×10^{-2} to 1.0×10^{-4} M were irradiated in the Rayonet reactor using 4 × 254 nm lamps for 30 min. The amount of isomerized olefin was measured by GC and was corrected for the fraction of light absorbed. The results are shown in Figure 4 and show a concentration dependence until ca. 1 mM steroid is reached.

Quantum Yields for Photosensitization of *cis*-2-Heptene Isomerization Using Different DPSO Models. The quantum yields for the sensitized isomerization of 12.5 M *cis*-2-heptene by 6.3 mM **4** and of 6.6 mM *cis*-2-heptene by 4.9 mM 3β-DPSO-5α-androstane, in cyclohexane, were determined at 266

Table 3. Quenching of *cis*-2-Heptene Isomerization Using Various Model Compounds as Sensitizers and Quenchers

sensitizer	quencher	$k_q\tau_{DPSO-H}$ (M^{-1})	R^2
4	**6a**	42 ± 4	0.97
4	**7a**	47 ± 2	0.99
8	**5**	221 ± 11	0.98
6b	**5**	50 ± 3[a]	0.99
7b	**5**	123 ± 4[b]	0.99

[a] $k_q\tau_{DPSO-5-H}$. [b] $k_q\tau_{DPSO-6-H}$; see text.

(21) For (*E*)-1-phenyl-2-butene, $\Phi_{E\rightarrow Z} = 0.20$: Morrison, H.; Peiffer, R. *J. Am. Chem. Soc.* **1968**, *90*, 3428.

(22) All olefin quantum yields are corrected for back-reaction, which takes into account the small amount of product isomer initially present. See: Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129. Palensky, F. J. Ph.D. Thesis, Purdue University, May 1977. See also: Saltiel, J.; Marinari, A.; Chang, D. W.-L.; Mitchener, J. C.; Megarity, E. D. *J. Am. Chem. Soc.* **1979**, *101*, 2982.

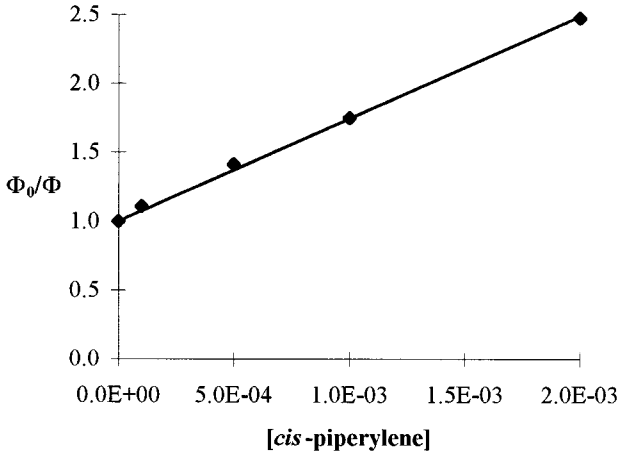

Figure 3. Stern−Volmer plot for quenching of C17 ethylidene isomerization in **1** using *cis*-piperylene as quencher.

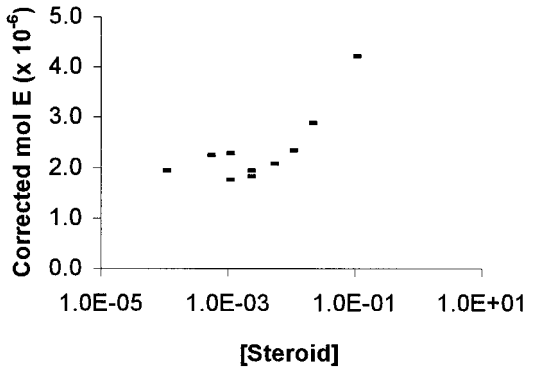

Figure 4. Irradiation of **1** at various concentrations (*y* axis normalized to photons absorbed).

nm by using the Nd:YAG laser at 30 mW power. The results were $\Phi_{Z\rightarrow E} = 3.34 \times 10^{-2}$ and 3.45×10^{-2} for the two sensitizers, respectively. Additionally, 5 mM *cis*-2-heptene was irradiated in cyclohexane (254 nm) using 10 mM **4** or 10 mM **8** as sensitizers. The amount of *trans*-2-heptene formed was 12.5% and 11.7% for **4** and **8**, respectively.

Discussion

Photochemistry. As with our earlier observations for 3α-DPSO-17-(*Z*)-ethylidene-5α-androstane,[3] excitation of compounds **1**, **2**, **3a**, and **3b** using light absorbed by the antenna DPSO group leads to olefin $Z \rightarrow E$ isomerization at the remote C17 position (cf. eq 1). Significantly, the photoisomerization in **1** was found to be quenchable by the addition of equimolar amounts of *cis*-2-heptene. The fact that the aryl fluorescence is unquenched by 75 mM *cis*-2-heptene confirms that the interaction involves the DPSO triplet state. Thus, at the 10 mM concentrations of **1** used in these experiments, TTET from C3 to C17 is not exclusively an intramolecular process.[23] That this is the case is also evidenced by the observed dependence of the photoisomerization reaction on the concentration of the substrate (cf. Figure 4). These observations contrast with our previous observations involving DPSO singlet−singlet energy transfer in steroid substrates, where no intermolecular component to the sensitization was observed.[3,4,5,8] As noted in the Introduction, this difference in behavior could be anticipated from the expectedly longer lifetimes of triplet states relative to their singlet counterparts. One might also anticipate a possible reduction in rates for triplet vs singlet intramolecular energy transfer. Both factors would result in a greater opportunity for the donor and acceptor chromophores on different molecules to interact.

Kinetics. Intrinsic DPSO Triplet Lifetime. Having noted that both intra- and intermolecular TTET play a role in the sensitized isomerization reaction, we set about to differentiate these two processes and to elaborate their relative efficiencies and rate constants. Our approach involved using a Stern−Volmer kinetic analysis of various triplet quenching reactions to calculate the inter- and intramolecular quantum efficiency components involved in the isomerization of the steroids. These quantum efficiencies were then used to predict the overall isomerization quantum yields ($\Phi_{Z\rightarrow E}$), which could be compared to the experimentally measured values as a check in the consistency of the method. We chose this approach over the obvious alternative of "isolating" the intramolecular process by reducing the steroid concentration to the point where intermolecular processes do not compete (see Figure 4) for two reasons. First, we found that the low concentrations involved in such high-dilution studies required very large corrections of the data to take into account the marginal light absorption of the solutions. Second, reproducibility in the irradiation of such dilute reaction solutions was problematic and gave less accurate results.

The quantum yields of isomerization ($\Phi_{Z\rightarrow E}$) were therefore determined at 6−10 mM steroid concentration, a range of concentrations in which the DPSO group absorbs at least 95% of the light. The data indicate that the overall $\Phi_{Z\rightarrow E}$ is most efficient for **1** (0.037) and is diminished in each of the additional steroids bearing an alkene group in ring B. The relative rate constants for interTTET and intraTTET at 10 mM steroid were then obtained by using *cis*-2-heptene in various competitive olefin quenching and sensitization experiments. Since such experiments only provide relative rates, our experiments were normalized to the quenching efficiency observed for **1** with *cis*-piperylene. The triplet energy of this quencher ($E_T = 57$ kcal/mol),[24] relative to that of the DPSO group ($E_T = 82$ kcal/mol), justifies the assumption that the rate of quenching of **1** by the diene would be diffusion-controlled.[25] The reported diffusion-controlled rate constants in cyclohexane are 7.0×10^9 and 1.3×10^{10} M^{-1} s^{-1}.[26,27] We have chosen to use the lower value because it has been shown that TTET is typically less than diffusion-controlled, especially in nonviscous solvents.[28,29]

Quenching of the C17 ethylidene isomerization in **1** by piperylene gave a slope in the Stern−Volmer plot of $k_{interP}\tau_{DPSO-17} = 744 \pm 13$ M^{-1}, where k_{interP} corresponds to the rate constant for TTET from 3β-DPSO to the piperylene (see Figure 3) and $\tau_{DPSO-17}$ is the triplet lifetime of the 3β-DPSO group in the presence of the C17 olefin. Using this slope and assuming that k_{interP} is diffusion-controlled, *the 3β-DPSO triplet lifetime in* **1** ($\tau_{DPSO-17}$) *is calculated to be 106 ± 2 ns at 10 mM concentration.*

(23) The reported[3a] lack of quenching of 3αDPSO/17Z was in error. Reanalysis of this compound showed ca. 30% quenching in the presence of equimolar amounts of *cis*-2-heptene, similar to **1** in the present study. The reported[3a] lack of quenching of 3αDPSO/6-ketone/17Z with equimolar *cis*-2-heptene has, however, been confirmed.

(24) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 71.

(25) The fluorescence emission of **1** was measured with and without 1 mM piperylene and showed no singlet quenching.

(26) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; p 314.

(27) Saltiel, J.; Atwater, B. W. In *Advances in Photochemistry*; Vollman, D. H., Hammond, G. S., Gollnick, K. K., Eds.; Interscience: New York, 1988; Vol. 14, p 1.

(28) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.

(29) All of the rate constants would be correspondingly altered were the actual intermolecular rate constant to be significantly different, but the quantum efficiencies we derive from these rates would remain unchanged.

The analogous experiment was run using *cis*-2-heptene as the quencher, with the resulting slope of the Stern−Volmer plot being $k_{\text{interH}}\tau_{\text{DPSO}-17} = 45 \pm 2\ \text{M}^{-1}$ (Table 2). Here k_{interH} is the bimolecular rate constant for energy transfer from the 3β-DPSO group to the *cis*-2-heptene quencher. Since $\tau_{\text{DPSO}-17}$ is the same for these two reactions, we calculate $k_{\text{interH}} = [4.2\ (\pm 0.2)] \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$.

We can now use this information to determine the intrinsic triplet decay rate constant for a DPSO group (k_{TS}) by irradiating the model compound **4** with varying amounts of *cis*-2-heptene.[30] The amount of *trans*-2-heptene formed was determined, and the data were plotted as $1/\Phi^{\text{hept}}_{Z\rightarrow E}$ vs. 1/[hept]. If one assumes that the only decay paths available to the DPSO triplet in this model compound are the intrinsic triplet decay and energy transfer to the heptene, the quantum efficiency of heptene isomerization and the energy transfer quantum efficiency are given by eqs 2 and 3, respectively. Here, $F_{D\rightarrow E}$ is the fraction

$$\Phi^{\text{hept}}_{Z\rightarrow E} = \Phi_{\text{isc}}\Phi_{\text{TTET}}F_{D\rightarrow E} \tag{2}$$

$$\Phi_{\text{TTET}} = \frac{k_{\text{interH}}[\text{hept}]}{k_{\text{interH}}[\text{hept}] + k_{\text{TS}}} \tag{3}$$

of heptene diradical triplets that decay to the *E* isomer. Substitution of eq 3 into eq 2 gives eq 4 as the overall expression for heptene isomerization. After inverting, this provides the final

$$\Phi^{\text{hept}}_{Z\rightarrow E} = \frac{\Phi_{\text{isc}}F_{D\rightarrow E}k_{\text{interH}}[\text{hept}]}{k_{\text{interH}}[\text{hept}] + k_{\text{TS}}} \tag{4}$$

expression (eq 5) in a form useful for plotting. A plot of the

$$\frac{1}{\Phi^{\text{hept}}_{Z\rightarrow E}} = \frac{1}{\Phi_{\text{isc}}F_{D\rightarrow E}} + \frac{k_{\text{TS}}}{\Phi_{\text{isc}}F_{D\rightarrow E}k_{\text{interH}}[\text{hept}]} \tag{5}$$

data using eq 5 is shown in Figure 2. From the slope and intercept (Table 2) we can calculate the ratio of rate constants for **4** (eq 6). Using eq 6 and the value for k_{interH} determined

$$\frac{k_{\text{interH}}}{k_{\text{TS}}} = 460 \pm 50\ \text{M}^{-1} \tag{6}$$

above we obtain $k_{\text{TS}} = [9.2\ (\pm 1.1)] \times 10^5\ \text{s}^{-1}$. *The intrinsic DPSO triplet lifetime* (τ_{DPSO}) *is therefore 1.1 ± 0.1 μs*.

