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Direct and Sensitized Valence Photoisomerization of a Substituted Norbornadiene. Examination of the Disparity between Singlet- and Triplet-State Reactivities

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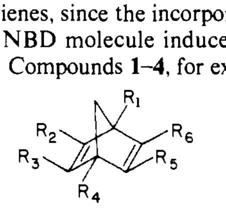
Abstract: Direct photolysis of 1,2,3-trimethyl-5,6-dicyanonorbornadiene (**4**) at 366 nm induces valence isomerization to the corresponding quadricyclene compound, **5**, with a quantum yield of 0.68 ± 0.01. The same transformation occurs in the presence of a number of triplet photosensitizers. Thus $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridine), whose emissive metal-to-ligand charge-transfer excited state is quenched by **4** with a rate constant of $2.0 \pm 0.2 \times 10^8$ M^{-1} s^{-1}, sensitizes the production of **5** at 546 nm with a limiting quantum yield of 0.06 ± 0.01. Limiting yields at 436 nm for the organic sensitizers biacetyl and 9-fluorenone are 0.11 ± 0.01 and 0.15 ± 0.01, respectively. The finding that direct photoisomerization occurs with much higher efficiency than the triplet-sensitized process suggests that the lowest excited singlet state of **4** is significantly more reactive than the triplet state. Interestingly, the opposite reactivity pattern obtains in the case of the unsubstituted norbornadiene molecule. Possible reasons for this substituent effect are discussed in terms of the excited-state potential energy surfaces that interconnect the norbornadiene and quadricyclene structures.

Most of the photochemical energy storage cycles presently under investigation are designed to produce gaseous or liquid fuels from small inorganic molecules. The light-induced dissociation of water into H_2 and O_2 is the archetype of such systems.[1] An alternative approach to energy storage that we[2] and others[3-8] have been exploring involves the use of endoergic photorearrangements of organic molecules. The best studied system of this type is based upon the interconversion of the valence isomers norbornadiene (NBD) and quadricyclene (Q) (eq 1). Although NBD absorbs very weakly above 290 nm and thus is essentially transparent to solar radiation, its transformation to Q can be driven with sunlight in the presence of various photosensitizers.[9] Once formed, the highly strained Q molecule is kinetically inert at ambient temperature because of orbital symmetry restrictions on the back reaction. In the presence of a suitable catalyst, however, rapid reversion to NBD ensues with the release of the stored energy as heat.[10]

NBD Q (1)

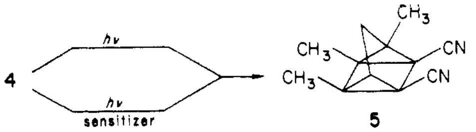
Despite intensive efforts to improve the overall efficiency and durability of the NBD–Q cycle,[2] several difficult problems remain to be solved. One of these arises from the relatively high energies of the electronic excited states in the NBD molecule and the consequent need for high-energy sensitizers which, even in the most favorable cases, absorb weakly in the region above 450 nm. Because ~90% of all solar photons lie in this wavelength region, the NBD–Q system in its present stage of development can store, at best, only a few percent of the sunlight striking the earth's surface.

This absorption problem has sparked considerable interest in substituted norbornadienes, since the incorporation of appropriate substituents into the NBD molecule induces a spectral shift to longer wavelengths.[11] Compounds **1**–**4**, for example, absorb above 300 nm (**3** absorbs above 500 nm) and undergo photoisomerization to the corresponding quadricyclenes upon direct irradiation with sunlight.[3-6] Moreover, Jones and co-workers reported[3b] that **1** can be converted to its quadricyclene with reasonable quantum efficiency via triplet–triplet energy transfer from organic sensitizers whose absorption extends to 500 nm. While the physical properties (many of the compounds are viscous liquids or solids) and greater cost of substituted norbornadienes are obvious drawbacks, these molecules merit additional study as models for energy storage media.



