# Steroids as Photonic Wires. $Z \rightarrow E$ Olefin Photoisomerization Involving Ketone Singlet → Triplet Switches by Through-Bond Energy Transfer[1,2]

**Joseph K. Agyin, Larry D. Timberlake, and Harry Morrison***

*Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907*

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**Abstract:** A series of steroids has been studied in which there is a dimethylphenylsiloxy (DPSO) group at the 3 position to serve as a light-absorbing antenna, a ketone group at C6 or C11 to serve as an energy "relay" or as a "singlet−triplet switch", and an olefin at C17 to serve as a triplet energy acceptor. These include 3α-(dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstan-11-one (**2**), its C6 carbonyl analog (**3**), and the C6 ketone 3$\beta$ isomer (**4**). The nonketonic steroid 3α-(dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstane (**1**) serves as a reference. Excitation of all four compounds with light absorbed by the DPSO chromophore leads to Z → E isomerization of the C17 ethylidene group. For the ketonic steroids this isomerization involves intramolecular singlet−singlet energy transfer (intraSSET) from the DPSO group to the carbonyl group, intersystem crossing to the carbonyl triplet, and intramolecular triplet−triplet energy transfer (intraTTET) to the alkene. For compound **1** there is modestly efficient (through-bond) intraTTET directly from C3 to C17. For **2**−**4** intraSSET is ca. 75−90% efficient and occurs with rate constants of $(1.1-1.7) \times 10^9$ s$^{-1}$. The C3 DPSO antenna transfers both singlet and triplet energy more efficiently when it is α (axial) than when it is $\beta$ (equatorial). IntraTTET from C6 and C11 to C17 is ca. 80% efficient; $k_{C6\rightarrow 17Z}$, determined from triplet quenching experiments, equals $8.3 \times 10^8$ s$^{-1}$. The C11 ketone has an unusually short singlet lifetime (0.4 ns), which can be attributed to an enhanced rate of radiationless decay caused by the proximity of the C19 angular methyl group.

## Introduction

As part of the surge of interest in the general area of nanotechnology[3] there has been developing attention to the potential use of molecular dimension "wires" to transmit photonic energy.[4] Examples of frameworks shown to be capable of through-bond transmission of electronic excitation include bicyclo[2.2.1]heptanes,[5a−c] bicyclo[2.2.2]octanes,[5d] oligo[1.1.1]-propellanes,[5e,f] polyenes and polyynes,[5g,h] polyphenylenes,[5i] oligothiophenes,[5j] polypeptides,[5k−m] polyethers,[5n] and block polymers.[5o,6] Steroids represent an additional group of transmitters, with recent work from our own[1,2,7] and other laboratories[8] providing ample confirmation that these rigid tetracyclics are excellent "photonic wires". These molecules provide a well-defined scaffold upon (and within) which one can insert different moieties to fulfill various electronic functions. The latter may include an "*antenna*" to absorb incident irradiation, *relays* and *gates* which facilitate and impede energy migration (the latter potentially multiplicity specific),[1] and *multiplicity switches* which convert singlet to triplet energy.

In our previous reports we have utilized the dimethylphenylsiloxy (DPSO) group as the antenna (because of its favorable properties as outlined earlier)[9] and the ketone functionality as the potential recipient of intramolecular singlet−singlet and triplet−triplet energy (intraSSET and intraTTET, respectively). The antenna and the ketone have been mounted on the 5α-androstane steroidal framework. We have shown that excitation of the DPSO chromophore in 3α-(dimethylphenylsiloxy)-5α-androstane-11,17-dione (3αDPSO/11/17) leads to triplet pho-

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(2) (a) Preliminary communication: Agyin, J. K.; Morrison, H.; Siemiarczuk, A. *J. Am. Chem. Soc.* **1995**, *117*, 3875−3876. (b) Abstracted from the Doctoral Dissertation of J. K. Agyin, Purdue University, August, 1996.

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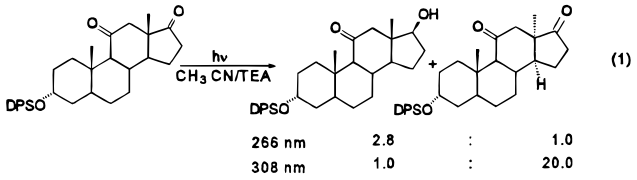
tochemistry at C17, although the C17 ketone itself intersystem crosses with very low efficiency; by contrast, direct photolysis of the carbonyl groups in this steroid primarily leads to singlet-derived epimerization in ring D (cf. eq 1).[7c] We proposed that



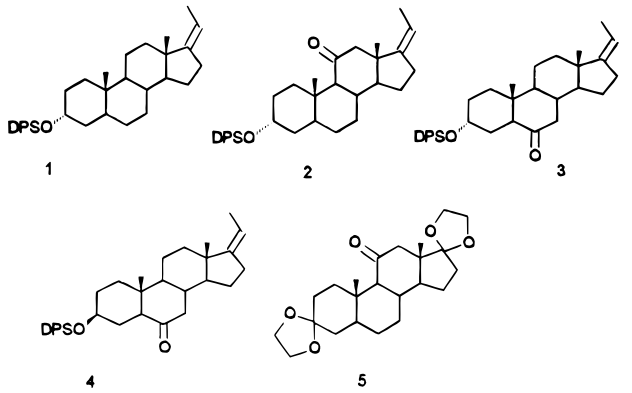

(1)

activation of C17 in 3αDPSO/11/17 occurs by intraSSET from the DPSO chromophore to C11, intersystem crossing of this ketone, and intraTTET from C11 to C17. To verify and expand this proposed role for the C11 carbonyl group as a "singlet → triplet switch", we have investigated energy migration in the trifunctional steroids 3α-(dimethylphenylsiloxy)-17-(Z)-ethylidene-5α-androstan-11-one (**2**), its C6 carbonyl analog (**3**), and the C6 ketone 3*β* isomer (**4**), (3αDPSO/11/17-Z, 3αDPSO/6/17-Z, 3*β*DPSO/6/17-Z, respectively). 3α-(Dimethylphenylsiloxy)-17-(Z)-ethylidene-5α-androstane (3αDPSO/17-Z, **1**) serves as a nonketonic reference. Compounds **2**−**4** were chosen to remove any ambiguity as to the source of excitation on the ultimate ring D acceptor, i.e. by contrast with a ketone, an olefin can only be activated by ketone or aryl donors through intraTTET.

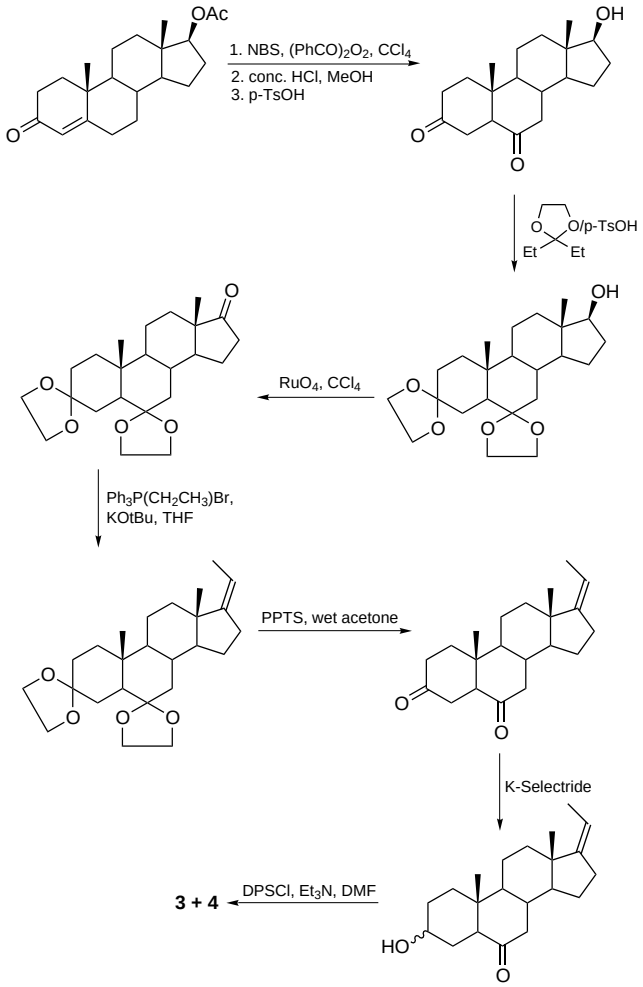
Our results demonstrate that excitation of the DPSO antenna with 266-nm light does indeed result in enhanced Z → E isomerization of the C17 ethylidene group in the ketonic steroids, thus confirming our proposal of the ketone as a multiplicity switch.