Rate Constants for InterTTET. The value for interTTET from the 3β-DPSO group to C17 was determined by using compound **8** sensitization of *cis*-2-heptene with **5** as quencher. The values for the rate constants corresponding to interTTET from a DPSO group to the B-ring olefins present in **2** and **3a** were determined by using the steroid−olefin model compounds, **6a** and **7a** as quenchers of the compound **4** (10 mM) DPSO-sensitized isomerization of *cis*-2-heptene (5 mM).[31] The results are summarized in Table 3, where the slope of the line is $k_q\tau_{\text{DPSO}-H}$, k_q is the intermolecular rate constant for energy transfer to the given olefin (k_{inter17}, k_{inter5}, or k_{inter6}), and $\tau_{\text{DPSO}-H}$ is the lifetime of the DPSO chromophore in the presence of 5 mM *cis*-2-heptene.[32] This lifetime is defined as shown in eq 7.

$$\tau_{\text{DPSO}-H} = \frac{1}{k_{\text{interH}}[\text{hept}] + k_{\text{TS}}} \tag{7}$$

Using the values of k_{interH} and k_{TS} determined above, we calculate the DPSO triplet lifetime in these runs to be $\tau_{\text{DPSO}-H} = 330 \pm 16$ ns. From this value, and the slopes of the Stern−Volmer plots (Table 3), we determined the intermolecular rate constants to be $k_{\text{inter17}} = [6.7\ (\pm 0.1)] \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$, $k_{\text{inter5}} = [1.3\ (\pm 0.1)] \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$, and $k_{\text{inter6}} = [1.4\ (\pm 0.1)] \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$. We note that the rate constant for intermolecular energy transfer to the C17 ethylidene group (k_{inter17}) is ca. 5-fold greater than the rate constants for transfer to either of the B-ring olefins.[33]

Rate Constants for IntraTTET. With a complete set of values of the rate constants for interTTET in hand, and the knowledge of the DPSO intrinsic triplet decay rate (k_{TS}), we can now calculate the intraTTET rate constants. First, for energy transfer from the C3β-DPSO group to the C17 ethylidene in compound **1** ($k^{(1)}_{\text{intra17}}$), the Stern−Volmer analysis of the quenching of the C17 isomerization with *cis*-2-heptene is represented by eq 8. As already noted, the slope of this line is $45 \pm 2\ \text{M}^{-1}$ (Table 2). In this equation, $\tau_{\text{DPSO}-17}$ is the triplet lifetime of the 3β-DPSO group in **1** (106 ± 2 ns) at 10 mM steroid concentration (eq 9) and Φ_0 is the quantum yield of the C17 ethylidene isomerization in **1** in the absence of the *cis*-2-heptene quencher.

$$\frac{\Phi_0}{\Phi} = 1 + k_{\text{interH}}\tau_{\text{DPSO}-17}[\text{hept}] \tag{8}$$

$$\tau_{\text{DPSO}-17} = \frac{1}{k^{(1)}_{\text{intra17}} + k_{\text{inter17}}[\text{DPSO}] + k_{\text{TS}}} \tag{9}$$

The 3β-DPSO triplet lifetime in **1** ($\tau_{\text{DPSO}-17}$) is concentration-dependent, since it depends on both intraTTET and interTTET to the C17 olefin (eq 9).[36] In this equation, $k^{(1)}_{\text{intra17}}$ and k_{inter17} correspond to the intramolecular and bimolecular rate constants for energy transfer from the 3β-DPSO donor to the C17 ethylidene, and k_{TS} is the intrinsic triplet decay rate constant for DPSO intersystem crossing to the ground state. Inserting the slope of $45 \pm 2\ \text{M}^{-1}$ as the value for $k_{\text{interH}}\tau_{\text{DPSO}-17}$ in eq 8, and solving for $k^{(1)}_{\text{intra17}}$ in eq 9, we obtain $k^{(1)}_{\text{intra17}} = [1.7\ (\pm 0.6)] \times 10^6\ \text{s}^{-1}$.

Alternatively, the value for $k^{(1)}_{\text{intra17}}$ can be derived from the same experiment, but by analyzing the amount of isomerized heptene using a reciprocal plot (Figure 2). The quantum yield for heptene isomerization as defined in eq 2 still applies. However, with the additional modes of triplet decay now

(30) We have demonstrated that the 17β-DPSO model (**4**), the 3β-DPSO model (**8**), and 3β-DPSO-5α-androstane are equally effective in sensitizing *cis*-2-heptene isomerizations (see Results).

(31) Compound **4** was used for these studies because **8** only became available in the latter part of this work. We believe that the *cis*-2-heptene results[30] justify our assumption that, for the relatively unencumbered C5 and C6 steroid olefins, the calculated intermolecular rate constants would not significantly differ for **4** vs **8**.

(32) Since the 3β-DPSO and 17β-DPSO chromophores display the same fluorescence quantum yields, singlet lifetimes, and phosphorescence/fluorescence ratios, we assume their intrinsic triplet lifetimes are the same.

(33) These relative rates presumably reflect a combination of sterics and relative triplet energies. Triplet energies for representative olefins are as follows (kcal/mol): $CH_2{=}C(CH_3)_2$, 80.5; $CH_2{=}C(CH_3)C_2H_5$, 78.3; $CH_3CH{=}C(CH_3)_2$, 77.2; $(CH_3)_2{=}C(CH_3)_2$, 75.8.[34] Sterics have been shown to have a modest effect on TTET by inhibiting favorable orbital overlap between a donor and an acceptor.[35]

(34) Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457.

(35) Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806.

(36) The [DPSO] term in this and subsequent equations represents the concentration of the appropriate DPSO−steroid for the system under consideration.

available to the DPSO group in **1** (i.e. intraTTET and interTTET), the efficiency of energy transfer from the antenna to the heptene is defined as in eq 10. Substitution of this expression

$$\Phi_{\mathrm{TTET}} = \frac{k_{\mathrm{interH}}[\mathrm{hept}]}{k_{\mathrm{interH}}[\mathrm{hept}] + k_{\mathrm{TS}} + k^{(1)}_{\mathrm{intra17}} + k_{\mathrm{inter17}}[\mathrm{DPSO}]} \quad (10)$$

into eq 2 and inverting provides a form useful for plotting (eq 11). The results of this analysis for the sensitization of *cis*-2-

$$\frac{1}{\Phi^{\mathrm{hept}}_{Z\rightarrow E}} = \frac{1}{\phi_{\mathrm{isc}} F_{\mathrm{D}\rightarrow E}} + \frac{k_{\mathrm{TS}} + k^{(1)}_{\mathrm{intra17}} + k_{\mathrm{inter17}}[\mathrm{DPSO}]}{\phi_{\mathrm{isc}} F_{\mathrm{D}\rightarrow E} k_{\mathrm{interH}}[\mathrm{hept}]} \quad (11)$$

heptene isomerization by compound **1** are given in Table 2. From the slope and intercept we calculate $k^{(1)}_{\mathrm{intra17}} = [1.7\ (\pm 0.7)] \times 10^6\ \mathrm{s}^{-1}$, which is the same as that obtained from the quenching data independently derived above. This rate constant is similar to that found by Tung et al. ($k = 1.5 \times 10^5\ \mathrm{s}^{-1}$) for intraTTET from C17 to C3 in a benzophenone donor/norbornadiene acceptor system.[6b,37]

To determine the rate constants for intraTTET from the 3β-DPSO group to the C5 and C6 olefins in **2** and **3a** (k_{intra5} and k_{intra6}, respectively), quenching of the **6b**- or **7b**-sensitized *cis*-2-heptene photoisomerization by **5** was conducted. In this Stern−Volmer analysis, Φ_0 is the quantum yield of *cis*-2-heptene isomerization in the absence of the compound **5** quencher. Beginning with **6b**, the lifetime of the DPSO group in the presence of the C5 olefin depends on both inter- and intramolecular energy transfer to that olefin, as shown in eq 12. The lifetime also depends on k_{interH} and k_{TS}, which were previously determined. Using the slope of the Stern−Volmer plot ($k_{\mathrm{inter17}}\tau_{\mathrm{DPSO-5-H}}$) of $50 \pm 3\ \mathrm{M}^{-1}$ and the values for the appropriate rate constants, we calculate $k_{\mathrm{intra5}} = [9.1\ (\pm 0.8)] \times 10^6\ \mathrm{s}^{-1}$. The analogous analysis using **7b** (eq 13) gives $k_{\mathrm{intra6}} = [1.0\ (\pm 0.3)] \times 10^6\ \mathrm{s}^{-1}$.

$$\tau_{\mathrm{DPSO-5-H}} = \frac{1}{k_{\mathrm{interH}}[\mathrm{hept}] + k_{\mathrm{inter5}}[\mathrm{DPSO}] + k_{\mathrm{intra5}} + k_{\mathrm{TS}}} \quad (12)$$

$$\tau_{\mathrm{DPSO-6-H}} = \frac{1}{k_{\mathrm{interH}}[\mathrm{hept}] + k_{\mathrm{inter6}}[\mathrm{DPSO}] + k_{\mathrm{intra6}} + k_{\mathrm{TS}}} \quad (13)$$

These results can now be used to determine the values of the intramolecular rate constant for energy transfer to the C17 olefins in **2** and **3a**, $k^{(2)}_{\mathrm{intra17}}$, and $k^{(3a)}_{\mathrm{intra17}}$, respectively. Using the *cis*-2-heptene quenching of the C17 ethylidene isomerization reaction for **2** and **3a**, (Table 2) the lifetimes of the 3β-DPSO triplet can be represented as shown in eqs 14 and 15, where all DPSO triplet-decay modes to the respective B-ring olefins are now included.

$$\tau_{\mathrm{DPSO-5-17}} = \frac{1}{k^{(2)}_{\mathrm{intra17}} + k_{\mathrm{inter17}}[\mathrm{DPSO}] + k_{\mathrm{intra5}} + k_{\mathrm{inter5}}[\mathrm{DPSO}] + k_{\mathrm{TS}}} \quad (14)$$

$$\tau_{\mathrm{DPSO-6-17}} = \frac{1}{k^{(3a)}_{\mathrm{intra17}} + k_{\mathrm{inter17}}[\mathrm{DPSO}] + k_{\mathrm{intra6}} + k_{\mathrm{inter6}}[\mathrm{DPSO}] + k_{\mathrm{TS}}} \quad (15)$$

Table 4. Summary of Kinetic Parameters[a]

	rate const	lifetime (ns)[b]
k_{TS}	$[9.2\ (\pm 1.1)] \times 10^5\ \mathrm{s}^{-1}$	$\tau_{DPSO} = 1090 \pm 130$
k_{interH}	$[4.2\ (\pm 0.2)] \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$\tau_{\mathrm{DPSO-H}} = 330 \pm 16$
k_{inter5}	$[1.3\ (\pm 0.1)] \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$\tau_{\mathrm{DPSO-17}} = 106 \pm 2$
k_{inter6}	$[1.4\ (\pm 0.1)] \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$\tau_{\mathrm{DPSO-5-17}} = 54 \pm 4$
k_{inter17}	$[6.7\ (\pm 0.1)] \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$\tau_{\mathrm{DPSO-6-17}} = 85 \pm 7$
k_{intra5}	$[9.1\ (\pm 0.8)] \times 10^6\ \mathrm{s}^{-1}$	$\tau_{\mathrm{DPSO-5-H}} = 75 \pm 5$
k_{intra6}	$[1.0\ (\pm 0.3)] \times 10^6\ \mathrm{s}^{-1}$	$\tau_{\mathrm{DPSO-6-H}} = 184 \pm 7$
$k^{(1)}_{\mathrm{intra17}}$	$[1.7\ (\pm 0.7)] \times 10^6\ \mathrm{s}^{-1}$	
$k^{(2)}_{\mathrm{intra17}}$	$[6.2\ (\pm 8)] \times 10^5\ \mathrm{s}^{-1}$	
$k^{(3a)}_{\mathrm{intra17}}$	$[1.6\ (\pm 1.2)] \times 10^6\ \mathrm{s}^{-1}$	

[a] All rates are relative to $k_{\mathrm{interP}} = k_{\mathrm{diff}} = 7.0 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. [b] $\tau_{\mathrm{DPSO-X}}$ represents the lifetime of the DPSO group in the presence of the given olefin, where H is heptene (5 mM) and 5, 6, and 17 are the olefinic positions on the steroid.