1, R_1=H; R_2=H; R_3=H; R_4=H; R_5=CO_2Me; R_6=CO_2Me
2, R_1=H; R_2=H; R_3=H; R_4=H; R_5=COOH; R_6=CONHPh
3, R_1=CH_3; R_2=Ph; R_3=Ph; R_4=CH_3; R_5=COEt; R_6=CO_2Me
4, R_1=CH_3; R_2=CH_3; R_3=CH_3; R_4=H; R_5=CN; R_6=CN

In this report we compare the direct and triplet-sensitized valence photoisomerization of **4** to the corresponding quadricyclene, **5** (eq 2). Several organic carbonyl compounds and the inorganic complex $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridine) were selected as sensitizers. The latter species proved to be especially attractive in this role owing to its strong absorption in the visible



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[†] University of Georgia.
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region, its photostability in polar solvents, and its easily measurable phosphorescence in room-temperature fluid solution.[12] This emission, which originates from a metal-to-ligand charge-transfer excited state of predominantly triplet spin multiplicity,[13] enables convenient monitoring of triplet-triplet interactions between the photoexcited complex and added substrates. Compound **4**, on the other hand, is representative of a growing class of substituted norbornadienes that contain both electron-donor and electron-acceptor substituents.[5,6] The bathochromic shift (relative to NBD) of the long-wavelength absorption band in these compounds has been attributed to an intramolecular charge-transfer interaction between the electron-rich and the electron-deficient double bonds. The primary aim of our investigation was to determine how this charge polarization influences the probability with which the lowest triplet state decays to the quadricyclene structure. Beside being of fundamental mechanistic interest, such information is needed to evaluate the generality and utility of triplet sensitization as a means of enhancing the wavelength response of energy storage cycles based upon substituted norbornadienes.

Experimental Section

Reagents. 1,2,3-Trimethyl-5,6-dicyanonorbornadiene (**4**) was synthesized by the Diels–Alder reaction of 1,2,3-trimethylcyclopentadiene[14,15] with dicyanoacetylene.[16] The product was purified (in the dark) by chromatography on a silica gel column with 1:1 hexane-dichloromethane as the eluting solvent. Evaporation of the eluant afforded **4** as a pale yellow solid, mp 85–86 °C (uncorrected). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.33; H, 6.57. Found: C, 78.38; H, 6.70. Quadricyclene **5** was prepared by irradiating a dichloromethane solution of **4** for 3 days with the filtered output (>350 nm) of a 450-W high-pressure mercury lamp. The photolyte was then chromatographed on a silica gel column. Unreacted **4** eluted as a pale yellow band with 1:1 hexane–dichloromethane, while **5** was obtained by elution with pure dichloromethane. Evaporation of the solvent gave **5** as a white solid, mp 101–102 °C (uncorrected). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.33; H, 6.57. Found: C, 77.90; H, 6.50. Proton NMR, mass spectral (m/e 184), and gas chromatographic analyses confirmed the structure and purity of **5**.

Commercially available $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (G.F. Smith) was recrystallized from water and then methanol; the spectral properties of the purified complex closely match those reported in the literature.[17] Samples of 9-fluorenone (Eastman) and thioxanthone (Aldrich) were recrystallized from methanol and benzene, respectively. Biacetyl (Aldrich) was purified by distillation under nitrogen. Solvents used in the spectral and photochemical experiments were of spectral grade quality.

Equipment and Procedures. Electronic absorption spectra were recorded on Cary 15 and 219 spectrophotometers. Luminescence spectra were taken with a Perkin-Elmer MPF-44B spectrofluorimeter. Luminescence lifetimes were measured by correlated single-photon counting techniques using an Ortec 9200 time-resolved spectrometer.

The half-wave reduction potentials of **4** and **5** in acetonitrile were determined polarigraphically at a dropping mercury electrode (t_d, 2 s; flow rate of Hg, 8.60×10^{-4} g/s) with a scan rate of 5 or 10 mV/s. Sodium or tetrabutylammonium perchlorate was used as the supporting electrolyte, and potentials were referenced to a $Ag/AgNO_3$ electrode (0.308 V vs. SCE). Half-wave oxidation potentials in acetonitrile were measured with a rotating platinum electrode at a scan rate of 50 mV/s. Lithium perchlorate was the supporting electrolyte, and potentials were again referenced to the $Ag/AgNO_3$ couple.