## Results

**Syntheses of the DPSO-Derivatized Steroids 1−4.** The C17 olefin, 3α-hydroxy-17-(*Z*)-ethylidene-5α-androstane, was prepared from androsterone by a Wittig reaction and silylated




**Scheme 1**




with chlorodimethylphenylsilane (DPSCl) to afford **1**. The reaction produced predominantly the *Z* isomer (97%), consistent with literature precedent[10] and with an X-ray analysis of **3** (see below). Epiandrosterone was used to prepare the 3*β* isomer of **1** (as the Z olefin) in like manner. The alcohol precursor for **2** (3α-hydroxy-5α-androstan-11,17-dione) was prepared by olefin reduction of $\Delta^4$-androstene-3,11,17-trione with lithium in ammonia followed by further regiospecific reduction at C3 with K-Selectride (the 3*β* hydrogen is evident as a singlet at *δ* 4.00; the C17 and C11 carbonyl carbons are seen as resonances at *δ* 217.81 and 209.32, respectively). A subsequent Wittig reaction is specific to C17 due to the steric encumbrance of C11. Again, the Z isomer predominates (97%). Compounds **3** and **4** were prepared from the commercially available testosterone acetate in 8 steps (Scheme 1). The two isomers were separated by flash chromatography. The structure assignment for **3** was confirmed by X-ray analysis (the X-ray structure and a table summarizing the crystal data and data collection parameters are provided as Supporting Information).

**Spectroscopy.** The UV absorption spectra of **2**−**4** in cyclohexane reflect the component aryl ($\lambda_{max}$ ca. 258 nm) and carbonyl ($\lambda_{max}$ 290−300 nm) chromophores and show no evidence of significant interaction between them. Compound **2** shows only aryl emission. Compounds **3** and **4** show dual emission with the aryl and ketone fluorescence maxima at ca. 285 and 430 nm, respectively. Compound **3** shows significantly

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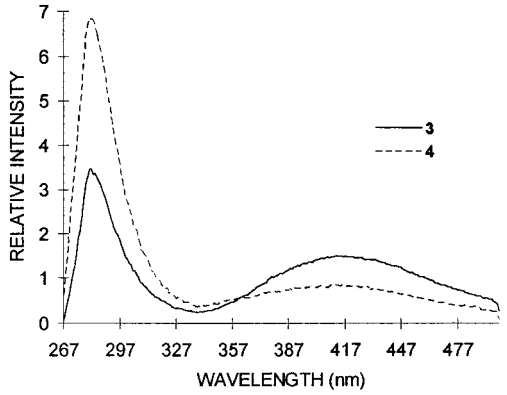


**Figure 1.** Normalized fluorescence spectra for **3** and **4** in cyclohexane.

**Table 1.** Fluorescence Quantum Efficiencies ($\phi_f$) and Lifetimes ($\tau_f$) for Compounds **1**, **2**, **3**, and **4** Using 254-nm Excitation[a,b]

| compd | $\phi_f$ | $\tau_f$ (ns) |
|---|---|---|
| **1** | 0.013 | 2.63 |
| **2** | 0.0024 | 0.55 |
| **3** | 0.0010 | 0.33 |
| **4** | 0.0027 | 0.67 |

[a] Solutions in cyclohexane with toluene emission in cyclohexane as the reference.[11] [b] $\phi_f$ and $\tau_f$ values estimated to be ±10% and ±0.1 ns, respectively.

**Table 2.** Fluorescence Quantum Efficiencies and Lifetimes Using 300-nm Excitation[a]

| compd | $\phi_f$(300 nm) | $\tau_f$ |
|---|---|---|
| **3** | $1.82 \times 10^{-3}$ | $4.0 \pm 0.2$ |
| **4** | $1.49 \times 10^{-3}$ | $3.6 \pm 0.1$ |
| 2-methylcyclohexanone | $1.43 \times 10^{-3}$ | $2.9 \pm 0.1$ |
| 3,17-diethylenedioxy-5α-androstan-11-one (**5**) | $4.5 \times 10^{-4}$ | $0.4 \pm 0.1$ |
| **2** | none detected | |

[a] Solutions in cyclohexane; acetone emission ($\phi_f = 9.3 \times 10^{-4}$) as the reference.[12]

more ketone emission than compound **4**, and its aryl fluorescence is considerably diminished relative to **4** (cf. Figure 1). The 0−0 transition energy for the DPSO $S_0 \rightarrow S_1$ transition is estimated from the onset at 270 nm to be 107 kcal/mol.

Fluorescence quantum efficiencies ($\phi_f$) and lifetimes ($\tau_f$) for compounds **1**−**4** were determined in cyclohexane at room temperature by using excitation of the DPSO antenna (254 nm) with toluene emission in cyclohexane ($\phi_f = 0.14$)[11] as the reference. The data are presented in Table 1.

Fluorescence quantum efficiencies and lifetimes were also measured for compounds **3**, **4**, 3,17-diethylenedioxy-5α-androstan-11-one (**5**), and 2-methylcyclohexanone in cyclohexane, using 300-nm excitation and with acetone emission in cyclohexane ($\phi_f = 9.3 \times 10^{-4}$)[12] as the reference. The results are summarized in Table 2.

Phosphorescence spectra for compounds **1** and **2** were obtained at 77 K in an ether/methylcyclohexane glass. An emission onset at 340 nm provided a triplet energy for the DPSO group of ca. $E_T = 84$ kcal/mol.

Table 3 summarizes the relevant singlet and triplet energies of the chromophores by using literature data (including our previous paper) and the current work.

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

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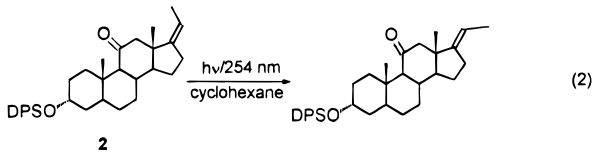
**Table 3.** Estimated Singlet and Triplet Energies[a]

| | DPSO | C6/C11 ketones | C17 olefin |
|---|---|---|---|
| $E_S$ | 107 | 84 | 135[b] |
| $E_T$ | 84 | 76 | 77[c] |

[a] Units of kcal/mol. [b] Estimated from ref 13a. [c] Estimated from ref 13b.

**Photochemistry. Photolysis of 2 in Cyclohexane.** Irradiation of an argon-degassed $1.1 \times 10^{-2}$ M solution of **2** in cyclohexane at 254 nm produced a single product (39.5%) (eq 2). The photoproduct has a GLC retention time identical with



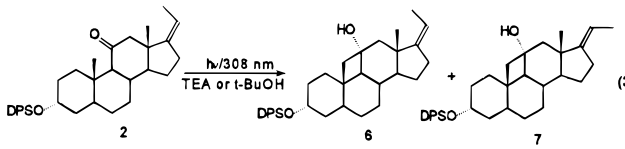

2 (2)

that of the small amount of E isomer formed as a side product in the synthesis of **2**. GC/MS with EI on the photolysis solution gave a parent ion at *m*/*e* 450. The $^1$H NMR spectrum of the reaction mixture further confirmed the presence of the E isomer with resonances at $\delta$ 5.02 (1 H, q) corresponding to the H-20 vinyl proton and at $\delta$ 1.53 (3 H, d, $J = 6$ Hz) for the allylic H-21 protons. The corresponding resonances for the Z isomer are at $\delta$ 5.11 and 1.66, respectively. The quantum efficiency for formation of the E isomer ($\phi_{Z\rightarrow E}$) was determined at 266 nm with a Nd:YAG laser and found to be 0.035.

In a separate photolysis with excitation at 308 nm with an excimer laser, the 17-E isomer was again observed as the only photoproduct. The quantum efficiency for formation of the E isomer at 308 nm was determined to be 0.041. The photostationary state was determined in cyclohexane with 254-nm light. The $[E]_{pss}/[Z]_{pss}$ ratio is 1.38.

**Photolysis of 2 at 308 nm in the Presence of Triethylamine (TEA).** It has been found that the reduction of the carbonyl group by TEA provides an effective means of testing for the creation, and involvement, of ketone triplet states in our steroid studies.[7c,d] Photolysis of an argon degassed cyclohexane solution of $1.1 \times 10^{-2}$ M **2** and $12.6 \times 10^{-2}$ M TEA with 308-nm light for 20 min showed a minimal effect of the amine, i.e. 5.8 and 6.3% of Z → E photoisomerization was observed with and without TEA, respectively.