The Stern−Volmer analysis of the quenching of the isomerization of the C17 ethylidene in **2** by *cis*-2-heptene gave $k_{\mathrm{interH}}\tau_{\mathrm{DPSO-5-17}} = 23 \pm 1\ \mathrm{M}^{-1}$ (Table 2). Using the value for k_{interH} determined above, we find $\tau_{DPSO-5-17} = 54 \pm 4$ ns. Using this value in eq 14, and the values of the other rate constants determined previously, gives $k^{(2)}_{\mathrm{intra17}} = [6.2\ (\pm 8)] \times 10^5\ \mathrm{s}^{-1}$. The high value for the error is a result of the propagation of errors, combined with the low value of the final result.

For **3a**, Stern−Volmer analysis of the quenching of the isomerization of the C17 ethylidene by *cis*-2-heptene gave $k_{\mathrm{interH}}\tau_{\mathrm{DPSO-6-17}} = 36 \pm 3\ \mathrm{M}^{-1}$ (Table 2). Using the value for k_{interH} determined above gives $\tau_{\mathrm{DPSO-6-17}} = 85 \pm 7$ ns. Insertion of this value, and the values of the other rate constants determined previously, into eq 15 gives $k^{(3a)}_{\mathrm{intra17}} = [1.6\ (\pm 1.2)] \times 10^6\ \mathrm{s}^{-1}$. All rate constants and lifetimes are summarized in Table 4.

We diverge briefly to discuss the intersystem crossing efficiency of a DPSO group, and the possibility of other quenching mechanisms, before proceeding to calculate the *quantum efficiencies* for intramolecular energy migration in these compounds.

Intersystem Crossing. The efficiency of intersystem crossing can be determined from the intercept of the reciprocal plots discussed above (Figure 2, Table 2) using eq 5 or 11. The fraction of heptene diradical triplets that decay to the *E* isomer ($F_{\mathrm{D}\rightarrow E}$) has been previously determined.[38] The calculated Φ_{isc} values, obtained using compounds **1** and **4** as sensitizers of *cis*-2-heptene isomerization, are 0.079 ± 0.004 and 0.086 ± 0.005, respectively. The average value is $\Phi_{\mathrm{isc}} = 0.083 \pm 0.005$.

A previous determination of Φ_{isc} for the DPSO group using photoacoustic calorimetry (PAC) gave $\Phi_{\mathrm{isc}} = 0.19$,[4c] a value considerably larger than the number obtained from our present triplet counting technique. If, during the interaction of the DPSO triplet with heptene, there were other modes of DPSO triplet decay that did not result in olefin isomerization (charge transfer, exciplex formation, etc.), then our value for Φ_{isc} would indeed be low. The existence of such processes would have the effect of adding a fractional term to eq 2 to account for incomplete energy transfer to the heptene by DPSO triplets. The fraction necessary to reduce the PAC Φ_{isc} value from 0.19 to our value of 0.083 is 0.44. Thus, instead of multiplying $\Phi_{\mathrm{TTET}}F_{\mathrm{D}\rightarrow E}$ by a

(37) It is interesting that a rate constant for electron transfer from a C16 biphenyl anion to a C3 naphthyl group has been determined to be $1.5 \times 10^6\ \mathrm{s}^{-1}$. See: Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. *J. Phys. Chem.* **1989**, *93*, 1173.

(38) We have used a value of 0.50 previously determined for $F_{\mathrm{D}\rightarrow E}$ for 2-heptene; see: Golub, M. A.; Stevens, C. L.; Brash, J. L. *J. Chem. Phys.* **1966**, *45*, 1503. Morrison, H.; Pajak, J.; Peiffer, R. *J. Am. Chem. Soc.* **1971**, *93*, 3978.

Table 5. Comparison of Measured[a] and Predicted $\Phi_{Z\rightarrow E}$ Values for 1−3a Using Φ_{TTET}[b] Calculated from either the Gate or the Relay Assumption[c]

	gate				relay		
	Φ_{TTET}	$\Phi_{intraTTET}$	$\Phi_{Z\rightarrow E}$ calcd[d] from Φ_{TTET} ($\times 10^{-2}$)	measd $\Phi_{Z\rightarrow E}$ ($\times 10^{-2}$)	Φ_{TTET}	$\Phi_{intraTTET}$	$\Phi_{Z\rightarrow E}$ calcd[d] from Φ_{TTET} ($\times 10^{-2}$)
1[e]	0.90 ± 0.10	0.18 ± 0.07	3.9 ± 0.4	3.7 ± 0.1	0.90 ± 0.10	0.18 ± 0.07	3.9 ± 0.4
2	0.39 ± 0.04	0.03 ± 0.04	1.7 ± 0.2	1.8 ± 0.2	0.95 ± 0.08	0.52 ± 0.07	4.1 ± 0.4
3a	0.71 ± 0.13	0.14 ± 0.11	3.1 ± 0.6	2.8 ± 0.2	0.92 ± 0.14	0.22 ± 0.11	4.0 ± 0.6

[a] Measured with a Nd:YAG laser at 266 nm, 30 mW power, 10 Hz pulse. [b] Φ_{TTET} and $\Phi_{intraTTET}$ refer to C3 → C17 energy transfer. [c] "Gate" assumes that all energy reaching the B-ring olefins is decayed and not transferred to the C17 olefin. "Relay" assumes that all energy reaching the B-ring olefins is passed on to the C17 olefin. [d] $\Phi_{Z\rightarrow E} = \Phi_{isc}\Phi_{TTET}F_{D\rightarrow E} = (0.083)\Phi_{TTET}(0.52)$, where $F_{D\rightarrow E}$ was obtained from photostationary data for the analogous 3α-DPSO-17-(*Z*)-ethylidene-5α-androstan-6-one.[3a] [e] Since no olefins are present in the B-ring, the "gate" and "relay" cases are equivalent.

Φ_{isc} value of 0.083, we would multiply by (0.19)(0.44); obviously, the net effect is the same. In other words, the involvement of additional decay paths during the interaction of DPSO triplets with heptene would not affect the calculated isomerization quantum yields. We are currently seeking an additional, independent, measurement of Φ_{isc} to resolve the discrepancy between the PAC value and the chemical triplet-counting value.[39,40]

Quantum Efficiencies of Energy Migration in 1. Having determined the rate constants for the various process that affect the triplet state in **1**, we can now calculate the quantum efficiency of energy transfer and dissect it into its inter- and intramolecular components. In **1**, the overall quantum efficiency of energy transfer from the 3*β*-DPSO group to the C17 ethylidene is given by eq 16. Substitution of the appropriate

$$\Phi_{TTET} = \frac{k^{(1)}_{intra17} + k_{inter17}[DPSO]}{k^{(1)}_{intra17} + k_{inter17}[DPSO] + k_{TS}} \qquad (16)$$

rate constants into eq 16 provides the calculated value for the overall TTET quantum efficiency as $\Phi_{TTET} = 0.90 \pm 0.10$. The intramolecular component, obtained by using only $k^{(1)}_{intra17}$ in the numerator, is $\Phi_{intraTTET} = 0.18 \pm 0.07$. The overall quantum efficiency for isomerization at C17 ($\Phi_{Z\rightarrow E}$) in **1** can be calculated an a manner analogous to that presented in eq 2 using the Φ_{TTET} value. This calculated value and the corresponding experimental result are presented in Table 5. We believe that the match between the calculated and experimentally measured $\Phi_{Z\rightarrow E}$ values is quite reasonable when one considers the multiple measurements involved in determining the calculated value.

Quantum Efficiencies of Energy Migration in 2 and 3a: The "Gate" Effect. There are two limiting possibilities for the TTET quantum efficiencies from the 3*β*-DPSO group to the C17 ethylidene in **2** and **3a**. In the first, we assume that all of the energy reaching the B-ring olefins decays unproductively and is not passed on to the C17 olefin. In this case, the B-ring olefins act as triplet energy gates. The TTET quantum efficiency is represented by eqs 17 and 18 for **2** and **3a**, respectively.

$$\Phi_{TTET} = \frac{k^{(2)}_{intra17} + k_{inter17}[DPSO]}{k^{(2)}_{intra17} + k_{inter17}[DPSO] + k_{intra5} + k_{inter5}[DPSO] + k_{TS}} \qquad (17)$$

$$\Phi_{TTET} = \frac{k^{(3a)}_{intra17} + k_{inter17}[DPSO]}{k^{(3a)}_{intra17} + k_{inter17}[DPSO] + k_{intra6} + k_{inter6}[DPSO] + k_{TS}} \qquad (18)$$

Alternatively, we may assume that *all* of the energy that reaches the B-ring olefins is passed on to the C17 olefin; i.e., the B-ring olefins are triplet energy relays. Such a situation will result in Φ_{TTET} expressions for **2** and **3a** as shown in eqs 19 and 20, respectively.

$$\Phi_{TTET} = \frac{k^{(2)}_{intra17} + k_{inter17}[DPSO] + k_{intra5} + k_{inter5}[DPSO]}{k^{(2)}_{intra17} + k_{inter17}[DPSO] + k_{intra5} + k_{inter5}[DPSO] + k_{TS}} \qquad (19)$$

$$\Phi_{TTET} = \frac{k^{(3a)}_{intra17} + k_{inter17}[DPSO] + k_{intra6} + k_{inter6}[DPSO]}{k^{(3a)}_{intra17} + k_{inter17}[DPSO] + k_{intra6} + k_{inter6}[DPSO] + k_{TS}} \qquad (20)$$

The results of both computations from these limiting cases for **2** and **3a** are presented in Table 5. It is clear from this table that the Φ_{TTET} values obtained using the gate assumption lead to calculated $\Phi_{Z\rightarrow E}$ values which best parallel the measured results, i.e., *the C5 and C6 olefins function as triplet energy gates and are not relays*. The relative efficiencies of the endocyclic and exocyclic gates can be illustrated by comparing just the intramolecular "wire" portion of the TTET. As shown in the gate section of Table 5, $\Phi_{intraTTET}$ is reduced in **2** by 83% relative to that calculated for **1**, i.e., the C5 gate allows only a small amount of energy to reach C17. The energy at C17 could be due to a small fraction of energy being relayed from C5. It is interesting, however, that the through-bond mode of energy transfer in the steroids allows for the possibility of multiple energy transfer pathways between C3 and C17, so that a "northern" route is available even if the "southern" route is completely blocked.[42] In either event, that we observe any C17 isomerization at all in **2** is due primarily to the interTTET that is present at the concentrations used.

