To facilitate quantitation, all deuteriated photodimers were labeled with [^{14}C]acetic anhydride at the 3'- and 5'-hydroxyl groups.[17] The protio photodimer was similarly labeled with [^{3}H]acetic anhydride.

Mixtures of protio and deuterio photodimers[18] were irradiated in the presence of the enzyme in a Rayonet photochemical reactor.[19] Products and unreacted substrates were purified by HPLC. Standard liquid scintillation counting techniques were used to accurately determine the percent conversion and the ^{3}H/^{14}C ratio in products and substrates. The secondary deuterium isotope effects, calculated using the integrated rate equations described by Cleland,[8] are summarized in Table I.

The enzymatic cleavage of the tetradeuterio photodimer shows a V/K isotope effect of 1.150. In contrast to our prediction, this effect is not primarily associated with either the cleavage of the 5,5' bond [$^D(V/K) = 1.082$] or the 6,6' bond [$^D(V/K) = 1.071$] of the photodimer but is almost equally distributed between the two bonds. Furthermore, the observation that the product of the V/K isotope effects for the 6,6'-dideuterio photodimer and the 5,5'-dideuterio photodimer equals the isotope effect for the tetradeuterio photodimer suggests that all four C–H bonds of the cyclobutane ring undergo a simultaneous hybridization change in a single transition state.

The simplest explanation is that the reaction proceeds via the dimer radical anion or cation and shows a large β-secondary isotope effect in addition to the α-secondary isotope effect on the first C–C bond cleavage. However, the β-isotope effects on radicals described in the literature are considerably smaller than the α-effects.[20] In addition, the magnitude of the β-effect is predicted to depend on cos^2 [ϕ] where ϕ is the dihedral angle between the bond undergoing cleavage and the β-C–H bond.[21] For the photodimer, this angle is 94°, suggesting that the β-effect will be small.

An alternative explanation is that the cleavage of the two C–C bonds from the dimer radical anion or cation is a concerted process. Radical anion **4** and radical cation **8** are both delocalized radicals. It is therefore not unreasonable that both the 5,5' and the 6,6' bonds are weakened by reduction/oxidation of the photodimer. Quasi-concerted [2 + 1] cycloadditions of a variety of alkene radical cations have been proposed on the basis of stereochemical[22] and theoretical[23] considerations. The cycloreversion of the *trans*-anethole cyclobutane radical cation has also been proposed to occur via a concerted pathway.[22b,c] While there is no precedent

for analogous chemistry with alkene radical anions, the dimer radical anion cannot be excluded as a possible intermediate. Experiments are currently in progress, using model systems, to determine if the surprising pattern of isotope effects observed for the enzymatic reaction is characteristic of photodimer cleavage from either a radical cation or a radical anion intermediate.

Synthesis and Characterization of Phenalenyl Cations, Radicals, and Anions Having Donor and Acceptor Substituents: Three Redox States of Modified Odd Alternant Systems

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Three redox states of an odd alternant hydrocarbon, phenalenyl cation, radical, and anion (**1$^+$**, **1$^\bullet$**, **1$^-$**), have already been isolated or generated.[2,3] The importance of this skeleton[4–6] has been renewed from recent growing interest in the multistage redox systems to explore new organic materials.[7–9] Extension of the

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(16) For the 5,5',6,6'-tetradeuterio photodimer, the levels of deuteration at the 5- and the 6-positions, as determined by NMR analysis, were 95.3 ± 0.7% and 93.9 ± 0.7%, respectively. For the 5,5'-dideuterio photodimer, the level of deuteration at the 5-positions was 95.9 ± 0.8%. For the 6,6'-dideuterio photodimer, the level of deuteration at the 6-positions was 84.1 ± 0.6%.

(17) Control experiments demonstrated that the esters were stable under our reaction conditions and that acetylation of the photodimer had a negligible effect on the enzymatic reaction.

(18) Mixtures of protio and deuterio photodimers were copurified by HPLC to >99% purity and to constant ^{3}H/^{14}C.

(19) λ_{max} = 350 nm; the reaction mixture (300 μL) consisted of 30 mM Tris, pH 7.2, 6.6 mM NaCl, 0.6 mM EDTA, 1 mM DTT, 1.7 mM substrates, and 7.4 μM enzyme.

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(1) (a) Institute for Molecular Science. (b) Faculty of Science, Osaka University. (c) Faculty of Engineering Science, Osaka University. (d) Kyoto University. (e) The University of Tokyo.

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(3) For the radical, see also: (a) Reid, D. H. *Tetrahedron* **1958**, *3*, 339–352. (b) Gerson, F. *Helv. Chim. Acta* **1966**, *49*, 1463–1467. (c) Gerson, F.; Heilbronner, E.; Reddock, H. A.; Paskovich, D. H.; Das, N. C. *Helv. Chim. Acta* **1967**, *50*, 813–821.