After prolonged photolysis (190 min) a mixture of two new products was formed (6.6% by GLC). Replacing TEA by *tert*-butyl alcohol in an analogous experiment gave 5.3% of the new product mixture after 190 min. The products were isolated by flash chromatography and identified as a 2:1 mixture of the E/Z cyclobutanol isomers **6** and **7** (cf. eq 3). Though the two

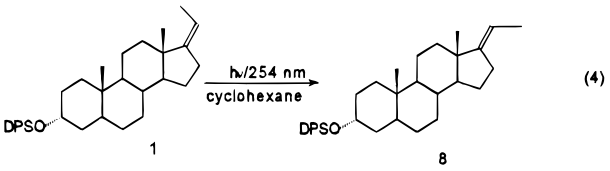



2 6 7 (3)

products could not be isolated in pure form, the $^1$H NMR spectrum of the mixture gave evidence of the cyclization through the absence of the characteristic resonance for the C19 angular methyl group. The C20 vinyl proton resonances at $\delta$ 5.07 (**6**) and 4.99 (**7**) and the C18 resonances at $\delta$ 0.99 (**6**) and 0.88 (**7**) were still evident. The IR spectrum of the mixture showed a broad peak at 2900 cm$^{-1}$ indicative of the presence of an alcohol.

**Photolysis of 1.** Irradiation of an argon-degassed cyclohexane solution of **1** at 254 nm produced a single photoproduct

(cf. eq 4). A $^1$H NMR spectrum of the product indicated

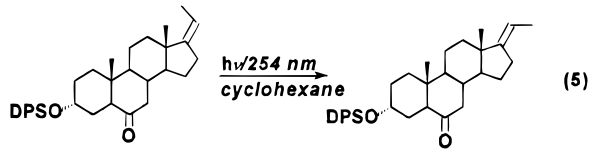



1 8 (4)

primary changes at the vinyl proton (to $\delta$ 5.02) and allylic methyl (to $\delta$ 1.54) resonances. Assignment as the 3αDPSO/17-E isomer was confirmed by comparison of the mass spectrum with an independently synthesized sample, prepared by silylation after *p-tert*-butyltoluene sensitized photolysis of the alcohol precursor of **1**. The quantum efficiency for Z → E isomerization of **1** was determined to be 0.043 with use of 266-nm light.

**Photolysis of 3*β*DPSO/17-Z.** Photolysis of the 3$\beta$ isomer of **1** with 254-nm light produced a single product that was identified as 3$\beta$DPSO/17-E by coinjection with a synthetic mixture of the two olefin isomers or with an independently prepared sample by using toluene sensitization of the precursor alcohol. The quantum efficiency for isomerization was determined by using **1** as a secondary actinometer and found to be 0.036. The 17-E isomer can also be formed by toluene sensitization of the 3$\beta$DPSO/17-Z substrate itself.

**Photolysis of 3.** Irradiation of an argon-degassed cyclohexane solution of **3** at 254 nm produced the 17-E isomer as a single product (cf. eq 5). A $^1$H NMR spectrum of a photostationary state mixture of the two olefins showed new resonances at $\delta$ 5.02 and 1.52 for the H-20 vinyl hydrogen and the allylic methyl group, respectively. The quantum efficiency for isomerization at 266 nm was found to be 0.36. The isomerization quantum efficiency was also measured at 308 nm and determined to be 0.46. The isomerization quantum efficiency at 254 nm was also determined for the 3$\beta$ isomer, **4**, and found to be 0.23. The photostationary state was determined in cyclohexane with 266-nm light and found to be $[E]_{pss}/[Z]_{pss} = 1.08$. An analogous experiment with 300-nm light gave a ratio of 1.13.




3 9 (5)

**Effect of Added *cis*-2-Heptene on the Photoisomerization of 1 and 3.** *cis*-2-Heptene was used to test for the possible involvement of intermolecular TTET by noting whether the added olefin quenched Z → E isomerization. For neither **1** nor **3** was any quenching observed when comparable concentrations of the olefin were present. Thus, for Z → E isomerization in the presence and absence of the heptene, at ca. $1 \times 10^{-2}$ M, concentrations of steroid and olefin were as follows: **1**, 16.9 and 16.7%; **3**, 36.1 and 36.5%, respectively.

**Effect of Added Triethylamine (TEA) on Z → E Photoisomerization of 3.** In a preliminary experiment $12.6 \times 10^{-2}$ M TEA was added to $1.02 \times 10^{-2}$ M **3** in cyclohexane and the solution photolyzed with 266-nm light. The extent of isomerization was reduced from 16.2% without the amine to 7.7% with TEA. The quenching was studied in greater detail by using 0.032−0.126 M TEA with $1.02 \times 10^{-2}$ M **3**. A Stern−Volmer plot of the data gave a slope and intercept of $k_q\tau = 8.5$ M$^{-1}$ and 1.0, respectively, with a correlation coefficient of 0.995.

**Table 4.** Efficiencies and Rate Constants for Intramolecular Singlet−Singlet Energy Transfer

| | from $\phi_f$ | | from $\tau_f$ | |
|---|---|---|---|---|
| compd | $\phi_{intraSSET}$ | $k_{intraSSET}$ ($\times 10^9$ s$^{-1}$) | $\phi_{intraSSET}$ | $k_{intraSSET}$ ($\times 10^9$ s$^{-1}$) |
| **2** | 0.82 | 1.5 | 0.79 | 1.4 |
| **3** | 0.92 | 2.8 | 0.88 | 2.7 |
| **4** | 0.79 | 1.2 | 0.75 | 1.1 |

## Discussion

**Photochemistry.** As shown in eqs 2−4, excitation of the antenna chromophore in each of the C3 DPSO steroids results in Z → E olefin isomerization at C17. The lack of quenching by external *cis*-2-heptene confirmed that energy transfer in these steroids is intramolecular, i.e. as with earlier cases, energy is being transmitted from the antenna in the A ring to the olefin in the ring D. Under normal conditions there is no observable chemistry at the C11 carbonyl group in **2** or at the C6 carbonyl in **3**. However, prolonged photolysis of **2** in cyclohexane containing TEA or *tert*-butyl alcohol produces, in addition to Z → E olefin isomerization, ca. 9% of a 2:1 mixture of Z and E isomers of product attributable to the C11 cyclobutanol.

**Energy Migration in Compounds 2, 3, and 4. Intramolecular Singlet/Singlet Energy Transfer (intraSSET).** It is clear from the fluorescence data in Table 1 that there is highly efficient intraSSET from the DPSO group to the carbonyl groups in compounds **2**−**4**. As one would expect, the aryl fluorescence efficiency (0.013) and lifetime (2.6 ns) in the bifunctional substrate, **1**, are typical of those observed for monofunctional DPSO substrates.[7] The presence of a carbonyl group at C11 (**2**) reduces the aryl $\phi_f$ to 0.0024, and the more proximal ketone at C6 further diminishes $\phi_f$ to 0.001. There is a corresponding reduction in the DPSO singlet lifetime to 0.55 and 0.33 ns, respectively. The quantum efficiency for intraSSET, $\phi_{intraSSET}(i)$, from the DPSO singlet to the ketone group in a substrate *i* can be calculated from either the $\phi_f$ or $\tau_f$ values by using the fluorescence data for **1** as a reference for the intrinsic photophysical properties of a DPSO group (cf. eqs 6 and 7).[7] The corresponding rate constants ($k_{intraSSET}(i)$) can then be calculated from the usual expression, $\phi_{intraSSET} = k_{intraSSET}\tau_f$.[14] The calculated values are given in Table 4.

$$\phi_{intraSSET}(i) = [\phi_f(\mathbf{1}) - \phi_f(i)]/\phi_f(\mathbf{1}) \quad (6)$$

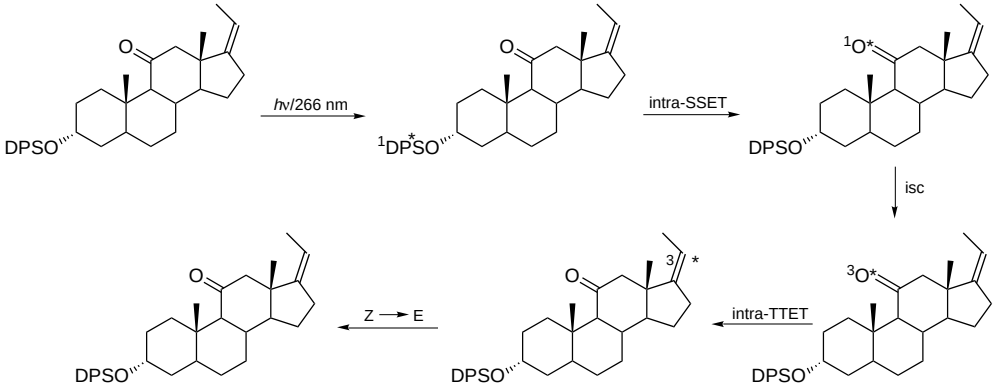
$$\phi_{intraSSET}(i) = [\tau_f(\mathbf{1}) - \tau_f(i)]/\tau_r(\mathbf{1}) \quad (7)$$

