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Antenna-Initiated Photochemistry of Distal Groups in Trifunctional Steroids. *Z*→*E* Olefin Photoisomerization Involving Ketone Singlet → Triplet Switches by Through-Bond Energy Transfer

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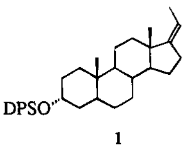
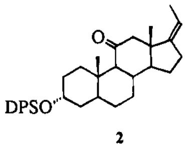
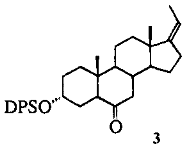
We have been interested in the potential use of "antenna" chromophores to harvest photon energy and effectively and selectively activate distal functionalities. Our studies have utilized the dimethylphenylsilyl (DPS) group as the antenna, because of its important characteristic properties outlined in an earlier report,[2] and the ketone functionality as the potential recipient of intramolecular singlet−singlet and triplet−triplet energy transfer (intra-SSET and intra-TTET, respectively). These have been mounted on the 5α-androstane steroid framework. In an earlier report[3] we showed that excitation of the DPS chromophore in 3α-(dimethylphenylsiloxy)-5α-androstane-11,17-dione (3αDPS/11/17) leads to triplet photochemistry at C17, although the C17 ketone itself intersystem crosses with very low efficiency. We proposed that activation at C17 occurs by efficient intra-SSET from the DPS chromophore to C11, intersystem crossing of this ketone, and intra-TTET from C11 to C17. Thus, the C11 carbonyl group serves as a *"singlet−triplet switch"*. To verify and expand this proposal we have investigated energy migration in the trifunctional steroids 3α-(dimethylphenylsiloxy)-17(*Z*)-ethylidene-5α-androstan-11-one, **2**, and its C6 carbonyl analog, **3** (3αDPS/11/17Z and 3αDPS/6/17Z, respectively). In these compounds, the ultimate olefin acceptor can only be activated by either the ketone or aryl donor through intra-TTET. The 3αDPS/17Z substrate **1** was used as our reference. These compounds were prepared by standard methods; the configurations of the DPS and olefin groups were assigned by NMR and confirmed by X-ray analysis of compound **3**.[4]



1



2

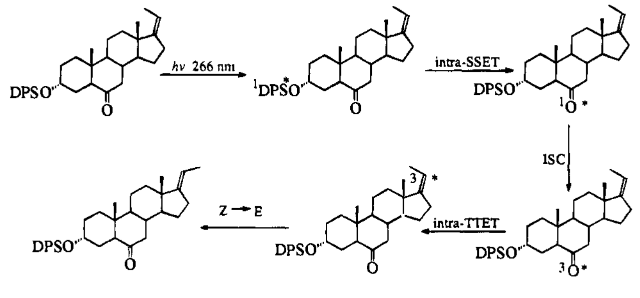


3

Table 1: Photophysical and Photochemical Data for Compounds **1**, **2**, and **3**

	ϕ_f	τ_f (ns)	$\phi_{Z\to E}$ (266 nm)	$\phi_{Z\to E}$ (308 nm)
1	0.013	2.63	0.12	
2	0.0024	0.55	0.11	0.15
3	0.001	0.33	0.55	0.67

Scheme 1



We find that excitation of the DPS antenna with 266 nm light (Nd:YAG laser; cyclohexane) does indeed result in *Z*→*E* isomerization of the C17 ethylidene group in all three of these steroids. This is the case even though it is clear from fluorescence data (Table 1) that there is highly efficient intra-SSET[5] from the DPS group to the carbonyl groups in both **2** and **3**. Thus, **1** shows strong DPS fluorescence with a ϕ_f of 0.013 but the presence of the carbonyl groups reduces ϕ_f to 0.0024 and 0.001 in **2** and **3**, respectively. These values correspond to ca. 82% and 92% efficient intra-SSET from the DPS group to C11 and C6, respectively.[6] These efficiencies of energy transfer, calculated from the steady state emission data, compare well with corresponding values (ca. 80% and 87%, respectively) calculated from lifetime data[6] and with intra-SSET values for 3αDPS to C6 and C11 obtained in earlier work with mono- and diketones.[3,6]

