ductivity at room temperature (compressed pellet, two-probe measurement) is found to be 10^{-5} S cm^{-1} with an activation energy of 0.3 eV.

In conclusion, we have synthesized and characterized for the first time the three redox states of the odd alternant phenalenyl system having donor and acceptor substituents. These results might be fundamentally important for exploration of new organic materials having interesting electrical and magnetic properties.[4,6,18]

Supplementary Material Available: Table II listing *g* values and coupling constants for **1·** and **2a·–2d·**, Tables III–VI listing ^{1}H and ^{13}C NMR data for the cations and anions of **1** and **2a–d**, Tables VII and VIII listing ^{1}H NMR data for **9a–c** and high-resolution mass spectral data for **9a–d**, respectively, and Figure 2 showing EPR spectra and computer simulations for **1·** and **2a·–2d·** (8 pages). Ordering information is given on any current masthead page.

(17) This absorption band might be attributed to the charge-transfer excitation from the singly occupied nonbonding molecular orbital (NBMO) in the neutral radical to the unoccupied NBMO in the cation.

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Photoactivation of Distal Functional Groups in Polyfunctional Molecules. Intramolecular Aryl Sensitized Ketone Photoreduction via an Internal Singlet–Triplet Switch[1]

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There has been recent interest in the phenomenon of aryl to ketone intramolecular singlet–singlet energy transfer (intra-SSET),[2,3] stimulated partially by the possibility that such intra-SSET might be used to achieve the selective photoreduction of a single carbonyl group in multiketonic systems.[4] In a prototypical study, it was shown that the dimethylphenylsiloxy (DPS) group provided an effective "antenna chromophore" to internally sensitize carbonyl photoreduction in, e.g., 4-(dimethylphenylsiloxy)cyclohexanone, using 254-nm light.[4c] We now report the application of this methodology to the steroidal ketones, 3α-(dimethylphenylsiloxy)-5α-androstane-11,17-dione (**1**) and 3α-(dimethylphenylsiloxy)-5α-androstan-17-one (**2**).[5] In the former system,

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(5) Compounds **1** and **2** were readily prepared by silylation of the parent steroids. Satisfactory spectral data and elemental analyses by high-resolution FAB mass spectrometry are in hand for these compounds as well as for compounds **3–6**.

Scheme I
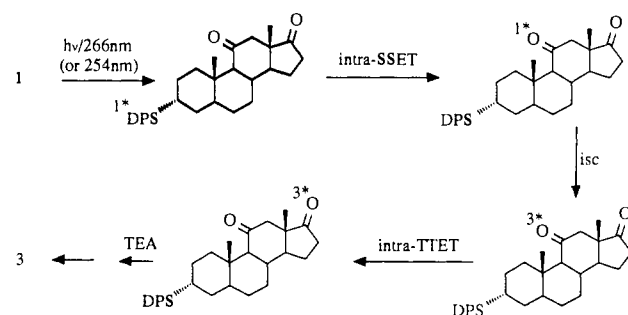
we have observed the self-sensitized, site-specific reduction of the 17-keto group via a remarkable energy relay mechanism in which the 11-keto moiety functions as an intermediate single–triplet switch.