These results are consistent with our earlier report of $\phi_{intraSSET} = 0.68$ for energy transfer from the C3 DPSO antenna to the C11 carbonyl in 3α-DPSO-17-$\beta$-hydroxy-5α-androstan-11-one and 0.73 for $\phi_{intraSSET}$ from the C3 DPSO group to a C6 ketone.[7c,d] Likewise, the rate constants in Table 4 match well with the values of $2.2 \times 10^9$ and $1.7 \times 10^9$ s$^{-1}$ we have previously observed for C3 DPSO energy transfer to C11 and C6, respectively.[7c,d]

The energy transfer parameters for C3 → C6 in the 3$\beta$ DPSO isomer, **4**, are also given in Table 4 and clearly indicate that, as a donor, the 3$\beta$ antenna is some 15% less efficient and greater than 2-fold slower relative to the 3α isomer (**3**). These relative energy transfer efficiencies are reflected in the quantum efficiencies for antenna initiated Z → E olefin isomerization in **3** vs **4**, 0.36 and 0.23 respectively. We have seen comparable

(14) We note that there is an error in eq 9 of ref 7c. The denominator has the labels interchanged; the denominator should read as the multiple of $\phi_f(6)\tau_f(i)$. Rate constants in parentheses in Table VII for compounds **3**, **4**, and **1** in this reference are 1.2, 19, and 25 ($\times 10^8$ s$^{-1}$), respectively.

**Scheme 2**




levels of reduced intraSSET efficiency for the equatorial 3$\beta$ antenna in previous studies involving DPSO sensitization of C6 and C17 ketones.[7c,d] Our observation that intraTTET from the 3$\alpha$ DPSO group to the C17 olefin in **1** leads to a $\phi_{Z\rightarrow E}$ of 0.043 vs a value of 0.036 for the 3$\beta$ isomer further demonstrates the "3$\beta$/3$\alpha$ effect" (see additional discussion below).

We note that these observations are contrary to the general conclusions of Closs *et al.*,[8a−c,15] using cyclohexane and *trans*-decalin as spacers and the 2-naphthyl and 4-benzophenonyl groups as intraTTET acceptor and donor, respectively. In these studies, groups occupying an equatorial position were found to be more efficient as energy transfer donors. In the Closs systems the triplet energy migration proceeds through a Dexter-exchange, through-bond mechanism.[16] This is likewise the only feasible mechanism for migration of triplet energy from C3 to C17 in **1**, where the interchromophore distance (i.e., silicon bonded aryl carbon to C17) from X-ray analysis of the crystal is 9.85 Å.[17] However, intraSSET from an aryl donor to a ketone acceptor can proceed through both the exchange and resonance energy transfer mechanisms.[7c,d] The possibility that the latter participates in, e.g., **3** and **4**, and therefore contributes a *through-space* component to the energy migration process, prevents us from rationalizing the 3$\alpha$/3$\beta$ ratio in **3** and **4** solely in terms of a TBI interaction. Studies are in progress which will address the equatorial/axial issue for intraSSET in the steroid wire.

**Intramolecular Triplet/Triplet Energy Transfer. Energy Migration from C3 to C17.** The DPSO initiated isomerization of the C17 ethylidene group is unambiguously a consequence of intraTTET. The efficiency of energy migration ($\phi_{\text{intraTTET}}$) from the C3 DPSO group to C17 can be calculated with eq 8.

$$\phi_{Z\rightarrow E} = \phi_{\text{isc}}\phi_{\text{intraTTET}}F_{D\rightarrow E} \qquad (8)$$

Thus, we have elsewhere shown that $\phi_{\text{isc}}$ for a steroidal DPSO chromophore is 0.19.[7c] If one assumes a decay ratio for the orthogonal alkylidene triplet ("D") such that $F_{D\rightarrow E} = 0.58$ (as it does in **2** (see below)), then a $\phi_{Z\rightarrow E}$ of 0.043 for **1** leads to a calculated value for $\phi_{\text{intraTTET}}$ of 0.39. This is similar to the value of 0.21 measured earlier for $\phi_{\text{intraSSET}}$ from the $\alpha$ C3 DPSO donor to a C17 ketone.[7c,18] The less than complete triplet energy transfer observed by olefin photoisomerization is also consistent with the observation of significant DPSO phosphorescence from **1**.

**The C6 and C11 Carbonyl Groups as Singlet → Triplet Switches.** As noted in the Introduction, a primary objective for the current study was to confirm our proposal that a C11 ketone can function as a singlet−triplet switch. This must certainly be the case, though at first glance this may not be obvious from the DPSO sensitized olefin isomerization efficiencies, $\phi_{Z\rightarrow E}$: 0.035 for **2** (with a C11 ketone) vs 0.043 for **1** (no ketone). Recall, however, that intraSSET from the DPSO group to the carbonyl group in **2** is highly efficient (ca. 80%, cf. Table 4). *Clearly, olefin isomerization could only be occurring in **1** and **2** at a comparable efficiency if a portion of the DPSO singlet energy transferred to C11 ends up as triplet energy at C17.* The argument is even more cogent for compounds **3** and **4**, where the insertion of a C6 carbonyl group raises $\phi_{(Z\rightarrow E)}$ with 266-nm excitation to 0.36 and 0.23, respectively, several fold higher than the value of 0.043 without a ketone present. For these compounds, the efficiencies of intraSSET from the C3 DPSO group to C6 are as high as ca. 90% (Table 4). The complete mechanism (illustrated for antenna initiated isomerization in **2**) is presented in Scheme 2.

It is possible to calculate the efficiency by which singlet energy at C6 or C11 ultimately surfaces as triplet energy at C17 by using eq 9. Here $\phi_{Cn\rightarrow 17Z}$ (C$n$ = C6 or C11) actually

$$\phi_{Z\rightarrow E}(266\text{ nm}) = \phi_{\text{DPSO}\rightarrow Cn}\phi_{Cn\rightarrow 17Z}F_{D\rightarrow E} \qquad (9)$$

represents the product of $\phi_{\text{isc}}$ for the C6 or C11 ketones × $\phi_{\text{intraTTET}}$ (this is discussed further below). The quantum efficiencies for intraSSET ($\phi_{\text{DPSO}\rightarrow Cn}$), and for the overall isomerization ($\phi_{Z\rightarrow E}$(266 nm)), have been previously discussed. This missing parameter is the fraction of the relaxed olefin triplet diradical that decays to the E isomer ($F_{D\rightarrow E}$). This value is obtainable from the photostationary state by using eq 10. For

$$[E]_{\text{pss}}/[Z]_{\text{pss}} = (\phi_{Cn\rightarrow 17Z})/(\phi_{Cn\rightarrow 17E})(F_{D\rightarrow E}/F_{D\rightarrow Z}) \qquad (10)$$

compound **2**, the $[E]_{\text{pss}}/[Z]_{\text{pss}}$ was found to be 1.38. Assuming that $(\phi_{C11\rightarrow 17Z})/(\phi_{C11\rightarrow 17E}) = 1$, and that $F_{D\rightarrow E} + F_{D\rightarrow Z} = 1$, the calculated value of $F_{D\rightarrow E}$ was 0.58. Using an averaged value for $\phi_{\text{DPSO}\rightarrow C11}$ of 0.80 (cf. Table 4), *one calculates an overall efficiency for energy transfer from C11 to C17 of 0.075.* (Note that this value would decrease slightly to the extent that there is direct TTET by the residual DPSO triplets formed by the short-lived DPSO singlet.)

One can do the same analysis by using the data for direct excitation of the ketone group with 308-nm light. Equation 9 then simplifies to eq 11. Insertion of the measured $\phi_{Z\rightarrow E}$(308

(15) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652−2653. Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751−3753.

(16) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836−850. Katz, J. L.; Jortner, J.; Choi, S. I.; Rice, S. A. *J. Chem. Phys.* **1963**, *39*, 1897−1900.