(39) We do have some evidence in hand, however, which discounts the existence of additional decay paths during the interaction of the DPSO triplet with heptene. The fact that we obtained the same intermolecular rate constants by a Stern−Volmer analysis of the quenching of the C17 ethylidene isomerization and by measuring the amount of isomerization that occurred in the quencher via a reciprocal plot lends support to there being no additional quenching processes.

(40) The sum of the intersystem crossing and fluorescence efficiencies for the DPSO group is $\Phi_{isc} + \Phi_f = 0.083 + 0.012 = 0.095$. This leaves the 91% of the DPSO singlets unaccounted for as nonradiative decay (Φ_{nr}). Clearly, this extensive nonradiative decay must be the source of the short singlet lifetime (ca. 1 ns) of the DPSO group. This is reminiscent of the "α-substitution effect" which we documented two decades ago[41] wherein a monosubstituted benzene having methyl, ethyl, isopropyl, or *tert*-butyl groups displayed fluorescence lifetimes of 35.2, 35.1, 24.5, and 10.0 ns, respectively. The Φ_{isc} values decreased accordingly (i.e. 0.52, 0.44, 0.34, and 0.086, respectively). The phenomenon was attributed to an increase in Φ_{nr} with increasing α methylation. The *tert*-butyl like substitution of the DPSO group may be causing a similar acceleration of radiationless decay.

(41) Froehlich, P. M.; Morrison, H. *J. Phys. Chem.* **1972**, *76*, 3506. Schloman, W. W., Jr.; Morrison, H. *J. Am. Chem. Soc.* **1977**, *99*, 3342.

Comparison of the gating ability of the exocyclic olefin in **3a** with the endocyclic olefin in **2** reveals that the exocyclic alkene is an ineffective gate, leading to a 22% reduction in $\Phi_{intraTTET}$ in **3a** vs **1**. This is due to the greatly diminished rate constant for intramolecular triplet energy transfer to the exocyclic alkene (k_{intra6}) relative to the endocyclic alkene (k_{intra5}) (Table 4) that makes the former much less effective. This was frankly unexpected, since we anticipated that the exocyclic methylene triplet would exhibit facile bond rotation and hence more rapidly and effectively dissipate triplet energy via the "free rotor effect".[43]

It is interesting that, in the benzophenone−steroid−norbornadiene system studied by Tung et al., the steroid contains an endocyclic B-ring olefin.[6b] Although these workers did not compare their results with a saturated B-ring analogue, there is no indication of impedance by the olefin. This is not surprising, since the olefin triplet energy is much higher than the triplet energies of the benzophenone and norbornadiene groups and, thus, should not act as a triplet gate in this system.

Comparison of 3*β*- vs 3α-DPSO as a Triplet Donor. Virtually all of our effort was devoted to the 3*β*-series of substrates represented by **1**, **2**, and **3a**. An insufficient quantity of the 3α-steroid **3b** prevented us from conducting a complete kinetic analysis of this compound. However, the remarkably low $\Phi_{Z\rightarrow E}$ found for **3b** (0.0035) vs that for **3a** (0.028) suggests that any intraTTET to C17 in this compound must be minimal. Using the measured $\Phi_{Z\rightarrow E}$ for **3b**, we calculate $\Phi_{TTET} = 0.08$.[44] This compares with the value $\Phi_{TTET} = 0.71$ for compound **3a** computed from the rate constants. Clearly, the lifetime of the axial 3α-DPSO triplet is much shorter than that for the 3*β*-isomer, due to the more efficient quenching by the C6 methylene group. We have seen a similar enhancement of singlet energy transfer for an axial vs equatorial DPSO donor with a ketone acceptor at C6[3a,4d] and noted that this result was inconsistent with the general observation that TBI in polycyclics is favored when donors and acceptors are equatorial.[45] We believe the more efficient energy transfer to C6 from the axial C3 donors now can be explained in terms of an added *through-space* mechanism. A molecular mechanics optimized structure for **3b** shows the distance from the aryl group to the methylene group to be about 4 Å in one conformation (Figure 5). In fact, an X-ray structure of a compound similar to **3b**, but with a carbonyl group at C6 in place of the exocyclic olefin, shows the DPSO group to indeed be tucked under the steroid. The distance from the aryl group to the C6 carbonyl is 6.45 Å.[46−48]

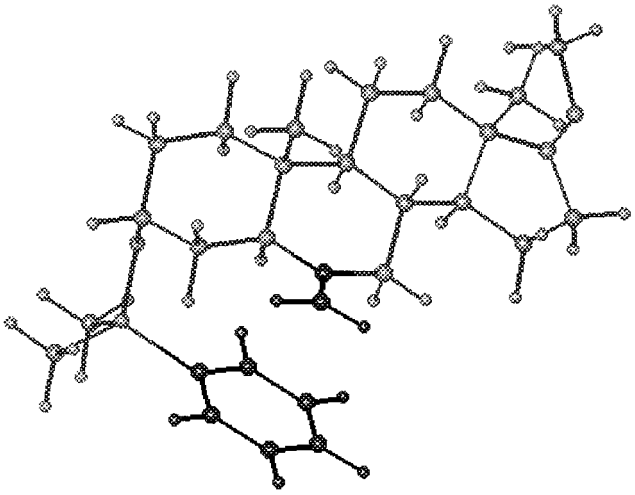

Figure 5. Molecular mechanics optimized structure for one rotamer of **3b**.

Energy Transfer in a Glass at Low Temperature. As one would expect, the total emission spectra for compounds **2**, **3a** and **3b** show no evidence of DPSO phosphorescence (Figure 1). This is consistent with complete intraTTET from the DPSO triplet to the alkenes in these compounds.[49] However, though compound **1** shows a diminution in the relative amount of phosphorescence emission compared with the nonolefinic model **4,** phosphorescence is not completely eliminated.[50] The observation of such emission is surprising, since the relatively slow triplet emission rate constants should not be competitive with the rate of intraTTET calculated for **1** above. We presume that the reduced rate of intraTTET in the glass may be a consequence of the restricted rotational movement of the DPSO group at 77 K. Thus, we speculate that conformations which are particularly inefficient in coupling to the steroid are extensively populated and frozen into place in the glass.

Conclusions

Triplet−triplet energy transfer in these steroid systems at millimolar concentrations consists of intra- and interTTET components. The use of external quenchers has allowed for the determination of a complete set of both the rate constants and the quantum efficiencies for these two modes of energy transfer. Partial gating of the through-bond intraTTET from C3 to C17 can be achieved by inserting endocylic and exocyclic alkenes in ring B, with the effect significantly more pronounced for the endocyclic alkene. The more efficient intraTTET from an axial C3 DPSO group to an exocyclic alkene at C6 is attributed to an added through-space intraTTET pathway between these groups.

The rate constant for intraTTET from the 3*β*-DPSO antenna to the C17 ethylidene acceptor ($k^{(1)}_{intra17}$) in **1** is 1.7×10^6 s^{-1}. The approximate distance between the DPSO and the ethylidene groups of 11 Å cannot support this magnitude of rate constant via a simple through-space exchange mechanism; for a donor and an acceptor at this distance the rate would be on the order of 10^3 s^{-1}.[51] We therefore invoke a TBI-mediated electron

(42) For discussions of multiple through-bond pathways, see: Paddon-Row, M. N.; Shephard, M. J. *J. Am. Chem. Soc.* **1997**, *119*, 5355. Paulson, B. P.; Curtiss, L. A.; Bal, B.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 378. Ratner, M. A. *J. Phys. Chem.* **1990**, *94*, 4877. Onuchic, J. N.; de Andrade, P. C. P.; Beratan, D. N. *J. Chem. Phys.* **1991**, *95*(2), 1131. Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771.

(43) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 8749. Zimmerman, H. E.; Albrecht, F. X.; Haire, M. J. *J. Am. Chem. Soc.* **1975**, *97*, 3726.

(44) Calculated by using $\Phi_{Z\rightarrow E} = \Phi_{isc}\Phi_{TTET}F_{D\rightarrow E}$: $0.0035 = (0.083)\Phi_{TTET}$-(0.52).

(45) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652. Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751.

(46) Agyin, J. K, Ph.D. Thesis, Purdue University, Aug 1996.

(47) For some examples of the involvement of through-space intramolecular energy transfer involving flexible tethers connecting donor and acceptor groups, see: Haggquist, G. W.; Katayama, H.; Tsuchida, A.; Ito, S.; Yamamoto, M. *J. Phys. Chem.* **1993**, *97*, 9270. Wagner, P. J.; El-Taliawi, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 8325. Katayama, H.; Ito, S.; Yamamoto, M. *J. Phys. Chem.* **1992**, *96*, 10115. Katayama, H.; Maruyama, S.; Ito, S.; Tsujii, Y.; Tsuchida, A.; Yamamoto, M. *J. Phys. Chem.* **1991**, *95*, 3480.

(48) There is evidence that for conformers having the donor and acceptor within 3−4 Å of each other, energy transfer occurs in 100 ps or less; cf.: Klán, P.; Wagner, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 2198.

(49) The total emission spectrum of **4** was measured at 77 K in a methylcylohexane glass containing an equimolar amount of **5** added as a competitive olefin quencher. The spectrum was unchanged, evidence that there is no interTTET in the steroidal olefins under these conditions.

(50) We have consistently observed phosphorescence emission from the α and *β* C3-DPSO/C17 and C17-DPSO/C3 olefins.

(51) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; p 320.

exchange mechanism for intraTTET in the steroid molecule; i.e., the steroid acts as a photonic wire, allowing excitation energy to be passed from donor to acceptor through the intervening σ-bond framework.[52] This study therefore represents our first unambiguous example of TBI within a steroid, since in the SSET cases we studied previously,[3−6] the possibility of resonance energy transfer was also present.

Experimental Section

Chemicals. The following chemicals were obtained from Aldrich Chemical Co., stored at room temperature, and used without further purification unless otherwise stated: epiandrosterone; chlorodimethylphenylsilane (stored in a desiccator); ethyltriphenylphosphonium bromide; methyltriphenylphosphonium bromide; triethylamine (distilled from CaH_2); *N*,*N*-dimethylformamide (anhydrous); potassium *tert*-butoxide (1.0 M in THF); 2-methyl-2-ethyl-1,3-dioxolane; *tert*-butyldimethylsilyl chloride; imidazole; *cis*-2-heptene and *cis*-piperylene (stored in the freezer and distilled prior to use); lithium tri-*tert*-butoxyaluminohydride (1.0 M in THF); *p*-toluenesulfonic acid monohydrate (*p*-TSA, stored in a desiccator). All silylated steroids synthesized in this study were stored at room temperature in amber vials in a desiccator.

The following chemicals were obtained from other suppliers and stored at room temperature unless otherwise indicated: 5α-androstane-17β-ol, dehydroepiandrosterone, and testosterone (all from Sigma); pyridine, chromium trioxide, and sodium bicarbonate (all from Mallinckrodt); chlororform-*d* (Cambridge Isotope Laboratories, stored over sodium carbonate); anhydrous magnesium sulfate (EM); hydrochloric and sulfuric acids (Fisher).