Our initial studies with compound **1** utilized 2-propanol as the reductant/solvent, the methodology successfully employed in the cyclohexanone series.[4c] Photolysis of the antenna chromophore with 254-nm light did indeed result in ketone photochemistry, solely at C-17, but with α-cleavage and epimerization of ring D,[6] rather than reduction, as the major process. Since the rate constant for the quenching of ketone triplets by triethylamine (TEA) is some 3 orders of magnitude greater than that for 2-propanol,[7] we anticipated that photoreduction by TEA would more effectively compete with the α-cleavage.[8] In fact, irradiation of **1** (14.8 mM) at 254 nm in the presence of TEA (36.0 mM) in degassed acetonitrile for 40 min again leads to photochemistry solely of the 17-keto functionality, but with the reduction product **3** formed in 83% yield by GC (57% isolated)[9] and only trace amounts of the epimerization product **4** (cf. eq 1).[10] A similar irradiation of the monoketone **2** (14.1 mM), gave a mixture of the reduced product **5** and the epimer **6** in a ratio of 3.6:1.0 (cf. eq 2).[11]
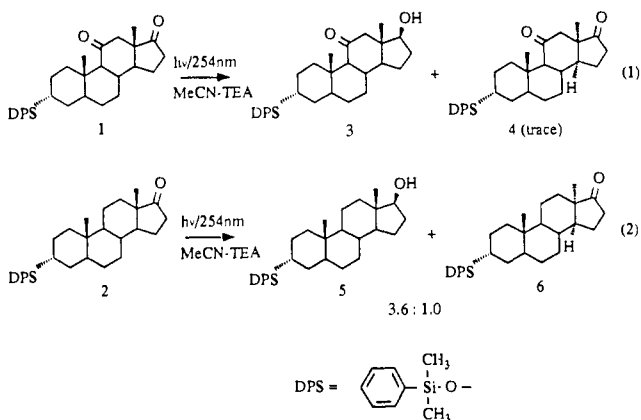
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(9) We found compound **3** to be relatively photostable in the presence of TEA in acetonitrile; photocyclization of related 11-keto steroids has been reported; cf.: Wehrli, H.; Heller, M. S.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1961**, *44*, 2162–2173. Iriarte, J.; Schaffner, K.; Jeger, O. *Ibid.* **1963**, *46*, 1599–1609.

(10) There is little likelihood of sensitized reduction by TEA excited states since the fluorescence of saturated tertiary amines is quenched by acetonitrile at a diffusion-control rate; cf.: Halpern, A. M.; Wryzykowska, K. *J. Photochem.* **1981**, *15*, 147–157.

(11) The alcohols were independently synthesized by reduction of the ketone with sodium borohydride in ethanol. Borohydride reduction of the 17-ketone functionality in the androstane series is known to give 17β-alcohols; cf.: Norymberski, J. K.; Woods, G. F. *J. Chem. Soc.* **1955**, 3426–3430.

The quantum efficiencies for the formation of **3** (ϕ_3) were measured as a function of the TEA concentration (32.3–91.5 mM) at [**1**] = 17.0 mM, using a Nd:YAG laser to provide monochromatic 266-nm light. The linear plot of $1/\phi_3$ vs $1/$[TEA] (slope = 2.02 (correlation coefficient = 0.999); intercept = 10.1) provides a limiting quantum efficiency for reduction of 0.099. The photochemistry of **2** is also dependent on the TEA concentration (e.g., 43.1–91.5 mM), with the quantum efficiencies for reduction increasing in this range from 0.018 to 0.031 while the quantum efficiencies for epimerization diminish more modestly from 0.038 to 0.027. The photoreduction of both **1** and **2** can be completely quenched by *cis*-piperylene (119 mM), whereas ϕ_0/ϕ for the photoepimerization of **2** is only 1.14. Both observations are consistent with the observation that the photoreduction of cycloalkanones is generally triplet derived[8b,12] whereas α-cleavage often has a significant singlet component[13a] (in 8-methyl-1-hydrindanone, 87%).[13b]

Of particular note is the observation that the photoproduct distribution for **1** depends on the wavelength of excitation. Photolysis of **1** with the 266-nm laser ([TEA] = 75.4 mM) gives only the reduced product **3** and no detectable epimer **4** (comparable to the observation at 254 nm; see above). However, excitation at 300 nm ([TEA] = 108 mM) gives rise to more epimerization than reduction (**4**/**3** = 1.8)! Since **3** is totally triplet derived while epimerization primarily occurs via the excited singlet state, *these differences in product distribution require that when excitation occurs through the aryl antenna, the 17-keto triplet is formed without the intermediacy of the 17-keto excited singlet state!* Direct irradiation of the carbonyl group(s) at 300 nm will, of course, generate both the 17-keto singlet and triplet states so that the formation of the epimer under these conditions is unexceptional. This situation is unique to the diketone; the product ratio from excitation of **2** is *independent* of the wavelength of excitation, and irradiation of the antenna at 254 or 266 nm leads to appreciable amounts of the primarily singlet derived epimer **6**.