(17) The X-ray analysis of **3** shows the $\alpha$ DPSO aromatic ring to be tucked under the steroid skeleton. This is in contrast to what was observed in the X-ray structure of the analogous 3$\alpha$ DPSO C17 ketone, where the DPSO group extends away from the steroid skeleton, and is therefore 12.85 Å from C17.[7d]

(18) We have elsewhere shown that singlet energy transfer from a C3 ketone to a C17 ketone is highly efficient.[1]

$$\phi_{Z\rightarrow E}(308\text{ nm}) = \phi_{C11\rightarrow 17Z}F_{D\rightarrow E} \quad (11)$$

nm) = 0.041 yields a value for energy transfer from C11 to C17 of 0.071, consistent with the number calculated from the 266-nm data. The analogous analysis for energy transfer from C6, employing the measured $[E]_{pss}/[Z]_{pss}$ of 1.08 for compound **3** (i.e. with $F_{D\rightarrow E} = 0.52$), and $\phi_{DPSO\rightarrow C6} = 0.90$ (Table 4), gives values of $\phi_{C6\rightarrow 17Z}$ of 0.77 and 0.87 (for 266 and 308 nm initiated isomerization, respectively). These values confirm that *triplet energy transfer from C6 to C17 is highly efficient.* The data obtained from the TEA quenching of alkene isomerization in **3** allow one to calculate the rate constant for C6 to C17 triplet energy transfer. Assuming that triplet quenching by the amine is diffusion controlled[19a,b] (in cyclohexane, $k_{diff} = 7 \times 10^9\ M^{-1}\ s^{-1}$),[19c] and that the ketone triplet lifetime (1.2 ns) calculated from the slope of the Stern−Volmer plot is entirely due to intraTTET, the calculated rate of intraTTET, $k_{C6\rightarrow 17Z}$, is $8.3 \times 10^8\ s^{-1}$.[20] This rate agrees well with the value of $1.3 \times 10^9\ s^{-1}$ determined for *trans*-1,4-(4-benzophenonyl-2-naphthyl)-cyclohexane in which the donor and acceptor are also separated by five bonds.[15]

The observation that *triplet* energy is efficiently transferred from C6 to C17 is consistent with our earlier observation that *singlet* energy also passes efficiently and rapidly between these two positions, i.e. $\phi_{intraSSET} = 0.85$ and $k_{intraSSET} \geq 4 \times 10^8\ s^{-1}$ for transfer between the C6 and C17 carbonyl groups.[7d] In effect, the C6 ketone serves as an excellent *energy relay* to C17 when an appropriate acceptor is at that site, and as an efficient *singlet−triplet switch/triplet donor* when there is no singlet acceptor available. The results at C11 (i.e. where $\phi_{C11\rightarrow 17Z}$ = ca. 7%) are strikingly different from that at C6, but again consistent with our earlier studies of the C11/C17 dione.[7c] There was also noted that only a small fraction (in this case, ca. 4%) of the singlet energy transferred to C11 from the C3 DPSO chromophore surfaced as C17 carbonyl triplet.

Some insight as to the origin of this energy loss at C11 is provided by the data in Table 2. There we note that the fluorescence quantum efficiencies ($\lambda_{exc}$ 300 nm) are ($\times 10^{-4}$): 18, 15, 14, and 4.5 for **3**, **4**, 2-methylcyclohexanone, and **5**, respectively. The corresponding lifetime data are 4.0, 3.6, 2.9, and 0.4 ns, respectively. Clearly, both $\phi_f$ and $\tau_f$ are markedly reduced for the ketone at C11 in **5** relative to the C6 keto steroids and a simplified model, 2-methylcyclohexanone. We attribute the diminution to deactivation of the C11 carbonyl singlet excited state by the proximate, axial C19 methyl group. In fact, the C11 carbonyl is known to form a cyclobutanol involving hydrogen abstraction from the C19 angular methyl group, reported, for example, upon photolysis of **5** in ethyl alcohol.[21] No quantum efficiency was reported but the reaction is very inefficient in our hands, i.e., $\phi_{dis} = 0.02$ in acetonitrile at 308 nm.[22,23] Thus, involvement of the methyl group would have to be primarily through an interaction with the ketone excited singlet state that was chemically unproductive, i.e., through reversible hydrogen abstraction or enhanced radiationless decay. In fact, recent reports confirm that n,$\pi^*$ excited singlet states are effectively deactivated by C−H bonds, an observation explained by the proposal that the reactants return to starting materials via an avoided crossing on the reaction surface which precedes the actual formation of a product radical pair.[24]

With these considerations in mind, we revisit the value for $\phi_{Cn\rightarrow 17E}$, which we noted above represents the product of intersystem crossing at C6 or C11 and the efficiency of triplet−triplet energy transfer to C17 ($\phi_{intraTTET}$). For C6, 77−87% of the singlet excitation at C3 ends up as triplet energy at C17, i.e., if $\phi_{isc}$ at C6 is essentially unity, these percentages are truly the corresponding values of $\phi_{intraTTET}$. However, the shortened singlet lifetime at C11 clearly will impact on the triplet yield at this position. An inefficient $\phi_{isc}$ would then be reflected in the 7% calculated overall efficiency of energy transferred and $\phi_{intraTTET}$ might also be quite high for C11 to C17. In fact, if one uses the $\phi_{Z\rightarrow E}$ of 0.041 observed for direct excitation of **2** with 308-nm light and *assumes* that $\phi_{intraTTET} = 1.0$,[25] one can use eq 8 to calculate a $\phi_{isc}$ for the C11 ketone of 0.07. This, combined with a plausible value for $k_{isc}$ of $2.5 \times 10^8$ to $3.0 \times 10^8\ s^{-1}$ (values obtained from the data for **3** and **4** in Table 2 assuming isc occurs in these compounds with unit efficiency), affords a singlet lifetime of 0.19−0.28 ns. Such a short lifetime would account for the failure to detect ketone fluorescence from **2** upon 300-nm irradiation. *We thus conclude that C11, like C6, efficiently transfers triplet energy to an olefin at C17, but the overall extent of energy transferred to the olefin suffers from a reduced triplet yield at C11.*

**Conclusions.** The trifunctional steroids 3αDPSO/6/17-Z, 3βDPSO/6/17-Z, and 3αDPSO/11/17-Z exhibit a rich array of photophysical and photochemical properties as a consequence of intramolecular singlet and triplet energy transfer. Of particular interest are the activation of the C17 ethylidene group through TBI-mediated triplet−triplet energy transfer and the ability of the C6 and C11 keto groups to act as "singlet → triplet switches" in relaying excitation energy from the DPSO antenna to the C17 alkene. This work, together with our previous reports,[1,7d] shows that groups at C6 can act as efficient (1) donors or relays of singlet energy, (2) singlet−triplet switches, and (3) transmitters of triplet energy. By contrast, the C11 ketone excited singlet state exhibits rapid radiationless decay, which prevents its function as a singlet energy relay and reduces its efficiency to act as a singlet−triplet switch + triplet energy relay.[26]

A complete summary of our observations to date on the steroid photonic wire is shown in Figure 2.

## Experimental Section

Only the salient experimental features are presented here; complete details may be found in ref 2b.

**Chemicals.** The following chemicals were obtained from Aldrich Chemical Company. Except where noted, they were used as received and stored at room temperature: adrenosterone; androsterone; chlo-

(19) (a) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419−1421. (b) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403−6406. (c) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; p 314.

(20) A referee has noted that the comparable rate constants may be fortuitous given the difference in triplet energies represented by the naphthalene/benzophenone and ketone/olefin donor/acceptor pairs. Unfortunately, we had insufficient material to do a similar analysis of **4**, and the classic steric impediments provided by neighboring axial methyl groups prevent TEA quenching at the C11 ketone in **2**.

(21) Wehrli, H.; Heller, M. S.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1961**, *44*, 2162−2173. Iriate, J.; Jeger, O. *Helv. Chim. Acta* **1963**, *46*, 1599−1609.

(22) Photolysis of **5** for 48 min with 300 nm light in a Rayonet Reactor, using *t*-butyl alcohol or triethylamine to facilitate ring closure,[23] led to a mixture of three products by glc which we attribute to α-cleavage products. Prolonged photolysis gave a fourth product at a longer retention time than **5** which we believe is the cyclobutanol. None of the fourth product was observable in the absence of added TEA or t-butyl alcohol.

(23) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898−5901. Wagner, P. J. *Tetrahedron Lett.* **1967**, 1753−1756. Wagner, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 5385−5388.