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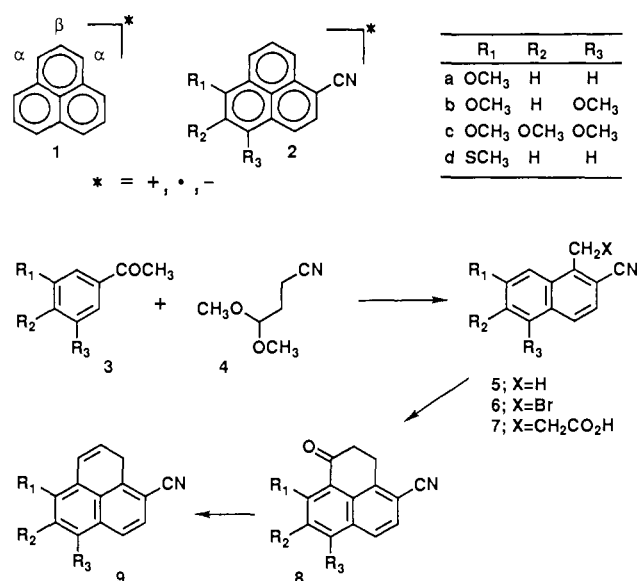
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Scheme I

	R₁	R₂	R₃
a	OCH₃	H	H
b	OCH₃	H	OCH₃
c	OCH₃	OCH₃	OCH₃
d	SCH₃	H	H

* = +, •, −

5; X=H
6; X=Br
7; X=CH₂CO₂H

Table I. Reduction Potentials of Phenalenyl Cations[a]

cations	$E_1^{red\,d}$	$E_2^{red\,d}$	$E_1 - E_2$
1⁺ [b]	+0.7	−0.9	1.60
2c⁺ [c]	+0.33 (0.09)	−0.76 (0.09)	1.09
2d⁺ [c]	+0.58 (0.06)	−0.59 (0.06)	1.17

[a] Volts vs SCE at room temperature. [b] CH₃CN/n-Bu₄NBF₄ (ref 5b). [c] CH₂Cl₂/n-Bu₄NClO₄. [d] Peak potential separations are shown in parentheses.

Figure 1. (a) EPR spectrum in CH₂Cl₂ and (b) computer simulation for 2d•.

conjugated system of the phenalenyl skeleton produced the highly amphoteric hydrocarbons[4] and the new planar neutral radical.[5] Introduction of both donor and acceptor substituents[10] can also modify the phenalenyl system and will produce the improved redox systems without addition of the extended conjugation. We now report the first realization of the three redox states of the phenalenyl modified by such substituents.

Our target phenalenyls contain methoxy or methylthio groups as the donors, and the cyano group as the acceptor at the electronically active α-positions rather than the inactive β-positions. No phenalenyl derivatives having cyano groups at the α-positions have been reported, in sharp contrast to a number of donor-substituted ones.[2a,11] The synthetic procedures are the construction of β-cyanonaphthalenes with the suitable substituents 5, and their conversions into the corresponding phenalenes 9, keeping the cyano group intact (Scheme I).

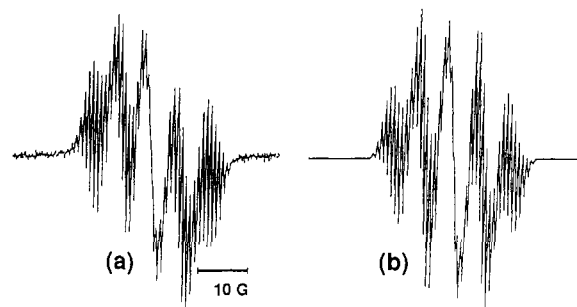Construction of the cyanonaphthalene skeletons 5 was performed by reaction of the acetophenones 3 with 4,4-dimethoxy-butanenitrile (4) in the presence of LDA followed by treatment with H₂SO₄, according to a similar procedure described by Teague and Roth[11] (5a, 74%; 5b, 74%; 5c, 82%; 5d, 63%). Bromination of 5 with NBS gave the bromides 6 (6a, 99%; 6b, 88%; 6c, 98%; 6d, 78%). Reaction of 6 with the anions derived from *tert*-butyl acetate and hydrolysis of the resulting esters with CF₃CO₂H or 1 N KOH afforded the two-carbon-elongated propionic acids (7a, 94%; 7b, 52%; 7c, 77%; 7d, 60%). Conversion of 7 into the phenalanone skeletons 8 was achieved by chlorination of 7 with PCl₅ followed by Friedel–Crafts cyclization with SnCl₄ (8a, 71%; 8b, 64%; 8c, 71%) or with AlCl₃ (8d, 74%). Reduction of 8 with NaBH₄ followed by dehydration with β-naphthalenesulfonic acid provided the phenalenes 9, which were more sensitive to the air than the unsubstituted phenalene, in 60–80% yields.