The following solvents were purchased from various suppliers and used as received: acetonitrile, 2-propanol, and methylene chloride (Fisher); acetone, ethyl acetate, hexanes, and toluene (Mallinckrodt). Tetrahydrofuran (THF, Fisher) was distilled under nitrogen from sodium−benzophenone ketyl before use. Spectrophotometric grade solvents were used in the photochemical and spectroscopic studies without further purification: cyclohexane (Fisher) and methylcylohexane (Aldrich). The photochemical solvents were stored under argon and purged with argon after removing a portion for use.

Instrumentation. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained in $CDCl_3$ with either a GE spectrometer operating at 300 MHz or a Varian Gemini spectrometer operating at 200 MHz, with chemical shifts reported relative to residual chloroform at 7.27 ppm. ^{13}C NMR were obtained in $CDCl_3$ with either a GE spectrometer operating at 75.6 MHz or a Varian Gemini spectrometer operating at 50 MHz, with chemical shifts reported relative to residual chloroform at 77.0 ppm unless otherwise noted. Mass spectra were recorded on Finnigan 4000 mass spectrometers operating with a source temperature of 250 °C with direct probe sample introduction. Electron impact (EI) and chemical ionization (CI) mass spectra were recorded at 70 eV, the latter with a 2-methylpropane pressure of 0.30 Torr. High-resolution mass spectra were recorded on a Kratos Model MS-50 instrument that was calibrated to a resolution of 10 000, with a 10% valley between peaks using perfluorokerosene. Absorption spectra were recorded in 1 cm cells against a solvent blank on a Cary Model 100 UV−vis spectrophotometer (dual beam) interfaced to a computer (Pentium P5-100) using Cary software. Steady-state fluorescence spectra were obtained on a SLM Aminco SPF-500 spectrophotometer using a 250 W xenon arc lamp operating in the A/B mode. Detection was normal to the excitation light. All fluorescence samples used 1 cm square fluorescence cells and were purged with argon at least 25 min prior to use. Fluorescence quantum efficiencies were obtained by using toluene as the reference[20] and correcting for differences in detector gain, absorbance, and refractive index. Total emission spectra were obtained in a methylcyclohexane glass using a 2 mm × 5 cm cylindrical quartz cell in an optical Dewar at 77 K after at least five freeze−pump−thaw degassing cycles (2×10^{-5} Torr).

Photochemical Apparatus. All irradiations were conducted at room temperature in solutions that were argon-degassed at least 25 min prior to use. The kinetic determinations were conducted in a Model RPR-100 Rayonet reactor available from Southern New England Ultraviolet Co. Cylindrical quartz tubes were used (1 cm × 9 cm). The reactor was equipped with 4 × 254 nm lamps and a merry-go-round turntable apparatus that was positioned approximately 2 cm from the lamps. Up to eight tubes could be irradiated simultaneously. Laser irradiations were conducted at 266 nm and 30 mW power with a Continuum NY-61 Nd:YAG laser equipped with a frequency quadrupler (10 Hz, ca. 3.0 mJ/pulse). A 2× beam enlarger was used in front of the sample cell to avoid cell damage. Square Vycor sample cells (1 cm) were used.

Chromatography. Samples were analyzed by analytical GLC using various capillary columns on a Varian Model Star 3400 CX gas chromatograph. Detection was with a flame-ionization detector utilizing a Hewlett-Packard 3390A integrator. Steroids were analyzed by using a DB-1 capillary column (15 m × 0.25 mm × 0.25 μm film thickness) with the following temperature parameters: injector and detector 300 °C, column 240 °C for 1 min, 5 °C/min to a final temperature of 280 °C. Retention times were 6−12 min for silylated steroids and 4−6 min for the steroid alcohols, depending on the structure. *cis*-2-Heptene and (*E*)-1-phenyl-2-butene were analyzed by using a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm film thickness) with injector and detector set at 250 °C and the column set at either 40 °C (*cis*-2-heptene, retention time 4 min) or 100 °C ((*E*)-1-phenyl-2-butene, retention time 6 min). Flash chromatography was performed by using hexane/ethyl acetate (v/v) solutions with a 50 mm × 36 in. column packed with 6 in. of 230 × 400 mesh silica gel (EM-9385). Analytical TLC was performed on silica gel 60 Å, 250 μm, coated on a glass support (Whatman) and visualized using a cerium sulfate/ammonium molybdate/sulfuric acid solution or a UV lamp as appropriate. Semipreparative HPLC was conducted by using a Waters 4000 HPLC system with a Waters 486 tunable absorbance detector set at 254 nm. The column used was a Beckman Model 235328 Ultrasphere 5 μm C-18 column of dimensions 10 mm × 25 cm with a mobile phase of 100% acetonitrile (isocratic) at a flow rate of 9 mL/min.

Syntheses. All reactions were conducted in oven-dried glassware, sealed with rubber septa, and run under nitrogen unless otherwise indicated.

3β-((Dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5α-androstane (1). Wittig Reaction: Illustration of General Procedure. Epiandrosterone (3.00 g, 10.3 mmol) was dissolved in 15 mL of THF. In a separate vessel, potassium *tert*-butoxide (53 mL, 1.0 M solution in THF) was added to a slurry of ethyltriphenylphosphonium bromide (19.2 g, 51.6 mmol) in 50 mL of THF. After 5 min of stirring, the steroid solution was added to the Wittig reagent via cannula over 5 min at ambient temperature. The mixture was stirred for 4.5 h and, after removal of a large portion of the Wittig byproducts by recrystallization from 7/3 hexane/ethyl acetate, the filtrate containing the crude product was concentrated and purified by flash chromatography (7/3 hexane/ethyl acetate). The 17-(*Z*)-ethylidene-3β-hydroxy-5α-androstane product was obtained in 92.1% yield (2.88 g; mp 138−144 °C from cyclohexane, lit.[9a] mp 152−154 °C) and used for the next reaction without further purification. ^{1}H NMR: δ 5.12 (q, 1 H), 3.59 (m, 1 H), 2.40−0.82 (m, 26 H), 0.86 (s, 3 H), 0.81 (s, 3 H). ^{13}C NMR: δ 150.3, 113.1, 71.2, 56.2, 54.3, 44.8, 44.3, 38.1, 37.1, 36.9, 35.5, 35.0, 31.8, 31.4, 31.3, 28.6, 24.3, 21.4, 16.8, 13.0, 12.3. MS (CI): *m*/*z* 302 (67, M^+), 287 (70). HRMS (CI): *m*/*z* calculated for $C_{21}H_{35}O$ (M + H) 303.2688, found 303.2672.

DPSO Reaction: Illustration of General Procedure. 17-(*Z*)-Ethylidene-3β-hydroxy-5α-androstane (2.62 g, 8.66 mmol) was dissolved in anhydrous DMF (30 mL) containing triethylamine (6.1 mL, 43.3 mmol). The solution was cooled in an ice bath, chlorodimethylphenylsilane (1.45 mL, 8.66 mmol) was added via syringe over 5 min, and the resulting slurry was mixed for 2.5 h. TLC (9/1 hexane/ethyl

(52) In the absence of a comprehensive rate vs distance study, one can use the relationship $k_{intraTTET} = k_0(\exp) - [\beta(\text{no. of bonds}) - 1]$, with k_0 as the commonly accepted value[53] of 10^{13} s^{-1} and an 11-bond separation, to estimate the value $\beta = 1.6$. This is close to the $\beta = 1.4$ value obtained from ab initio calculations for TBI mediated intraTTET in a naphthyl−polynorbornyl−naphthyl system.[54]

(53) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(54) Clayton, A. H. A.; Scholes, G. D.; Ghiggino, K. P.; Paddon-Row, M. N. *J. Phys. Chem.* **1996**, *100*, 10912.

acetate) showed the reaction to be complete. The slurry was diluted with 100 mL of toluene and washed successively with cold 5% aqueous sodium bicarbonate, cold 5% HCl, and cold 5% aqueous sodium bicarbonate. The organic phase was dried ($MgSO_4$) and concentrated under vacuum to give a colorless oil. The material was purified by using flash chromatography (9/1 hexane/ethyl acetate) to provide 3*β*-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5α-androstane as a colorless oil, which was recrystallized (2×) from acetonitrile to give a white solid (2.39 g, 63.3% yield, mp 57−58 °C). GC analysis showed the product to contain ca. 2.5% of the *E* isomer. ^{1}H NMR: *δ* 7.36−7.61 (m, 5 H), 5.10 (q, 1 H), 3.59 (m, 1 H), 2.04−0.86 (m, 25 H), 0.85 (s, 3 H), 0.79 (s, 3 H), 0.38 (s, 6 H). ^{13}C NMR: *δ* 150.5, 138.6, 133.5, 129.4, 127.7, 113.2, 72.3, 56.2, 54.4, 44.9, 44.4, 38.4, 37.2, 37.1, 35.5, 35.0, 31.9, 31.7, 31.4, 28.7, 24.4, 21.4, 16.9, 13.1, 12.3, −0.9, −1.0. MS (CI): *m*/*z* 437 (13, M + H), 285 (100). HRMS (CI): *m*/*z* calculated for $C_{29}H_{45}OSi$ (M + H) 437.3240, found 437.3241.

3*β*-((Dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5-androstene (2). 17-(*Z*)-Ethylidene-3*β*-hydroxy-5-androstene was obtained from dehydroisoandrosterone (2.89 g, 10.0 mmol) in 92.7% yield (2.79 g) using the general Wittig procedure and used for the next reaction without further purification (mp 133−135 °C from cyclohexane, lit.[10] mp 136−137 °C). ^{1}H NMR: *δ* 5.36 (m, 1 H), 5.13 (q, 1 H), 3.53 (m, 1 H), 2.42−1.04 (m, 23 H), 1.02 (s, 3 H), 0.90 (s, 3 H). ^{13}C NMR: *δ* 150.3, 140.8, 121.6, 113.5, 71.7, 56.5, 50.1, 44.0, 42.3, 37.2, 36.9, 36.5, 31.7, 31.6, 31.42, 31.37, 24.5, 21.2, 19.4, 16.6, 13.1. MS (EI): *m*/*z* 300 (100, M^+), 285 (38), 267 (70);. HRMS (CI): *m*/*z* calculated for $C_{21}H_{33}O$ (M + H) 301.2531, found 301.2530.

17-(*Z*)-Ethylidene-3*β*-hydroxy-5-androstene (1.08 g, 3.61 mmol) was treated with chlorodimethylphenylsilane (0.61 mL, 3.61 mmol) according to the general DPSO procedure. The material was purified by using flash chromatography (20/1 hexane/ethyl acetate) to provide the product as a white solid, which was recrystallized (2×) from acetonitrile to give white crystals (0.953 g, 60.7% yield). GC analysis showed the product to contain ca. 2.0% of the *E* isomer (mp 73−74 °C). ^{1}H NMR: *δ* 7.36−7.60 (m, 5 H), 5.26 (m, 1 H), 5.14 (q, 1 H), 3.56 (m, 1 H), 2.42−1.02 (m, 22 H), 1.00 (s, 3 H), 0.88 (s, 3 H) 0.390 (s, 3 H), 0.385 (s, 3 H). ^{13}C NMR: *δ* 150.3, 141.3, 138.5, 133.4, 129.5, 127.7, 121.2, 113.4, 72.7, 56.5, 50.1, 44.0, 42.5, 37.2, 37.0, 36.6, 31.8, 31.7, 31.42, 31.37, 24.5, 21.2, 19.3, 16.6, 13.1, −1.0, −1.1. MS (EI): *m*/*z* 434 (16, M^+), 356 (48), 135 (100). HRMS (CI): *m*/*z* calculated for $C_{29}H_{43}OSi$ (M + H) 435.3083, found 435.3083.