(24) Nau, W. M.; Cozens, F. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1996**, *118*, 2275−2282. Nau, W. M.; Cozens, F. L.; Adam, W.; Scaiano, J. C. *Book of Abstracts*; XVIth IUPAC Symposium on Photochemistry, July 21−26, 1996, Helsinki, Finland, pp 67 and 68.

(25) A referee has noted that an interaction with the angular methyl group may diminish $\phi_{intraTTET}$.

(26) The Z → E quantum efficiencies reported for compounds **1**, **2**, and **3** correct and replace those reported in the preliminary communication.

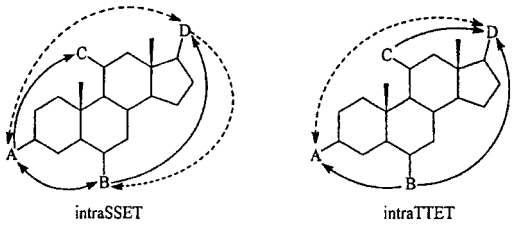



**Figure 2.** Summary diagram showing efficient (solid arrow, >50% ET) and inefficient (broken arrow, <50% ET) energy transfer pathways through the steroid photonic wire. Donors for intraSSET and intraTTET are aryl and keto chromophores. The acceptor for intraSSET is the keto group. Acceptors for intraTTET are both the keto and alkene moieties.

rodimethylphenylsilane; epiandrosterone; ethyltriphenylphosphonium bromide; 2-ethyl-2-methyl-1,3-dioxolane; K-Selectride, 1.0 M solution in tetrahydrofuran (THF); 2-methylcyclo-hexanone, distilled; palladium, 10% on activated carbon; pyridinium−*p*-toluene sulfonic acid (PPTS); ruthenium(IV) oxide hydrate; silica gel, Merck, grade 10181; and sodium periodate. Testosterone acetate was from Sigma.

Spectrograde solvents were used in the photochemical and spectroscopic studies without further purification: acetonitrile (Fisher and Baxter); cyclohexane (Aldrich); toluene (Fisher); acetone (Fisher). Tetrahydrofuran (THF, Mallinckrodt) and diethyl ether (Mallinckrodt) used in syntheses were distilled under nitrogen from sodium benzophenone ketyl. *N*,*N*-Dimethylformamide (Mallinckrodt) was treated with 4-Å molecular sieves followed by distillation under reduced pressure.

**Instrumentation.** Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1800 Fourier transform infrared spectrophotometer and a Perkin-Elmer Model 1420 ratio recording spectrophotometer. $^1$H NMR spectra were obtained in $CDCl_3$ with a GE 300-MHz NMR spectrometer with chemical shifts recorded in ppm relative to TMS at 0.0 ppm or relative to residual chloroform at 7.26 ppm. $^{13}$C and attached proton test (APT) spectra were also acquired on the GE spectrometer operating at 75.6 MHz. Carbon chemical shifts were recorded relative to $CDCl_3$ at 77.0 ppm. Mass spectra were recorded on Finnigan 4000 mass spectrometers, operating with a source temperature of 250 °C, interfaced to a gas chromatograph containing either packed or capillary columns. Electron impact (EI) and chemical ionization (CI) mass spectra were recorded at 70 eV, the latter with isobutane at a pressure of 0.30 Torr. High-resolution mass spectra were recorded on a Kratos Model MS-50 instrument operated at 70 eV for EI spectra. Ultraviolet absorption spectra were recorded on a Perkin-Elmer model Lambda 3B spectrophotometer interfaced to a Zenith microcomputer (Z-386/20) controlled by Perkin-Elmer computerized spectroscopy software (PECSS). Steady state fluorescence spectra were recorded on an SLM Aminco SPF-500C spectrofluorometer, using the A/B mode in all experiments. Fluorescence quantum efficiencies were obtained with reference to toluene or acetone and corrected for differences in absorbance, detector gain, and solvent refractive index; the spectral areas were numerically integrated by using SLM software ("500"). Fluorescence lifetimes were obtained with PTI Model 100 or LaserStrobe lifetime spectrophotometers at room temperature with the solutions purged with argon for at least 15 min prior to measurement. Phosphorescence spectra were run in an ether−methylcyclohexane glass at 77 K, which was degassed by using at least 3 freeze−pump−thaw cycles at $10^{-4}$ Torr.

**Photochemical Apparatus.** All photochemical studies were conducted at room temperature with solutions purged with argon for at least 15 min prior to use. Laser photolyses at 266 nm were conducted with a Continuum NY-61 Nd:YAG laser equipped with a frequency quadrupler (10 Hz, 3.0−3.3 mJ/pulse). A 2× beam enlarger was used in front of the photolysis cell to avoid cell damage. Photolyses with 308-nm light utilized a minics EX-700 Pulse Master Excimer Laser (10 Hz, 3.5 mJ/pulse) equipped with a Pyrex glass beam splitter and a laser beam mask with an open area 7 × 9 mm for photolysis of small solution volumes. All sample solutions for photolysis were purged with argon for at least 15 min prior to use. All photochemical reactions were run at room temperature. The power meters used in the photolyses were OPHIR Models 3A-P-CAL-S or 30A-P. Qualitative and quantitative photochemical experiments employing 254- (quartz tubes) and 300-nm (Pyrex tubes) light were performed in a Model RPR-100 Rayonet Reactor available from Southern New England Ultraviolet Company. The reactor was equipped with a merry-go-round turntable that positioned photolysis tubes approximately 2 cm from the lamps.

**Chromatography.** Analytical GLC was performed on a capillary gas chromatograph (Varian model 3700) equipped with a flame ionization detector utilizing a Hewlett-Packard 3390A integrator. The following J & W Scientific DB-1 capillary columns, 0.25 $\mu$m film thickness, were used in this work: A, 15.0 m × 0.25 mm i.d.; B, 12.5 m × 0.25 mm i.d. Analytical thin layer chromatography utilized silica gel 60A, 0.25 mm, coated on glass support (Whatman) visualized by using anisaldehyde or potassium permanganate spray reagent and a hand-held UV lamp. Flash chromatography was performed with silica gel 60 (E. Merck 9285, 230−400 mesh). Preparative separations were performed on a Chromatotron Model 7924T made by Harrison Research.

**Syntheses. 3α-(Dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstane (1).** To a slurry of ethyltriphenylphosphonium bromide (3.83 g, 10.33 mmol), dry THF (27 mL), and *t*-BuOK (1.2 g, 10.45 mmol) under an atmosphere of nitrogen in a 50-mL round-bottom flask was added 3α-hydroxy-5α-androstane-17-one (0.65 g, 2.15 mmol) dissolved in 2.5 mL of dry THF. After the mixture was stirred for 3 h at room temperature, additional ethyltriphenylphosphonium bromide (3.83 g, 10.33 mmol) and tBuOK (1.2 g, 10.45 mmol) were added. The mixture was stirred at room temperature for 60 h, poured into 100 mL of ice−water, and extracted 3 times with 25 mL of EtOAc. The combined extracts were washed with 3 × 25 mL of water and 25 mL of brine and dried over anhydrous $Na_2SO_4$. Filtration, solvent removal, and chromatography on silica gel (hexane−ether, 2:1) afforded 0.73 g (71% yield) of 3α-hydroxy-17-(*Z*)-ethylidene-5α-androstane as white crystals (GLC analysis of the product on column B indicated ca. 3% of the E isomer was present), mp 158−160 °C. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 5.12 (q, 1 H, H-20 vinyl H), 4.05 (s, 1H, 3$\beta$-H), 2.42−0.93 (m, 26 H), 0.87 (s, 3H, 19-$CH_3$), 0.79 (s, 3H, 18-$CH_3$); $^{13}$C NMR ($CDCl_3$, 75.6 MHz) $\delta$ 150.61 (17-C═C), 113.26 (20-C═C), 66.70, 56.40, 54.46, 44.20, 39.22, 37.35, 36.26, 36.02, 35.16, 32.26, 31.96, 31.52, 29.14, 28.64, 24.45, 21.07, 17.01, 13.20, 11.25.