The quantum efficiencies ($\phi_{Z\to E}$) for olefin isomerization upon excitation with 266 nm light are also given in Table 1. The model, **1**, gives a value of 0.12, not surprising since the DPS group is known to intersystem cross with ϕ_{isc} = ca. 0.16[6] and intra-TTET from C3 to C17 has been demonstrated by us and others.[3,6] However, the $\phi_{Z\to E}$ for **2** (0.11) is comparable to that for **1**, and a much higher value (0.55) is measured for **3**. Clearly, with 80−90% of the DPS singlet states diverted to the carbonyl groups the only way olefin triplet isomerization can be occurring with comparable or higher efficiency is if a large fraction of the ketone singlets are being "switched" to ketone triplets prior to energy transfer to C17. This is depicted in Scheme 1 using **3**; a comparable mechanism could be drawn for **2**.[7]

The rate constants for singlet energy transfer from DPS to C11 and C6 in **2** and **3** can be calculated from the ϕ_f and τ data as 1.7×10^9 and 4.6×10^9 s^{-1}, respectively, values which are again in good agreement with earlier data.[3,6] As to the rate constants for the second energy transfer steps (intra-TTET), we have indirectly measured this for **3** by using triethylamine (TEA) to quench the C6 triplet in competition with energy transfer to C17. A Stern−Volmer plot of the data provides a slope and intercept which are $k_q\tau$ = 8.5 and 1.0, respectively, with a correlation coefficient of 0.995.[8] Assuming that triplet quenching by the amine is diffusion controlled (in cyclohexane, $k_q = 7 \times 10^9$ M^{-1} s^{-1})[9] and that the intrinsic triplet lifetime (1.2 ns) calculated from the slope is entirely due to intra-TTET (not entirely true; see below), a maximum rate for TTET from C6 to C17 is calculated to be 8.3×10^8 s^{-1}.[10]

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(1) Organic Photochemistry. 106. Part 105: Terrian, D. J.; Mohammad, T.; Morrison, H. *J. Org. Chem.* in press.

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

(3) Wu, Z.-Z.; Nash, J.; Morrison, H. *J. Am. Chem. Soc.* **1992**, *114*, 6640−6648.

(4) Satisfactory analytical data for all new compounds are in hand; spectral data will be presented in the full paper.

(5) The intramolecularity of the energy transfer was confirmed by control studies using *cis*-2-heptene as an external quencher. We found that the presence of *cis*-2-heptene did not affect the efficiency of *Z* → *E* isomerization in compounds **1**, **2**, and **3**.

(6) Wu, Z.-Z.; Morrison, H. *J. Am. Chem. Soc.* **1992**, *114*, 4119−4128.

(7) It is interesting that the role of C6 as a potential singlet−triplet switch was masked in our earlier work with 3αDPS/6/17 because of the very facile intra-SSET that occurs in this compound.[3] As already noted, such SSET is not feasible with the 17 olefin.

(8) Reduction at C6 results from this quenching; the products will be discussed in the full paper.

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

(10) TEA does not quench the C11 ketone triplet, presumably due to either steric inhibition or an even faster rate of intra-TTET.

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Further insight into the details of energy migration is provided by the quantum efficiencies for $Z \rightarrow E$ isomerization when the ketone groups are directly excited using 308 nm (XeCl laser) light. These values (Table 1) are 0.15 and 0.67 for **2** and **3**, respectively, slightly larger than the efficiencies measured for initial DPS excitation. That there should be some loss in excitation energy between the first and second energy transfer steps is not surprising, but the low 266 and 308 nm values for **2**, given the closer proximity of C11 to C17, were unexpected. A likely source of energy loss in **2** would be the C19 angular methyl group, which may be interacting with, and thus deactivating, the C11 ketone excited states.[11]

In summary, the trifunctional steroids **2** and **3** exhibit a rich array of photophysical and photochemical properties as a consequence of intra-SSET and intra-TTET processes. These compounds provide further evidence for the activation of a C17 functionality by a C3 antenna through intervening ketone functionalities acting as single–triplet switches.[12]

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(11) Photoinduced hydrogen abstraction from a C19 angular methyl group by a C11 ketone to give a cyclobutanol has been reported; see: (a) Wehrli, H.; Heller, M. S.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1961**, *44*, 2162–2173. (b) Iriarte, J.; Jeger, O. *Ibid.* **1963**, *46*, 1599–1609. No quantum efficiencies are reported, but the reaction, in our hands, appears to be quite inefficient. Our studies of this process will be given in the full paper.

(12) For another example of the conversion of singlet energy to triplet energy within a polyfunctional molecule, see the studies of 4,4-di-β-naphthylcyclohexa-2,5-dien-1-one in the following: Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745–7756.