This proposal is consistent with the sequence presented in Scheme I.

Excitation of the aryl antenna with 254- or 266-nm light leads to the 11-keto excited singlet state via intra-SSET.[14] Rapid intersystem crossing generates the 11-keto triplet, which undergoes triplet–triplet energy transfer (intra-TTET), to form the 17-keto triplet, which is ultimately reduced by TEA. The 11-keto group acts as an internal *singlet-triplet switch*, which effectively limits excitation of the 17-keto functionality to the triplet manifold.

This mechanism for activation of the 17-keto group is supported by a comparison of the fluorescence data for compounds **1–3** and **5** (cf. Figure 1). The ϕ_f values for **1**, **2**, **3**, and **5** in acetonitrile are 0.0017, 0.0047, 0.0020, and 0.0053, respectively, and one notes that (a) those compounds containing a keto moiety (i.e., **1–3**) show a diminution in the aryl fluorescence intensity relative to the emission of the aryl alcohol **5** and (b) the two substrates containing an 11-keto group (**1** and **3**) have considerably reduced aryl fluorescence relative to compound **2**, which has only the more distant 17-keto acceptor group. Particularly noteworthy is the small additional diminution in aryl fluorescence in **1** (containing both the 11- and 17-keto groups) vs **3** (containing only the 11-keto group). The first observation confirms that there is intra-SSET in all three aryl ketones while the second is consistent with intra-SSET to the 11-keto chromophore being appreciably more efficient than energy transfer to the more remote 17-keto functionality, i.e., direct SSET from the antenna to the 17-keto group in **1** may be assumed to be minimal. The latter conclusion explains
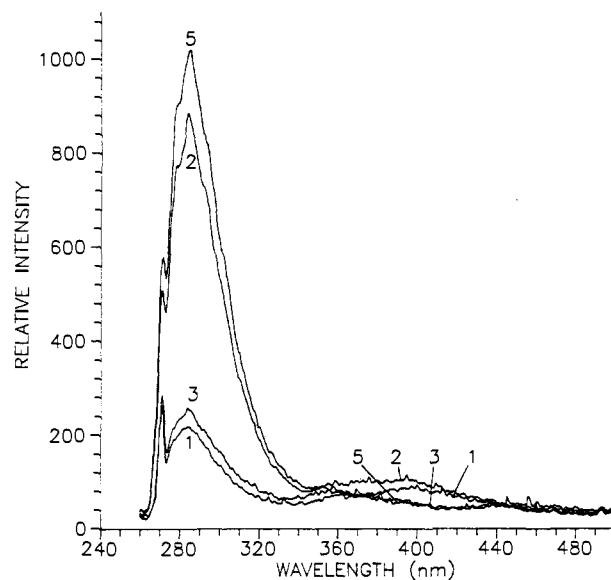

Figure 1. Fluorescence spectra of compounds 1–3 and 5 in cyclohexane with λ_{ex} = 254 nm.

why there is no evidence for the 17-keto singlet upon excitation of the antenna; excitation is totally funneled through the 11-keto group, which transfers energy to the 17-keto group after intersystem crossing. The quantum efficiencies for intra-SSET within these keto steroids may be calculated by using their aryl ϕ_f values with **5** as a model system (cf. eq 3), where n represents one of

$$\phi_{\text{intra-SSET}}^{n} = (\phi_f^5 - \phi_f^n)/\phi_f^5 \tag{3}$$

the aryl ketone substrates. The corresponding $\phi_{\text{intra-SSET}}$ valus are 0.68, 0.11, and 0.62 for compounds **1**, **2**, and **3**, respectively. Using the ϕ_f (0.0053) and $^1\tau$ (ca. 0.63 ns)[14] values for **5**, and assuming that the k_f values for the DPS group are comparable in **2**, **3**, and **5**, one can calculate[3,4c] the rate constants for intra-SSET ($k_{\text{intra-SSET}}$) for energy transfer from the antenna to the 11-keto group in **3** and the 17-keto group in **2**. These are 2.6 × 10⁹ and 2.0 × 10⁸ s⁻¹, respectively. The more rapid transfer to the 11-keto group is due to the closer interchromophore distance in this case (ca. 6.4 Å) relative to that for the 17-keto functionality (ca. 10.2 Å).[15,16] The antenna to 11-keto rate constant is comparable to that (2.9 × 10⁹ s⁻¹) previously determined[4c] for a cyclohexanone model system where the interchromophore distance is also ca. 7 Å.