Photolyses were performed with a 200-W high-pressure mercury arc lamp (Illumination Industries). A high-intensity monochromator or a combination of interference and blocking filters was used to isolate the desired Hg emission line. Incident light intensity was determined by ferrioxalate[18] or Reineckate actinometry.[19]

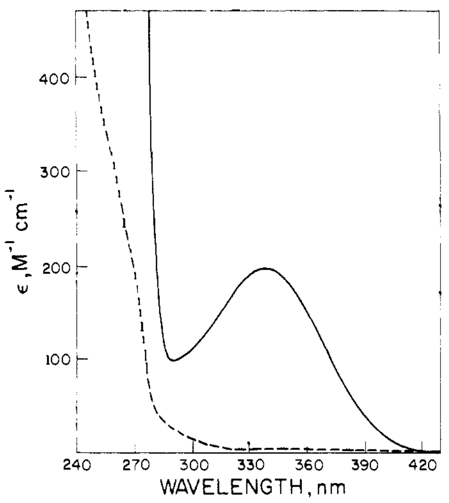

Figure 1. Electronic absorption spectra of **4** (—) and **5** (---) in acetonitrile.

Table I. Half-Wave Oxidation and Reduction Potentials of **4** and **5**

compound	$E_{1/2}^{ox}$, V^a	$E_{1/2}^{red}$, V^a
4	1.82	−1.39
5	1.76	<−2.4

^{a}Measured in acetonitrile; potentials are relative to SCE.

Acetonitrile solutions of $Ru(bpy)_3^{2+}$ and **4** were degassed by five freeze–pump–thaw cycles and then irradiated with stirring in a thermostated, 1-cm rectangular cell. The concentration of the metal complex was sufficiently high (typically 4.3×10^{-3} M) to ensure >99% absorption of the incident light. Photolyzed samples were poured onto a short glass column packed with 70–230 mesh silica gel. This material retained $Ru(bpy)_3^{2+}$ while **4** and **5** were eluted with acetonitrile. The concentration of **5** in the eluant was determined by reverse-phase high-pressure liquid chromatography on an IBM LC/9533 chromatograph containing a 25-cm C_1 column and equipped with a fixed-wavelength (254 nm) UV detector. The following operating conditions were employed: mobile phase, 70:30 water-acetonitrile; flow rate, 1 mL/min; pressure, 140–190 bar.

Benzene solutions containing **4** and an organic sensitizer were deaerated by bubbling with N_2 for 20 min. Photolyzed samples were evaporated to dryness,[20] redissolved in acetonitrile, and then analyzed for **5** by liquid chromatography as described above.

Results

Spectral, Photochemical, and Electrochemical Properties of 4 and 5. Substituted norbornadiene **4** is a low-melting, light-yellow solid that dissolves in a number of organic solvents. Its electronic absorption spectrum in acetonitrile is shown in Figure 1. The band at 337 nm shifts to 335 nm in benzene and 325 nm in cyclohexane.

Irradiation of **4** at 366 nm induces isomerization to the corresponding quadricyclene, **5**. Since the latter compound absorbs weakly above 320 nm (Figure 1), the extent of reaction can be determined with reasonable accuracy from the decrease in intensity of the long-wavelength band of **4**. The quantum yield for direct photoisomerization, ϕ_{isom}^{dir}, obtained by this procedure is 0.68 ± 0.01 in degassed acetonitrile for conversions ranging from 4% to 24%.[21] Switching the solvent to benzene has no significant effect upon the quantum efficiency.

Table I lists the half-wave oxidation and reduction potentials of **4** and **5** in acetonitrile. While the two compounds undergo oxidation at comparable potentials,[22] they possess markedly different tendencies toward reduction. In particular, **5** strongly resists the addition of an electron.

$Ru(bpy)_3^{2+}$-Sensitized Photoisomerization of 4. Excitation of $Ru(bpy)_3^{2+}$ with 546-nm light produces the characteristic orange-red phosphorescence which, in acetonitrile at 25 °C, decays

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[20] Benzene was removed from the sample since it absorbs strongly at the monitoring wavelength of the liquid chromatograph detector.

[21] An independent measurement of the extent of reaction by high-pressure liquid chromatography afforded a value of 0.82 for ϕ_{isom}^{dir}.