3*β*-((Dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-6-methylene-5α-androstane (3a). 17*β*-Hydroxy-5α-androstane-3,6-dione was prepared by following the reported literature procedure in 65% overall yield from testosterone acetate.[11] ^{1}H NMR: *δ* 3.69 (t, 1 H), 2.61−1.18 (m, 21 H), 0.97 (s, 3 H), 0.78 (s, 3 H).

17*β*-Hydroxy-5α-androstane-3,6-dione was treated on the basis of the procedure of Rosenkranz et al.[12] This steroid (11.53 g, 37.9 mmol) was placed in a dry flask with 138 mL of 2-methyl-2-ethyl-1,3-dioxolane and 0.46 g of *p*-TSA. The mixture was quickly heated to reflux and held at reflux for 5 min. The resulting reaction solution was cooled in an ice bath, during which time crystals appeared. Isolation of the filter cake gave 5.59 g of 3-(ethylenedioxy)-17*β*-hydroxy-5α-androstan-6-one (42.4% yield, GC assay 97.6%; mp 189−190 °C from cyclohexane/ethyl acetate). ^{1}H NMR: *δ* 3.87−3.99 (m, 4 H), 3.69 (t, 1 H, C17αH), 2.55−1.13 (m, 21 H), 0.78 (s, 3 H, C19−CH_3), 0.75 (s, 3 H, C18−CH_3). ^{13}C NMR: *δ* 211.1. 109.1, 81.6, 64.4, 64.3, 56.2, 53.8, 51.5, 46.2, 43.5, 41.0, 38.0, 36.4, 35.8, 30.9, 30.5, 29.9, 23.3, 21.2, 12.6, 11.2. MS (EI): *m*/*z* 348 (91, M^+), 319 (47), 99 (100). HRMS (CI) *m*/*z* calculated for $C_{21}H_{33}O_4$ (M + H) 349.2379, found 349.2378.

3-(Ethylenedioxy)-17*β*-hydroxy-5α-androstan-6-one (5.59 g, 16.1 mmol) was treated with potassium *tert*-butoxide (48.2 mL, 1.0 M solution in THF) and methyltriphenylphosphonium bromide (17.2 g, 48.15 mmol) according to the general Wittig procedure. The mixture was stirred overnight, and the isolated product was purified by flash chromatography (1/1 hexane/ethyl acetate). The 3-(ethylenedioxy)-6-methylene-5α-androstan-17*β*-ol product[13] was obtained in 93% yield (5.2 g) and used for the next reaction without further purification. ^{1}H NMR: *δ* 4.7 (d, *J* = 1.47 Hz, 1 H), 4.4 (d, *J* = 1.47 Hz, 1 H), 3.96−3.93 (m, 4 H), 3.54 (t, 1 H), 2.24−1.00 (m, 21 H), 0.72 (s, 3 H, C19−CH_3), 0.70 (s, 3 H, C18−CH_3). ^{13}C NMR: *δ* 149.9, 110.1, 105.2, 82.3, 64.6, 54.9, 51.5, 48.8, 43.6, 41.9, 38.2, 38.0, 37.1, 36.1, 34.0, 31.4, 31.0, 23.8, 21.6, 12.2, 11.6.

3-(Ethylenedioxy)-6-methylene-5α-androstan-17*β*-ol (4.9 g, 14.1 mmol) was dissolved in 300 mL of acetone in an open flask equipped with a mechanical stirrer. Jones reagent (18 mL) was added by pipet while the ca. 20 °C reaction temperature was maintained. (The Jones reagent was prepared by dissolving 67 g of chromium trioxide in 125 mL of water and slowly adding 58 mL of sulfuric acid with cooling.) After the reaction slurry was stirred for 1 h, a small amount of 2-propanol was added to destroy any excess oxidant. The slurry was worked up by removing most of the acetone under reduced pressure and pouring the residue into 400 mL of water. The product was extracted with ethyl acetate (3×), and the organic phase was washed with 5% sodium bicarbonate and water. The product solution was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude 6-methylene-5α-androstane-3,17-dione was used in the next reaction without further purification (GC assay 92.9%). An analytical specimen was purified by recrystallization from cyclohexane (mp 186−187 °C, lit.[15] mp 187−188 °C). ^{1}H NMR: *δ* 4.82 (d, 1 H), 4.47 (d, 1 H), 2.55−0.95 (m, 20 H), 0.91 (s, 3 H), 0.87 (s, 3 H). ^{13}C NMR: *δ* 220.4, 211.8, 147.2, 107.3, 54.1, 51.1, 50.8, 47.7, 40.5, 40.4, 38.0, 37.9, 37.7, 36.7, 35.7, 31.3, 21.7, 20.9, 13.8, 11.6.

6-Methylene-5α-androstane-3,17-dione (3.4 g, 11.4 mmol) was dissolved in 115 mL of THF. The solution was cooled to −78 °C, and a 1.0 M solution of lithium tri-*tert*-butoxyaluminohydride (18.6 mL) was added over 2.5 h with reaction monitoring by GC. The solution was poured into 500 mL of 5% HCl, and the resulting slurry was extracted with methylene chloride (3×). The combined methylene chloride layers were washed with water and 5% sodium bicarbonate. The solution was dried ($MgSO_4$), concentrated under reduced pressure, and purified with flash chromatography (1/1 hexane/ethyl acetate) to give 2.4 g of 3*β*-hydroxy-6-methylene-5α-androstan-17-one (**15**; mp 135−136 °C, toluene) and 0.5 g of recovered starting material (83% yield based on recovered starting material). ^{1}H NMR: *δ* 4.76 (d, 1 H), 4.51 (d, 1 H), 3.64 (m, 1 H), 2.49−0.88 (m, 21 H), 0.85 (s, 3 H), 0.71 (s, 3 H). ^{13}C NMR: *δ* 220.9, 148.5, 106.6, 71.2, 54.7, 51.3, 49.3, 47.9, 40.7, 37.8, 36.9, 36.5, 35.8, 33.6, 31.4, 31.2, 21.7, 20.7, 13.8, 12.4. MS (EI): *m*/*z* 302 (100, M^+), 284 (41), 269 (42), 91 (72). HRMS (CI): *m*/*z* calculated for $C_{20}H_{31}O_2$ (M + H) 303.2324, found 303.2323.

3*β*-Hydroxy-6-methylene-5α-androstan-17-one (1.0 g, 3.3 mmol) was treated with potassium *tert*-butoxide (16.6 mL, 1.0 M solution in THF) and ethyltriphenylphosphonium bromide (6.1 g, 16.6 mmol) according to the general Wittig procedure. The 17-(*Z*)-ethylidene-3*β*-hydroxy-6-methylene-5α-androstane product was obtained in 75% yield (0.78 g, mp 155−157 °C, cyclohexane) and used for the next reaction without further purification. ^{1}H NMR: *δ* 5.12 (q, 1 H), 4.73 (d, *J* = 1.46, 1 H), 4.47 (d, *J* = 1.46, 1 H), 3.65 (m, 1 H), 2.36−0.89 (m, 24 H), 0.86 (s, 3 H), 0.70 (s, 3 H). ^{13}C NMR: *δ* 150.1, 149.4, 113.4, 106.0, 71.5, 56.1, 54.7, 49.3, 44.4, 41.8, 37.8, 37.1, 37.0, 36.5, 33.7, 31.4, 31.3, 24.3, 21.7, 16.9, 13.1, 12.4. MS (EI): *m*/*z* 314 (100, M^+), 299 (68), 281 (24). HRMS (CI): *m*/*z* calculated for $C_{22}H_{35}O$ (M + H) 315.2688, found 315.2688.

17-(*Z*)-Ethylidene-3*β*-hydroxy-6-methylene-5α-androstane (0.76 g, 2.42 mmol) was treated with chlorodimethylphenylsilane (0.41 mL, 2.4 mmol) according to the general DPSO procedure. The material was purified by using flash chromatography (9/1 hexane/ethyl acetate) to provide **3a** as a colorless oil. After it was held under vacuum overnight, the material formed a fused solid, which was crystallized from acetonitrile to give white needles (0.70 g, 80% yield; mp 82−83 °C). GC analysis showed the product to contain ca. 1.0% of the *E* isomer. The material was recrystallized again prior to use (0.4% *E* isomer). ^{1}H NMR: *δ* 7.63−7.35 (m, 5 H), 5.12 (q, 1 H), 4.70 (m, 1 H), 4.44 (m, 1 H), 3.62 (m, 1 H), 2.33−1.16 (m, 23 H), 0.85 (s, 3 H), 0.68 (s, 3 H) 0.40 (s, 6 H). ^{13}C NMR: *δ* 150.2, 149.6, 138.5, 133.5, 129.5, 127.8, 113.3, 105.9, 72.5, 56.1, 54.7, 49.4, 44.4, 41.8, 37.8, 37.1, 37.0, 36.6, 34.0, 31.5, 31.4, 24.3, 21.6, 16.9, 13.1, 12.4, −0.9, −1.0. MS (EI): *m*/*z* 448 (97, M^+), 433 (39), 281 (44), 137 (100). HRMS (CI): *m*/*z* calculated for $C_{30}H_{45}OSi$ (M + H) 449.3240, found 449.3240.

3α-((Dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-6-methylene-5α-androstane (3b). 3α-Hydroxy-5α-androstane-6,17-dione was prepared

as described earlier.[4d] ^{1}H NMR: δ 4.18 (s, 1 H, 3β H), 0.88 (s, CH_3), 0.77 (s, CH_3).

3α-Hydroxy-5α-androstane-6,17-dione (1.0 g, 3.3 mmol, contaminated with a small amount of the 3β-hydroxy isomer) was dissolved in 12 mL of THF. In a separate vessel, potassium *tert*-butoxide (9.9 mL, 1.0 M solution in THF) was added to a slurry of methyltriphenylphosphonium bromide (3.5 g, 9.9 mmol) in 12 mL of THF. After 5 min of stirring, the Wittig reagent was cooled to −60 °C and the steroid solution was added via cannula over 8 min. The mixture was stirred for 3 h, and the temperature was slowly increased to −15 °C. The reaction mixture was poured into ice−water and extracted with methylene chloride. The crude product was purified by flash chromatography (1/1 hexane/ethyl acetate). 3α-Hydroxy-6-methylene-5α-androstan-17-one was isolated in 39% yield (0.38 g, mp 151−171 °C) and contained a trace of the 3β-alcohol impurity. ^{1}H NMR: δ 4.74 (d, J = 1.52 Hz, 1 H), 4.45 (d, J = 1.52 Hz, 1 H), 4.17 (m, 1 H), 2.41−1.24 (m, 21 H), 0.85 (s, 3 H), 0.68 (s, 3 H). ^{13}C NMR: δ 221.4, 149.5, 106.1, 66.1, 55.0, 51.5, 48.0, 43.6, 41.0, 38.5, 37.1, 35.9, 31.7, 31.5, 31.3, 28.6, 21.8, 20.4, 13.96, 11.6. MS (EI): *m*/*z* 302 (21 M^+), 284 (75), 269 (75), 55 (100). HRMS (CI): *m*/*z* calculated for $C_{20}H_{31}O_2$ (M + H): 303.2324, found 303.2320.