In summary, we have discovered a novel intramolecular energy relay pathway that utilizes a S_1–T_1 switch. One advantage of this switch is that it bypasses the normally inefficient intersystem crossing characteristic of cyclopentanones by utilizing the more facile intersystem crossing observed for cyclohexanones.[18] Studies with other steroids containing a photolabile keto group in the

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(14) The absence of inter-SSET was demonstrated by the observation that neither the photochemistry of **1** nor that of **2** is significantly affected by the addition of an "external" ketone, cyclohexanone.[4a,c] The short lifetime of the antenna (ca. 0.63 ns as estimated from a Stern–Volmer analysis of the fluorescence quenching of **4** by TEA) is important to assure the absence of such inter-SSET.

(15) The actual efficiency for intra-SSET in the presence of TEA will be reduced by quenching of the aryl singlet by the amine. When the Stern–Volmer parameter, $k_q\tau_0$ = 15.3 M⁻¹, from the quenching of the fluorescence of **1** (4.0 mM) by TEA (7.2–36.0 mM) in acetonitrile on excitation at 269 nm is used, the $\phi_{\text{intra-SSET}}^1$ in the presence of 91.9 mM TEA is calculated to be 0.28.

(16) In principle, one should also be able to estimate the efficiency for intramolecular triplet energy transfer between the 11- and 17-keto groups since, according to the scheme given above, the limiting quantum efficiency (ϕ_3) for formation of **3** should equal the product ($\phi_{\text{intra-SSET}}$)($\phi_{\text{isc}}^{11\text{-keto}}$)($\phi_{\text{intra-TTET}}$)($\phi_r$), where ϕ_r represents the efficiency of formation of **3** from the 17-keto triplet. Because ϕ_r is not readily determined, one can only say that the value of $\phi_{\text{intra-TTET}}$ lies between 0.40 and 1.0. One potential source of inefficiency in the triplet transfer step would be quenching of the 11-keto triplet by the aryl antenna.[17]

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"switch" position are now in progress.

Direct Measurement of the Rate Constant for β-Scission of the Cumyloxyl Radical by Laser Flash Photolysis with Time-Resolved IR Detection[1]

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The combination of laser flash photolysis (LFP) with time-resolved infrared (TRIR) detection provides a new and potentially extremely powerful tool for the measurement of absolute rate constants for fast reactions and for structural studies on reactive intermediates. However, IR bands generally have small extinction coefficients relative to UV bands, and this has restricted the application of the LFP/TRIR technique almost entirely to the study of metal carbonyl systems.[4-7] The single exception in organic chemistry is Schuster and co-workers' investigation of 1,2-didehydroazepines.[8]

It seemed important to us to widen the organic applications of this valuable new technique. The β-scission of alkoxyl radicals in solution should be an ideal reaction to study since ketones (and aldehydes) have rather strong IR absorptions within the 1600–2000-cm^{-1} range of line-tunable carbon monoxide lasers. There has been only one direct, time-resolved measurement of an alkoxyl β-scission in solution (vis.,[9] $C_6H_5CH_2CH_2O^\bullet \rightarrow C_6H_5CH_2{}^\bullet + CH_2O$). Reliable β-scission rate data for other systems are required in order to understand why solvents would appear to have such a profound effect on $k_\beta{}^{9-13}$ as well as to correlate k_β with structure.