[22] For comparison, the $E_{1/2}^{ox}$ values for NBD and Q are 1.56 and 0.91 V (vs. SCE), respectively. Gassman, P.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

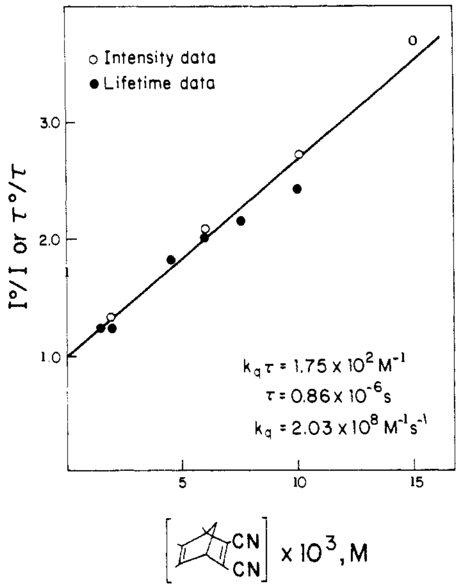

Figure 2. Stern–Volmer plot of intensity and lifetime quenching of the luminescent excited state of $Ru(bpy)_3^{2+}$ by **4**; data measured in acetonitrile at 25 °C.

Table II. Limiting Quantum Yields for Triplet-Sensitized Conversion of **4** to **5**

sensitizer	λ_{excit}, nm	ϕ_{isom}^{sen}	E_T, kcal $(\phi_T)^a$
$Ru(bpy)_3^{2+}$	546	0.06 ± 0.01^b	$47^c\ (1.0)^d$
9-fluorenone	436	0.15 ± 0.01^e	$53.3^d\ (0.93)^g$
biacetyl	436	0.11 ± 0.01^h	$56.3^i\ (1.0)^i$
thioxanthone	405	$<0.3^e$	$65.5^j\ (1.0)^j$

[a] Triplet-state energy (efficiency of forming triplet state). [b] Corrected for incomplete quenching of sensitizer. [c] Reference 13. [d] Reference 12. [e] Obtained from intercept of plot of ϕ^{-1} vs. $[\mathbf{4}]^{-1}$. [f] Reference 25a. [g] Reference 25b. [h] Measured under conditions of complete sensitizer quenching. [i] Reference 25d. [j] Reference 25e.

with a lifetime of 0.86 μs. Addition of **4** to the solution quenches this emission with no discernible alteration in peak shape. Quenching data obtained from lifetime and steady-state intensity measurements obey the Stern–Volmer relationship given by eq 3, where I^0 and τ^0 denote the emission intensity and lifetime,

$$\frac{I^0}{I} = \frac{\tau^0}{\tau} = 1 + K_{SV}[\mathbf{4}] \qquad (3)$$

respectively, in the absence of **4**, I and τ represent the corresponding quantities in the presence of the diene, and K_{SV} is the Stern–Volmer quenching constant. As seen in Figure 2, plots of I^0/I and τ^0/τ vs. [**4**] are linear with a common slope, K_{SV}, equal to 175 ± 10 M^{-1}. Such behavior establishes that **4** quenches the emissive state of $Ru(bpy)_3^{2+}$ via a dynamic, collisional process.[23] Dividing K_{SV} by τ^0 yields a value of $2.0 \pm 0.2 \times 10^8\ M^{-1}\ s^{-1}$ for the bimolecular quenching constant, k_q. In contrast to the behavior of **4**, **5** is an extremely poor quencher ($K_{SV} < 2$) of the emissive excited state of $Ru(bpy)_3^{2+}$.

Acetonitrile solutions of $Ru(bpy)_3^{2+}$ and **4** produce **5** when irradiated at 546 nm. The quantum efficiency of this sensitized isomerization, ϕ_{isom}^{sen}, was determined at short irradiation times (20–30 min) and under conditions in which **4** quenches >80% of the emissive excited state of the metal complex. Several independent measurements afford a limiting value (i.e., corrected for incomplete quenching) of 0.06 ± 0.01 for ϕ_{isom}^{sen}.

In one long-term photolysis experiment, an acetonitrile solution of $Ru(bpy)_3^{2+}$ and 1.5×10^{-2} M **4** was irradiated for 7 h. Analysis of the photolyte revealed that 56% of the diene had isomerized to **5**. Some decomposition of the sensitizer[24] also occurred, as evidenced by changes in the absorption spectrum of the sample.