The olefinic alcohol (0.51 g, 1.69 mmol) was dissolved in 5 mL of DMF in a 15-mL round-bottom flask under nitrogen. The flask was flushed with nitrogen for 10 min, and freshly distilled triethylamine (0.5 mL) was added by syringe under ice−salt cooling and constant stirring. Chlorophenyldimethylsilane (0.34 mL, 2.02 mmol) was added dropwise. After 1 h TLC analysis indicated that the reaction was complete. The mixture was diluted with 20 mL of benzene and then quickly washed with 2 × 4.0 mL of cold 5% $NaHCO_3$, 4.0 mL of cold 2% aqueous HCl, and again with 4.0 mL of $NaHCO_3$. The separated organic layer was dried with anhydrous $MgSO_4$. The crude product was purified by silica gel chromatography (5% EtOAc/95% hexane) to afford 0.59 g (80% yield) of the pure product as white crystals. These were further recrystallized from acetonitrile to afford the analytically pure title compound (GLC analysis indicated 1.1% of the E isomer to be present), mp 88−90 °C. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.63−7.37 (m, 5 H, arom), 5.14 (q, 1H, 20-vinyl H), 4.05 (s, 1H, 3$\beta$-H), 2.37−2.15 (m, 3 H), 1.69 (d, $J$ = 7.2 Hz, 3H, 21-allylic $CH_3$), 1.67−0.97 (m, 22 H), 0.89 (s, 3H, 19-$CH_3$), 0.78 (s, 3H, 18-$CH_3$), 0.38 (s, 3H, Si$CH_3$), 0.37 (s, 3H, Si$CH_3$); $^{13}$C NMR ($CDCl_3$, 75.6 MHz) $\delta$ 150.73, 139.27, 133.56, 129.40, 127.81, 113.25, 67.61, 56.46, 54.38, 44.54, 39.04, 37.40, 36.61, 36.14, 35.20, 32.48, 32.08, 31.62, 29.70, 28.69, 24.53, 21.12, 17.06, 13.27, 11.50, −0.77, −0.91. MS (EI) *m*/*e* 436 ($M^+$), 269 (100); high-resolution MS (EI) *m*/*e* calcd for $C_{29}H_{44}SiO$ 436.3161, found 436.3148.

**3α-(Dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstan-11-one (2).** This compound was prepared in a manner virtually identical with that described above. The crude product was purified by silica gel chromatography (5% EtOAc/95% hexane) to afford **2** in 69% yield as a white solid. GLC analysis indicated 2.7% of the E isomer was present, mp 117−119 °C. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.60−7.35 (m, 5 H, arom), 5.18 (q, 1H, 20-vinyl H), 4.00 (s, 1H, 3$\beta$-H), 2.74 (d × d, 2H, 12-$CH_2$), 2.46−1.66 (m, 9 H), 1.61 (d, $J$ = 7.0 Hz, 3H, 21-allylic $CH_3$), 1.60−1.13 (m, 9 H), 0.98 (s, 3H, 19-$CH_3$), 0.83 (s, 3H, 18-$CH_3$), 0.36 (s, 3H, Si$CH_3$), 0.35 (s, 3H, Si$CH_3$); $^{13}$C NMR ($CDCl_3$,

75.6 MHz) $\delta$ 211.38 (11-C=O), 147.61, 139.18, 133.52, 129.42, 127.80, 114.85, 67.35, 64.96, 56.19, 55.77, 47.62, 38.92, 36.16, 35.99, 35.80, 32.59, 31.82, 31.17, 29.39, 28.03, 24.20, 18.16, 13.02, 11.27, −0.78, −1.00. MS (EI) *m*/*e* 450 ($M^+$), 137 (100); high-resolution MS (EI) *m*/*e* calcd for $C_{29}H_{42}SiO_2$ 450.2954, found 450.2949.

**3α-(Dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstan-6-one (3) and 3*β*-(Dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstan-6-one (4): 17-(*Z*)-Ethylidene-3,6-diethylenedioxyandrostane.** To a slurry of ethyltriphenylphosphonium bromide (5.2 g, 14.0 mmol), dry THF (46 mL), and tBuOK (1.62 g, 14.5 mmol) under an atmosphere of nitrogen in a 250-mL round-bottom flask was added 3.0 mL of dry THF containing 1.82 g (4.67 mmol) of 3,6-diethylenedioxyandrostan-17-one (from 17*β*-hydroxy-5α-androstan-3,6-dione which had been prepared from testosterone acetate). After the mixture was stirred for 3 h at room temperature, additional ethyltriphenylphosphonium bromide (5.2 g, 14.0 mmol) and *t*-BuOK (1.62 g, 14.5 mmol) was added. The mixture was stirred at room temperature for 60 h and then poured into 400 mL of ice−water and extracted with ethyl acetate (3 × 100 mL). The combined extract was washed with 3 × 100 mL of water and 100 mL of brine and dried over anhydrous sodium sulfate. Filtration, evaporation of solvent, and chromatography on silica gel (40% EtOAc, 60% hexane) afforded 1.6 g (84% yield) of pure product as a white solid. A sample was recrystallized from acetone to afford white needles, mp 184−186 °C. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 5.10 (q, 1 H), 3.94−3.73 (m, 8 H), 2.37−1.02 (m, 23 H), 0.95 (s, 3H, 19-$CH_3$), 0.88 (s, 3H, 18-$CH_3$); $^{13}$C NMR ($CDCl_3$, 75.6 MHz) $\delta$ 150.206, 113.522, 109.779, 65.535, 64.320, 55.849, 53.464, 49.653, 44.487, 41.193, 37.319, 37.125, 37.002, 33.062, 31.434, 31.144, 29.390, 24.453, 21.309, 16.975, 13.620, 13.245, 0.122. MS (EI) *m*/*e* 402 ($M^+$); MS (CI) 403 (M + 1); high-resolution MS (EI) *m*/*e* calcd for $C_{25}H_{38}O_4$ 402.2770, found 402.2766.

**17-(*Z*)-Ethylidene-5α-androstan-3,6-dione.** A solution of 3,6-diethylenedioxy-17-(*Z*)-ethylidene-5α-androstane (1.54 g, 3.84 mmol) in wet acetone (40.0 mL) containing pyridinium tosylate (0.579 g, 2.3 mmol) was refluxed for 6 h. Excess solvent was then removed *in vacuo*, ether (100 mL) was added, and the mixture was washed with saturated $NaHCO_3$ (3 × 20 mL) and once with 20 mL of brine. The organic phase was dried with anhydrous $Na_2SO_4$ and the solvent removed *in vacuo* to give the diketone. GLC analysis indicated 95.7% C17 (Z) ethylidene and 3.2% of the corresponding E isomer. After the solution was dried under high vacuum, 0.9 g (75%) of product was obtained as a white solid. A sample was recrystallized from acetone, mp 174−176 °C. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 5.14 (q, 1H, 20-CH), 2.60−1.72 (m, 14 H), 1.65 (d, 3H, 21-$CH_3$, $J$ = 7.2 Hz), 1.58−1.20 (m, 6 H), 0.96 (s, 3H, C-19 $CH_3$), 0.89, (s, 3H, C-18 $CH_3$). $^{13}$C NMR ($CDCl_3$, 75.6 MHz) $\delta$ 211.269, 209.069, 149.075, 114.177, 57.583, 56.372, 53.555, 46.532, 44.717, 41.367, 38.129, 37.655, 37.467, 37.079, 36.705, 31.199, 24.319, 21.916, 16.949, 13.226, 12.642. MS (EI) *m*/*e* 314 ($M^+$), 299 (M − $CH_3$); MS (CI) *m*/*e* 315 (M + 1); high-resolution MS (EI) *m*/*e* calcd for $C_{21}H_{30}O_2$ 314.2246, found 314.2259.

**3-Hydroxy-17-(*Z*)-ethylidene-5α-androstan-6-one.** A 50-mL round-bottom flask with a side arm capped with a rubber septum was fitted with a magnetic stir bar and a condenser with a nitrogen inlet tube. The apparatus was flame dried under nitrogen and a solution of 3,6-dioxo-17-(*Z*)-ethylidene-5α-androstane (0.85 g, 2.71 mmol) in dry THF (12 mL) was syringed into the flask. The solution was stirred and cooled in a dry ice bath to −78 °C. A solution of K-Selectride (3.0 mL, 1 M in THF) was then added dropwise to the flask, and the yellowish mixture was stirred at −78 °C for 3 h. The mixture was warmed to room temperature, stirred for 20 min, and hydrolyzed by the addition of 8 mL of 50% ethanol in water. The organoborane was oxidized by the addition of 1.0 mL of 6 N sodium hydroxide and 3.2 mL of 30% hydrogen peroxide. The reaction mixture was saturated with anhydrous $K_2CO_3$ and the layers were separated. The aqueous layer was extracted with ether/THF (1:1). The organic layers were combined, washed with 1 N HCl solution and brine, and dried over anhydrous $Na_2SO_4$. After removal of the solvent *in vacuo*, the crude product was dried under high vacuum overnight to afford 0.84 g (98%) of product as a white solid. GLC analysis of the product indicated a mixture of 78% C-3 α-alcohol and 22% of the corresponding *β*-isomer. The crude product was used for the next reaction without further purification.