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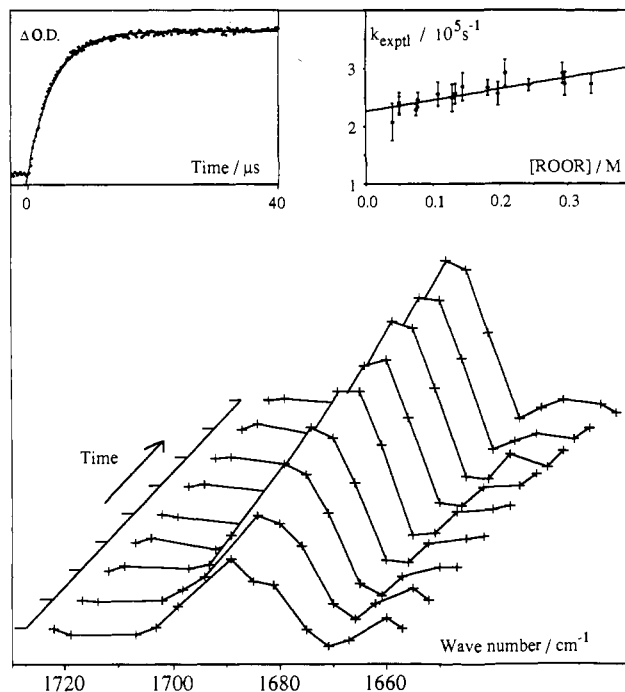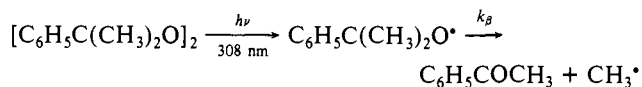

Figure 1. Time-resolved infrared difference absorption spectra observed following laser flash photolysis (308 nm, 2.8 mJ/cm^2) of dicumyl peroxide (0.16 M) in Ar-saturated CCl_4. The spectra are shown at 1.5-μs intervals from 0.75 to 12.75 μs. The spectra were constructed from kinetic traces taken at CO laser frequencies indicated by the + symbols. The left-hand inset shows transient absorbance at 1689 cm^{-1} as a function of time (top $\Delta OD = 0.0056$), the solid line being a first-order fit to the points which yields k_{exptl}. The right-hand inset shows $k_{exptl}/(10^5 \text{ s}^{-1})$ as a function of [dicumyl peroxide]/M; points obtained in Ar- and in O_2-saturated solution are included.

For our initial study, we chose to measure the β-scission of the cumyloxyl radical, which was generated by 308-nm LFP of dicumyl peroxide (0.06–0.5 M) in CCl_4 at room temperature (23 °C) in a flow system (1.3 mL/min) within a calcium fluoride cell (path length, 2 mm). The apparatus has been described.[14,15] TRIR spectra derived from kinetic traces show first-order growth of a band at 1689 cm^{-1}, as expected for acetophenone (see Figure 1).

$$[C_6H_5C(CH_3)_2O]_2 \xrightarrow[\text{308 nm}]{h\nu} C_6H_5C(CH_3)_2O^\bullet \xrightarrow{k_\beta}$$
$$C_6H_5COCH_3 + CH_3{}^\bullet$$

The experimental rate constant for growth, k_{exptl}, was identical for argon- and oxygen-saturated solutions (a result consistent with the formation of acetophenone from an oxygen-centered precursor) and for laser doses varying from 2 to 6 mJ/cm^{-2} (a result that shows that cumyloxyl radicals are not destroyed by radical–radical reactions). However, k_{exptl} does decrease slightly as the peroxide concentration is decreased (see right-hand inset in Figure 1) because the cumyloxyl radicals can be destroyed by attack on the peroxide:

$$C_6H_5C(CH_3)_2O^\bullet + [C_6H_5C(CH_3)_2O]_2 \xrightarrow{k_p} \text{products}$$

Since $k_{exptl} = k_\beta + k_p[C_6H_5C(CH_3)_2O]_2$, the slope of this plot yields k_p and the intercept k_β. We also measured the rate constant for hydrogen abstraction from cyclohexane, k_a, by the addition of various concentrations of cyclohexane with a fixed concentration of peroxide ($k_{exptl} = k_0 + k_a[\text{c-C}_6H_{12}]$). These rate constants ($\pm 2\sigma$) are as follows: $k_p = (1.94 \pm 0.62) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $k_a = (9.53 \pm 1.35) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, and $k_\beta = (2.27 \pm 0.13) \times 10^5 \text{ s}^{-1}$.

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