The cationic species 2⁺ were isolated as orange to violet solids by treatment of 9 with trityl perchlorate in CH₂Cl₂. These salts are stable on drying and constitute rare examples of isolable carbocations containing the cyano group.[13] Their structures were

confirmed by ¹H and ¹³C NMR spectra in CF₃CO₂D. Furthermore, the most stable cation, 2c⁺, gave satisfactory elemental analysis as (2c)₁(ClO₄)₁. Interestingly, the elemental analysis of 2d⁺ showed a nonstoichiometric ratio of the components, (2d)₁-(ClO₄)₀.₇ (see below). The anionic species 2⁻ were generated as deep red solutions by treatment of 9 with n-BuLi in THF-d₈ at −78 °C and characterized by ¹H and ¹³C NMR spectra. The ¹H NMR data for both ionic species indicate that the charge distributions are large on the α-positions and small on the β-positions.

Table I shows the reduction potentials of 2c⁺ and 2d⁺ measured by cyclic voltammetry. The observed potentials are less positive for the first reduction (2•/2⁺) and less negative for the second one (2⁻/2•) than the corresponding values reported for 1⁺.[5b] This indicates that both the cation and the anion states interact to a larger extent with the donor and the acceptor substituents, respectively, and therefore, the amphoteric redox nature of the radicals is enhanced.

The radical species 2• were generated by applying the electrochemical oxidation technique[14] to the phenalenes 9 in a CH₂Cl₂ solution containing n-Bu₄NBF₄ as supporting electrolyte at 3.10 V and characterized by EPR spectra, which were well reproduced by computer simulations. Figure 1 shows the spectra of 2d• as an example. The hyperfine proton coupling constants for 2a•–2d• are large at α-positions (5.32–6.33 G) and small at β-positions (0.86–1.67 G), showing a highly spin polarized nature. Both the EPR and NMR spectra of 2• and 2⁺, 2⁻, respectively, reveal that these modified phenalenyl species still maintain the characteristics of odd alternant electronic systems.

It should be noted that the cation salt (2d)₁(ClO₄)₀.₇ is paramagnetic not only in the solid state[15] but also in solution. The average g factor, ḡ = 2.0036 (2), in the solid EPR spectrum coincides with g = 2.0032 (2) in a CH₂Cl₂ solution of the salt. In addition, the solution spectrum is essentially identical with that of the radical species generated by the electrochemical oxidation of 9d (see above). Therefore, the EPR absorption of the salts must arise from the 3-cyano-7-(methylthio)phenalenyl radical species 2d•.[16]

The compressed pellet of (2d)₁(ClO₄)₀.₇ dispersed in KBr shows a broad electronic absorption band at 5000 cm⁻¹.[17] The con-

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(15) The EPR intensity was virtually invariant for 1 month. The spin susceptibility follows the Curie law with a Curie constant of 5.9 × 10⁻³ emu K mol⁻¹ at temperatures below 20 K. This constant suggests that only about 5% of the radicals contained contribute to the spin susceptibility as Curie spins. At room temperature, 17% of the radicals are active.

(16) For perchlorophenalenyl radical, see: Haddon, R. C.; Chichester, S. V.; Stein, S. M.; Marshall, J. H.; Mujsce, A. M. *J. Org. Chem.* **1987**, *52*, 711–712.

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.

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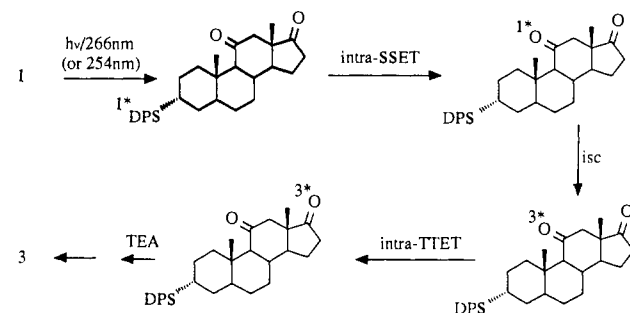
we have observed the self-sensitized, site-specific reduction of the 17-keto group via a remarkable energy relay mechanism in which the 11-keto moiety functions as an intermediate single–triplet switch.

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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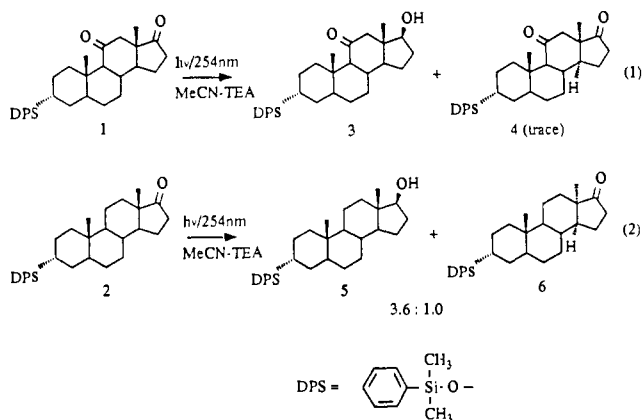
(6) Wehrli, A.; Schaffner, K. *Helv. Chim. Acta* **1962**, *45*, 385–389. (b) Schaffner, K.; Jeger, O. *Tetrahedron* **1974**, *30*, 1891–1902 and references therein.

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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.; Wrzyzykowska, 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.