**3α-(Dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstan-6-one (3) and 3*β*-(Dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstan-6-one (4).** The alcohol mixture (0.72 g, 2.29 mmol), DMF (8.0 mL), and TEA (0.9 mL) was added to a dry three-neck flask equipped with a magnetic stir bar, rubber septa, and a nitrogen inlet. Stirring was commenced under nitrogen, and chlorodimethylphenylsilane (0.47 g, 2.75 mmol) was syringed into the reaction mixture at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was then diluted with benzene (40 mL) and washed successively with cold 5% $NaHCO_3$ (5 mL), 1 N HCl (5 mL), and 5% $NaHCO_3$ (5 mL). The organic layer was dried with anhydrous $NaSO_4$ and evaporated to give a crude product that was purified by silica gel chromatography (5% EtOAc, 95% hexane) to give 142 mg of crude 3*β*-(dimethylphenylsiloxy)-17-(*Z*)-ethylidene-5α-androstan-6-one (**4**) and the desired 3α isomer, **3**, as a white solid. Compound **3** was further purified by two recrystallizations from acetonitrile to afford 500 mg of product as white needles (100% GLC pure), mp 145−146 °C. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.58−7.36 (m, 5 H, arom), 5.15 (q, 1H, 20-CH), 4.11 (s, 1H, 3*β*-H), 2.75−1.21 (m, 23 H), 0.87 (s, 3H, 19-$CH_3$), 0.71 (s, 3H, 18-$CH_3$), 0.35 (s, 6H, $Si(CH_3)_2$). MS (EI) *m*/*e* (rel intensity): 451 (M + 1), 450 ($M^+$, 50), 435 (M − $CH_3$, 33), 135 (100); MS (CI) *m*/*e* 451 (M + 1, 100), 299 (89); high-resolution MS (EI) *m*/*e* calcd for $C_{29}H_{42}SiO_2$ 450.2954, found 450.2945.

Compound **4** (142 mg) was also obtained from the silica gel chromatography and was recrystallized from acetonitrile, mp 115−116 °C; MS (EI) *m*/*e* 450 ($M^+$, 7), 135 (100); high-resolution MS (EI) *m*/*e* calcd for $C_{29}H_{42}SiO_2$ 450.2954, found 450.2948.

Crystals of **3** were prepared by recrystallization from acetonitrile. A colorless plate of crystal having approximate dimensions of 0.25 × 0.20 × 0.13 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Cu Kα radiation ($\lambda$ = 1.54184 Å) on an Unroof-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained for least-squares refinement by using the setting angles of 25 reflections in the range $17 < \theta < 43°$ measured by the computer-controlled diagonal slit method of centering. The data were collected at a temperature of 295 ± 1 K by using the $\omega - 2\theta$ scan technique. Data were collected to a maximum of $2\theta$ of 136.3°.

**Photolysis of 3 with 266-nm Light.** A degassed solution of **3** in cyclohexane (10.46 mM, 1.0 mL) was irradiated for 2 min with the 266-nm laser at a power of 4 mJ/pulse. GLC analysis on column A at 240 °C indicated a new peak at $t_R$ = 8.12 min, which corresponded to the E isomer ($t_R$ for the Z isomer = 8.78 min). A $^1$H NMR spectrum of the reaction mixture indicated an upfield shift of the C20 vinyl proton resonance from $\delta$ 5.18 to $\delta$ 5.13 and an upfield shift of the allylic C21 methyl resonance from $\delta$ 1.66 to $\delta$ 1.52 (d, $J$ = 6.9 Hz) for the E isomer. Compound **1**, **2**, and **4** were similarly photolyzed in cyclohexane and analyzed by GLC. In all cases the E isomer was the only photoproduct detected.

**Photolysis of 3 with 300-nm Light.** A degassed solution of **3** in cyclohexane (13.1 mM, 3.0 mL) was irradiated for 26.0 min with 300-nm light. GLC analysis on column A at 240 °C indicated the formation of a new product with a retention time identical with that obtained from the 266-nm irradiation. Likewise, the $^1$H NMR spectrum of the product mixture matched that obtained from the 266-nm irradiation.

**Photolysis of 3*β*DPSO/17Z with 254-nm light.** Irradiation of a 5.0-mL solution of argon degassed 11.0 mM 3*β*DPSO/17-Z in cyclohexane with 254-nm light for 1 produced a single product (16.7%) by GLC analysis on column B. The product was identified as 3*β*DPSO/17-E by coinjection on the gas chromatograph with the starting material (which contains ca. 3% of the E isomer).

**Determination of the Photostationary State for 3.** A degassed solution of **3** in cyclohexane (13 mM, 3.0 mL) was photolyzed at various time intervals with use of 308-nm light and analyzed by GLC to determine the amount of the E isomer formed. The results are summarized in Table 5. A photostationary state ratio (E/Z) of 1.2 was obtained. The same experiment repeated with 254-nm lamps gave a photostationary state ratio of 1.08.

**Determination of the Photostationary State for 2.** A degassed solution of **2** in cyclohexane (6.61 mM, 5.0 mL) was photolyzed at various time intervals with 254-nm light and analyzed by GLC on

**Table 5.** Photostationary State Data for **3** at 266 nm

| photolysis time (min) | % E isomer | % Z isomer |
|---|---|---|
| 1.5 | 30.9 | 67.7 |
| 2.5 | 39.4 | 59.5 |
| 3.5 | 44.3 | 54.8 |
| 4.5 | 48.1 | 49.9 |
| 5.5 | 48.6 | 51.4 |
| 9.5 | 51.9 | 48.1 |
| 11.5 | 51.9 | 48.1 |

**Table 6.** Photostationary State Data for **2** at 266 nm[a]

| photolysis time (min) | % E isomer | % Z isomer |
|---|---|---|
| 40.0 | 35.4 | 64.6 |
| 80.0 | 50.4 | 48.6 |
| 100.0 | 54.4 | 45.6 |
| 130.0 | 58.2 | 41.8 |
| 160.0 | 58.4 | 41.6 |

[a] In cyclohexane.

column B at 240 °C. The photostationary state ratio (E/Z) was determined to be 1.38. The data are presented in Table 6.

**Quantum Efficiency Determinations.** A quartz cuvette containing 1.0−2.0 mL of argon degassed sample solution of ca. 7−15 mM was placed in a sample holder and irradiated with the 266- or 308-nm laser for 3−9 min. Dark control experiments were carried out at the same temperature for each of the quantum efficiency measurements.

**Photolysis of 1 and 3 in the Presence of *cis*-2-Heptene.** Degassed cyclohexane solutions of **3** (15.34 mM, 3 mL) with and without 15 mM *cis*-2-heptene were photolyzed in matched quartz tubes with 254-nm light. GLC analysis of the photolysates indicated 36.1 and 36.5% formation of the E isomer with and without *cis*-2-heptene, respectively. The same experiment conducted with **1** (11 mM, 3 mL) and 11 mM 2-heptene in cyclohexane gave 16.9% and 16.7% Z → E olefin isomerization with and without *cis*-2-heptene, respectively.

**Table 7.** Effect of Added Triethylamine (TEA) on *Z* → *E* Olefin Photoisomerization of **3**

| [TEA] (mM) | $\phi$ | $\phi_0/\phi$ |
|---|---|---|
| 0.0 | 0.55 | 1.00 |
| 32.1 | 0.46 | 1.31 |
| 64.7 | 0.39 | 1.54 |
| 96.8 | 0.34 | 1.78 |
| 125.5 | 0.29 | 2.09 |

**Photolysis of 2 and 3 with TEA.** Two degassed cyclohexane solutions of **2** (2 mL, 10.7 mM), with and without TEA (35 $\mu$L, 125.5 mM), were irradiated in quartz cells at room temperature for 10 min with the 308-nm excimer laser (3.4 mJ/pulse). The solutions were analyzed by GLC on column A at 240 °C. The E isomer was formed to the extent of 5.8 and 6.3% with and without TEA, respectively. The experiment was repeated with compound **3** (1 mL, 10.6 mM), with and without TEA (35 $\mu$L, 125.5 mM), to give 7.7 and 16.2% E isomer with and without TEA, respectively. An analysis with varying concentrations of TEA gave the data shown in Table 7.

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**Supporting Information Available:** The X-ray structure and a table summarizing the crystal data and data collection parameters for compound **3** (4 pages). See any current masthead page for ordering and Internet access instructions.

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