3α-Hydroxy-6-methylene-5α-androstan-17-one (0.38 g, 1.3 mmol) was dissolved in 6 mL of THF and treated with potassium *tert*-butoxide (6.3 mL, 1.0 M solution in THF) and ethyltriphenylphosphonium bromide (2.3 g, 6.3 mmol) according to the general Wittig procudure. The solid crude product was purified by flash chromatography (1/1 hexane/ethyl acetate). The 17-(*Z*)-ethylidene-3α-hydroxy-6-methylene-5α-androstane product was obtained in 59% yield (0.23 g) and used for the next reaction without further purification. ^{1}H NMR: δ 5.12 (q, 1 H), 4.70 (d, J = 1.5, 1 H), 4.41 (d, J = 1.5, 1 H), 4.17 (m, 1 H), 2.34−1.21 (m, 24 H), 0.86 (s, 3 H), 0.67 (s, 3 H). ^{13}C NMR: δ 150.3, 113.5, 105.5, 66.4, 56.3, 54.7, 44.6, 43.6, 42.1, 38.5, 37.2, 31.7, 31.5, 31.4, 28.6, 24.4, 21.3, 17.0, 13.2, 11.5. MS (EI): *m*/*z* 314 (48 M^+), 299 (23), 281 (59), 91 (100). HRMS (FAB, CH_2Cl_2−PEG): *m*/*z* calculated for $C_{22}H_{35}O$ (M + H) 315.2688, found 315.2687.

17-(*Z*)-Ethylidene-3α-hydroxy-6-methylene-5α-androstane (0.22 g, 0.68 mmol) was treated with chlorodimethylphenylsilane (0.11 mL, 0.68 mmol) according to the general DPSO procedure. The material was purified by using flash chromatography (9/1 hexane/ethyl acetate) to provide **3b** as a colorless oil. The product was then purified by semipreparative HPLC. The product could not be recrystallized and was isolated as an oil (0.14 g, 47% yield). GC analysis showed the product to contain ca. 1.8% of the *E* isomer. After NMR analysis, the material was purified again by twice repeating the HPLC purification and drying on high vacuum for several days before use (1.7% *E*). ^{1}H NMR: δ 7.61−7.37 (m, 5 H), 5.13 (q, 1 H), 4.68 (d, J = 1.5 Hz, 1 H), 4.35 (d, J = 1.5 Hz, 1 H), 4.12 (s, 1 H), 2.35−1.22 (m, 23 H), 0.87 (s, 3 H), 0.65 (s, 3 H), 0.35 (s, 6H). ^{13}C NMR: δ 151.0, 150.4, 139.0, 133.6, 129.5, 127.9, 113.5, 105.2, 67.3, 56.3, 54.7, 44.6, 43.7, 42.1, 38.4, 37.25, 37.23, 32.0, 31.98, 31.6, 29.3, 24.5, 21.4, 17.1, 13.3, 11.8, −0.8, −0.9. MS (EI): *m*/*z* 448 (21, M^+), 370 (35), 296 (38), 281 (100). HRMS (FAB, PEG): *m*/*z* calculated for $C_{30}H_{45}OSi$ (M + H) 449.3240, found 449.3250.

17β-((Dimethylphenylsilyl)oxy)-5α-androstane (4). 5α-Androstan-17β-ol (1.98 g, 7.18 mmol) was treated with chlorodimethylphenylsilane (1.20 mL, 7.18 mmol) according to the general DPSO procedure. Flash chromatography (9/1 hexane/ethyl acetate) provided the product as a colorless oil, which was crystallized from acetone to give a white solid (1.787 g, 60.6% yield, mp 59−60 °C). ^{1}H NMR: δ 7.35−7.59 (m, 5 H), 3.56 (t, 1 H), 1.82−0.80 (m, 24 H), 0.77 (s, 3 H), 0.74 (s, 3 H), 0.333 (s, 3 H), 0.328 (s, 3 H). ^{13}C NMR: δ 138.9, 133.5, 129.3, 127.6, 82.1, 55.0, 50.7, 47.1, 43.2, 38.7, 37.1, 36.3, 35.6, 31.8, 30.8, 29.05, 28.97, 26.8, 23.5, 22.2, 20.4, 12.3, 11.5, −0.9, −1.0. MS (EI): *m*/*z* 410 (15, M^+), 332 (26), 258 (32), 135 (100). HRMS (CI): *m*/*z* calculated for $C_{27}H_{43}OSi$ (M + H) 411.3083, found 411.3080.

3β-((*tert*-Butyldimethylsilyl)oxy)-17-(*Z*)-ethylidene-5α-androstane (5). TBDMS Reaction: Illustration of General Procedure. 17-(*Z*)-Ethylidene-3β-hydroxy-5α-androstane (1.20 g, 3.97 mmol) and imidazole (0.68 g, 9.92 mmol) were dissolved in anhydrous DMF (10 mL) at 40 °C under nitrogen. *tert*-Butyldimethylsilyl chloride (0.72 g, 4.76 mmol) was added all at once to produce a thick slurry. The reaction slurry was held at 40 °C for 2.5 h, and TLC analysis (7/3 hexane/ethyl acetate) indicated the reaction was complete. The reaction mixture was diluted with 50 mL of toluene and washed successively with water, 5% bicarbonate, and water. The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a white solid. The crude solid was purified by using flash chromatography with 20/1 hexane/ethyl acetate as the eluant. The isolated material was recrystallized from acetonitrile containing a small amount of ethyl acetate to give 1.2 g of white needles. A second crop of crystals provided an additional 0.12 g (overall yield 82%). The main crop was recrystallized again before use (GC 99.74% *Z*, 0.26% *E*; mp 143−144 °C). ^{1}H NMR: δ 5.12 (q, 1 H), 3.57 (m, 1 H), 2.45−0.95 (m, 25 H), 0.89 (s, 9 H), 0.86 (s, 3 H), 0.81 (s, 3 H), 0.05 (s, 6 H). ^{13}C NMR: δ 150.5, 113.2, 72.2, 56.3, 54.5, 45.0, 44.4, 38.7, 37.3, 37.1, 35.6, 35.1, 32.0, 31.4, 28.7, 26.0, 24.4, 21.4, 18.3, 16.9, 13.1, 12.3, −4.6. MS (CI): *m*/*z* 417 (7, M + H), 285 (100). HRMS (CI): *m*/*z* calculated for $C_{27}H_{49}OSi$ (M + H) 417.3553, found 417.3552.

3β-((*tert*-Butyldimethylsilyl)oxy)-17-ethylenedioxy-5-androstene (6a). Dehydroisoandrosterone (2.00 g, 6.94 mmol), 2-ethyl-2-methyl-1,3-dioxolane (10 mL), and *p*-TSA (0.066 g, 0.35 mmol) were mixed, and the reaction slurry was heated to reflux, producing a solution. The reaction solution was held at reflux for 4.5 h and cooled to room temperature. The solution was diluted with ether and washed successively with 5% sodium bicarbonate and water. The organic layer was dried ($MgSO_4$) and the ether was removed under reduced pressure to give a light yellow solid. The crude solid was purified by using flash chromatography (7/3 hexane/ethyl acetate). Recrystallization from cyclohexane containing a trace of ethyl acetate gave 1.37 g of 17-(ethylenedioxy)-3β-hydroxy-5-androstene (59.2% yield; mp 163−165 °C, lit.[17a] mp 161−165 °C).

17-(Ethylenedioxy)-3β-hydroxy-5-androstene (1.365 g, 4.106 mmol) was treated with *tert*-butyldimethylsilyl chloride (0.74 g, 4.93 mmol) according to the general TBDMS procedure. The solid product was purified by using flash chromatography (9/1 hexane/ethyl acetate) followed by crystallization from acetonitrile to give 1.5 g of **6a** (81% yield) as white flakes (mp 121−122 °C). ^{1}H NMR: δ 5.31 (m, 1 H), 3.88 (m, 4 H), 3.45 (m, 1 H), 2.35−1.05 (m, 19 H), 1.01 (s, 3 H), 0.89 (s, 9 H), 0.86 (s, 3 H), 0.06 (s, 6 H). ^{13}C NMR: δ 141.4, 120.9, 119.5, 72.5, 65.1, 64.5, 50.6, 50.0, 45.7, 42.8, 37.3, 36.6, 34.2, 32.2, 32.0, 31.3, 30.6, 25.9, 22.8, 20.4, 19.4, 18.2, 14.2, −4.6. MS (CI): *m*/*z* 447 (100, M + H), 315 (66). HRMS (CI): *m*/*z* calculated for $C_{27}H_{47}O_3Si$ (M + H) 447.3295, found 447.3294.

3β-((Dimethylphenylsilyl)oxy)-17-(ethylenedioxy)-5-androstene (6b). 17-(Ethylenedioxy)-3β-hydroxy-5-androstene (1.50 g, 4.51 mmol) was treated with chlorodimethylphenylsilane (0.76 mL, 4.51 mmol) according to the general DPSO procedure. The material was purified by using flash chromatography (9/1 hexane/ethyl acetate) to provide **6b** as a white solid. The product was crystallized from acetonitrile (2×) to give 1.5 g of white needles (74% yield, mp 115−116 °C). ^{1}H NMR: δ 7.61−7.36 (m, 5 H), 5.25 (m, 1 H), 3.83−3.92 (m, 4 H), 3.52 (m, 1 H), 2.40−1.34 (m, 19 H), 0.99 (s, 3 H), 0.85 (s, 3 H), 0.39 and 0.38 (s, 6 H). ^{13}C NMR: δ 141.3, 138.6, 133.6, 129.6, 127.9, 121.2, 119.6, 72.7, 65.3, 64.7, 50.7, 50.1, 45.8, 42.6, 37.4, 36.7, 34.3, 32.3, 31.9, 31.4, 30.7, 22.9, 20.6, 19.5, 14.3, −0.86, −0.95. MS (CI): *m*/*z* 467 (60, M + H), 315 (100). HRMS (CI): *m*/*z* calculated for $C_{29}H_{43}O_3Si$ (M + H) 467.2982, found 467.2982.

3β-((*tert*-Butyldimethylsilyl)oxy)-6-methylene-5α-androstan-17β-ol (7a). 3β-Hydroxy-6-methylene-5α-androstan-17-one (1.4 g, 4.6 mmol) was treated with *tert*-butyldimethylsilyl chloride (0.84 g, 5.6 mmol) according to the general TBDMS procedure. The crude solid product was purified by using flash chromatography (8/2 hexane/ethyl acetate), giving 1.7 g (87% yield) of 3β-((*tert*-butyldimethylsilyl)oxy)-6-methylene-5α-androstan-17-one. The material was used in the next reaction without further purification. GC: 96.6%. ^{1}H NMR: δ 4.76 (s, 1 H), 4.52 (s, 1 H), 3.58 (m, 1 H), 2.41−1.24 (m, 20 H), 0.90 (s, 9 H), 0.85 (s, 3 H), 0.71 (s, 3 H), 0.06 (s, 6 H). ^{13}C NMR: δ 220.9, 148.8, 106.5, 72.2, 54.9, 51.4, 49.5, 47.9, 40.8, 37.9, 37.0, 36.7, 35.8, 34.1, 31.7, 31.5, 26.0, 21.7, 20.8, 18.3, 13.8, 12.5, −4.6. MS (EI): *m*/*z* 416 (2, M^+), 401 (1), 359 (100). HRMS (CI): *m*/*z* calculated for $C_{26}H_{45}O_2Si$ (M + H) 417.3189, found 417.3184.

3β-((*tert*-Butyldimethylsilyl)oxy)-6-methylene-5α-androstan-17-one (1.6 g, 3.8 mmol) was dissolved in 25 mL of THF, and the solution was cooled to −20 °C. Lithium tri-*tert*-butoxyaluminohydride (5 mL, 1.0 M in THF) was added via syringe, and the reaction solution was held at −20 °C for 2 h. The reaction solution was worked up by dilution with 80 mL of toluene, followed by pouring into 20 mL of 5% HCl. The mixture was immediately washed with 5% sodium bicarbonate and water. The organic phase was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography using 7/3 hexane/ethyl acetate to give 1.4 g of **7a** (87% yield). The product was crystallized (2×) from acetonitrile prior to use (mp 140−141 °C). ^{1}H NMR: δ 4.71 (d, J = 1.20 Hz, 1 H), 4.47 (s, J = 1.20 Hz, 1 H), 3.64 (m, 2 H), 2.31−0.91 (m, 21 H), 0.90 (s, 9 H), 0.72 (s, 3 H), 0.69 (s, 3 H), 0.06 (s, 6 H). ^{13}C NMR: δ 149.3, 106.0, 81.8, 72.3, 54.9, 51.0, 49.5, 43.1, 41.5, 38.0, 37.5, 36.7, 36.6, 34.1, 31.7, 30.5, 25.9, 23.3, 21.1, 18.2, 12.5, 11.1, −4.6. MS (CI): *m*/*z* 419 (64, M + H), 401 (25), 287 (100). HRMS (CI): *m*/*z* calculated for $C_{26}H_{47}O_2Si$ (M + H) 419.3345, found 419.3345.

3β-((Dimethylphenylsilyl)oxy)-6-methylene-5α-androstan-17β-ol (7b). 3β-Hydroxy-6-methylene-5α-androstan-17-one (1.4 g, 4.6 mmol) was treated with chlorodimethylphenylsilane (0.78 mL, 4.6 mmol) according to the general DPSO procedure. The material was purified by using flash chromatography (8/2 hexane/ethyl acetate) to provide 3β-((dimethylphenylsilyl)oxy)-6-methylene-5α-androstan-17-one as a colorless oil (1.3 g). ^{1}H NMR: δ 7.64−7.37 (m, 5 H), 4.75 (d, 1 H), 4.49 (d, 1H), 3.62 (m, 1 H), 2.39−1.27 (m, 20 H), 0.85 (s, 3 H), 0.70 (s, 3 H), 0.41 (s, 6 H). ^{13}C NMR: δ 220.9, 148.6, 138.4, 133.4, 129.5, 127.8, 106.5, 72.3, 54.7, 51.3, 49.4, 47.8, 40.7, 37.8, 36.9, 36.6, 35.8, 33.9, 31.4, 21.7, 20.7, 13.8, 12.4, −0.96, −1.05. MS (EI): *m*/*z* 436 (9, M^+), 421 (100). HRMS (CI): *m*/*z* calculated for $C_{28}H_{41}O_3Si$ (M + H) 437.2876, found 437.2875.

3β-((Dimethylphenylsilyl)oxy)-6-methylene-5α-androstan-17-one (1.2 g, 2.7 mmol) was dissolved in 10 mL of THF, and the solution was cooled to −10 °C. Lithium tri-*tert*-butoxyaluminohydride (4.1 mL, 1.0 M in THF) was added via syringe, and the reaction solution was held at −10 °C for 30 min. The reaction solution was worked up by dilution with 80 mL of cold toluene, followed by pouring into 20 mL of cold 5% HCl and quickly washing the mixture with 5% sodium bicarbonate and water. The organic phase was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography using 7/3 hexane/ethyl acetate to give 0.9 g of **7b** as a white solid. The product was crystallized (2×) from hexane prior to use in photolysis experiments (mp 102−104 °C). ^{1}H NMR: δ 7.62−7.37 (m, 5 H), 4.70 (d, 1 H), 4.49 (d, 1 H), 3.61 (m, 2 H), 2.39−1.00 (m, 20 H), 0.72 (s, 3 H), 0.69 (s, 3 H), 0.40 (s, 6 H). ^{13}C NMR δ 149.2, 138.5, 133.4, 129.4, 127.7, 106.0, 81.8, 72.4, 54.8, 51.0, 49.4, 43.1, 41.5, 37.7, 37.5, 36.6, 33.9, 31.5, 30.5, 23.3, 21.1, 12.5, 11.1, −0.9, −1.0. MS (CI): *m*/*z* 439 (52, M + H), 421 (34), 287 (100). HRMS (CI): *m*/*z* calculated for $C_{28}H_{43}O_2Si$ (M + H) 439.3032, found 439.3031.

3β-((Dimethylphenylsilyl)oxy)-17-(ethylenedioxy)-5α-androstane (8). Epiandrosterone (2.0 g, 6.9 mmol) was refluxed in 20 mL of 2-ethyl-2-methyl-1,3-dioxolane with *p*-TSA (0.07 g) overnight to give 17-(ethylenedioxy)-5α-androstan-3β-ol (mp 141−148 °C, lit.[18] mp 152−154 °C). This compound (1.76 g, 5.27 mmol) was treated with chlorodimethylphenylsilane (0.88 mL, 5.27 mmol) according to the general DPSO procedure. The product was isolated by flash chromatography (9/1 hexane/ethyl acetate) to give 1.92 g of **8** (78% yield). The material was crystallized (2×) from methanol before use (mp 106−108 °C). ^{1}H NMR: δ 7.62−7.36 (m, 5 H), 3.91−3.83 (m, 4 H), 3.48 (m, 1 H), 1.97−0.88 (m, 22 H), 0.83 (s, 3 H), 0.79 (s, 3 H), 0.38 (s, 6 H). ^{13}C NMR: δ 138.6, 133.4, 129.4, 127.7, 119.5, 72.2, 65.1, 64.5, 54.1, 50.3, 45.9, 44.9, 38.4, 37.1, 35.7, 35.5, 34.2, 31.7, 31.3, 30.7, 28.5, 22.6, 20.6, 14.4, 12.3, −0.9, −1.0. MS (EI): *m*/*z* 468 (29, M^+), 453 (4), 99 (100). HRMS (CI): *m*/*z* calculated for $C_{29}H_{45}O_3Si$ (M + H) 469.3138, found 469.3140.

Fluorescence Quantum Yields. A 1 cm square quartz fluorescence cell was filled with a given steroid solution at an optical density of ca. 0.1 at the excitation wavelength. The solution was argon-degassed for 30 min and sealed with a rubber septum wrapped with Parafilm. A solution of toluene was also placed in a fluorescence cell and treated with the same procedure. The fluorescence emission for the sample was acquired at 254 nm excitation, and the instrumental conditions were optimized to give ca. 90% of full intensity at the maximum emission wavelength. The toluene standard was run using identical instrumental conditions.

Total Emission Spectra. A steroid sample in methylcylohexane giving an optical density of ca. 0.3 in a 1 cm cuvette was transferred to a 2 mm phosphorescence cell equipped with a vacuum stopcock. After it was degassed with at least five freeze−pump−thaw cycles, the sample was inserted into a liquid nitrogen optical Dewar and the spectrum was acquired with 254 nm excitation.

Steroid Quantum Yields $\Phi_{Z\rightarrow E}$. Several laser cells were filled with 2 or 3 mL of steroid solution at 10 mM concentration in cyclohexane (optical density ca. 2.5). The solutions were argon-degassed for 25 min and sealed with rubber septa. The power was monitored with a OPHIR Model AN/2 power meter. The solutions were placed in the 266 nm beam of the laser and irradiated for ca. 5 min (30 mW power, 10 Hz rep rate). Typical product conversions were 5−7%. This was repeated with the other sample cells, and the results were averaged. All results were corrected for the small amount of back-reaction. A dark control sample was analyzed simultaneously. The product formed was determined by GC analysis using an internal standard of 3α-((dimethylphenylsilyl)oxy)-17-methylene-5α-androstane or **6a**.

The quantum yields obtained using this laser technique were compared with those obtained using the 254-nm Rayonet reactor for the compound 3α-((dimethylphenylsilyl)oxy)-17-(*Z*)-ethylidene-5α-androstane. The results were $\Phi_{Z\rightarrow E}$ = 0.043 and 0.041, respectively. Thus, two-photon processes occurring due to laser irradiation can be ruled out.

Stern−Volmer Quenching of C17 Isomerization in 1 with *cis*-2-Heptene. Illustration of Typical Procedure. Stock solutions of **1** and *cis*-2-heptene in cyclohexane were prepared. Six quartz tubes were filled with **1** to give a final concentration of 10 mM, and four of the tubes were filled with various amounts of *cis*-2-heptene to produce final concentrations of 0.2×10^{-2}, 1×10^{-2}, 2×10^{-2}, and 5×10^{-2} M. The final volume was 3.0 mL. The tubes were argon-degassed for 25 min with a slow stream of argon and were sealed with rubber septa. The tubes were irradiated at 254 nm in the Rayonet reactor simultaneously for 15 min. After irradiation, a cyclohexane solution of the internal standard (3α-((dimethylphenylsilyl)oxy)-17-methylene-5α-androstane) was added and the tubes were analyzed by GC to determine the amount of product formed. The results were corrected for the small amount of back-reaction.

Quenching of 8-Sensitized *cis*-2-Heptene Isomerization with Steroid−Olefin Quencher. Illustration of Typical Procedure. Stock solutions of **8, 5**, and *cis*-2-heptene in cyclohexane were prepared. Seven photolysis tubes were filled with 10 mM **8** and 5 mM *cis*-2-heptene. Five of the tubes were filled with various concentrations of **5** at 1×10^{-2}, 5×10^{-2}, 10×10^{-2}, and 15×10^{-2} M (includes one replicate). The final volume was 3.0 mL. The tubes were argon-degassed for 25 min with a slow stream of argon and were sealed with rubber septa. The tubes were irradiated at 254 nm in the Rayonet reactor simultaneously for 15.0 min, and the amount of *trans*-2-heptene was determined by GC analysis. The amount of *trans*-2-heptene formed ranged between 3.5% and 11.2%. The initial amount of *trans*-2-heptene present in the *cis*-2-heptene solution was 1.2%. After correction for back-reaction, the data were plotted according to the Stern−Volmer equation.

***cis*-2-Heptene Isomerization with Steroid Sensitizer. Illustration of Typical Reciprocal Plot Procedure**. Stock solutions of **4,** *cis*-2-heptene, and (*E*)-1-phenyl-2-butene (actinometer) in cyclohexane were prepared. Five quartz tubes were filled with 10 mM **4** and various amounts of *cis*-2-heptene to produce final concentrations of 2×10^{-3}, 5×10^{-3}, 10×10^{-3}, 15×10^{-3}, and 30×10^{-3} M. Three quartz tubes were filled with 21 mM of (*E*)-1-phenyl-2-butene solution. All tubes contained 2.7 mL of solution. The tubes were argon-degassed for 30 min with a slow stream of argon and were sealed with rubber septa. The tubes were irradiated at 254 nm in the Rayonet reactor. The steroid samples were irradiated for 25 min, and the actinometer samples were irradiated for 7−8 min simultaneously. The amounts of *trans*-2-heptene and (*E*)-1-phenyl-2-butene were determined by GC analysis. The results were corrected for the small amount of back-reaction.

Acknowledgment. We are grateful for financial support of this research from the National Science Foundation (Grant No. CHE 9311828). A research grant from Great Lakes Chemical Corp. is also gratefully acknowledged. We thank Ms. Fatemeh Olang for the quenching study on 3αDPSO/6-ketone/17Z.

Supporting Information Available: Stern−Volmer plots for all quenching reactions not shown in the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9808595