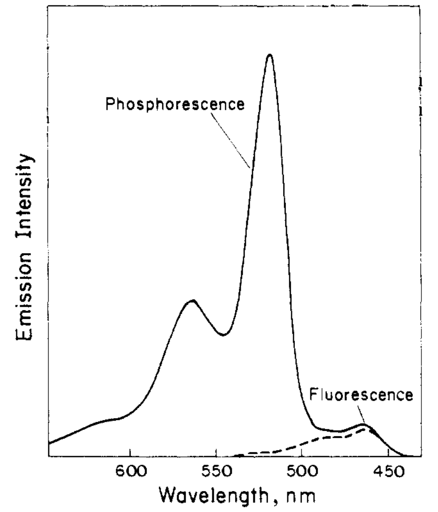

Figure 3. Effect of **4** on the phosphorescence and fluorescence of biacetyl in benzene: (—) no **4** present; (---) 6.5×10^{-2} M **4** present.

Organic Triplet-Sensitized Photoisomerization of 4. Table II summarizes the results of photochemical experiments in which organic compounds having triplet-state energies, E_T,[25] higher than that of $Ru(bpy)_3^{2+}$ were tested as sensitizers for the isomerization of **4** to **5**. Samples containing 9-fluorenone or biacetyl were irradiated at a wavelength where competitive absorption by **4** could be neglected. This was not possible for thioxanthone, and hence it was necessary to correct for the amount of **5** formed by direct photolysis. Owing to considerable uncertainty in this correction, only a conservative upper limit to ϕ_{isom}^{sen} is given for thioxanthone.

As seen in Figure 3, 6.5×10^{-2} M **4** completely quenches the phosphorescence of biacetyl while causing no change in the fluorescence. Since ϕ_{isom}^{sen} has attained its limiting value under these conditions, we conclude that sensitization by biacetyl proceeds entirely via its lowest triplet state. Estimates of quenching rate constants can be obtained by using the Stern–Volmer expression in eq 3. Given a singlet lifetime of 10 ns for biacetyl in benzene[26] and assuming that at most 5% quenching could go undetected yield $1 \times 10^8\ M^{-1}\ s^{-1}$ as an upper limit to k_q for fluorescence quenching by **4**. Similarly, the finding that even 6.9×10^{-4} M diene completely quenches (i.e., $I^0/I \geq 50$) phosphorescence can be used in conjunction with the biacetyl lifetime of 65 μ's[27] to set a lower limit of $1 \times 10^9\ M^{-1}\ s^{-1}$ on k_q for phosphorescence quenching.

Only fluorescence is observed for 9-fluorenone[25c] and thioxanthone,[25e] and in neither case does **4** quench the emission. Here again, the results support the view that **4** interacts solely with the triplet state of the organic sensitizer.

Side products were not evident in the liquid chromatograms of photolyzed samples, suggesting that the sensitized isomerization of **4** to **5** proceeds with high chemical specificity. This point was checked more thoroughly in the following experiment. A benzene solution of **4** and biacetyl was irradiated for 80 min. Analysis of the photolyte revealed that 40% of the diene was converted to **5**, while the total concentration of the two isomers had decreased by 5–6%. These results indicate that biacetyl-sensitized isom-

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[23] If static quenching were important, we might expect to find evidence of ground-state complex formation between $Ru(bpy)_3^{2+}$ and **4**. The additivity of their electronic absorption spectra argues against this possibility and supports the assignment of a collisional quenching mechanism.

[24] Photosubstitution of a bpy ligand occurs with a quantum yield of $<10^{-2}$ in acetonitrile. Jones, R. F.; Cole-Hamilton, D. J. *Inorg. Chim. Acta* **1981**, *53*, L3.

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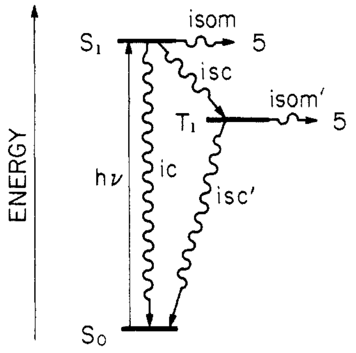


Figure 4. Schematic energy-level diagram showing the ground (S_0), excited singlet (S_1), and excited triplet (T_1) states of **4**; indicated processes are internal conversion (ic), intersystem crossing (isc and isc′), and valence isomerization to quadricyclene **5** (isom and isom′).

erization of **4** to **5** occurs with a specificity of 85% or higher.

Discussion

Our results reveal a significant disparity between the quantum yields for direct and sensitizer-mediated photoisomerization of substituted norbornadiene **4**. Thus direct photolysis affords the corresponding quadricyclene with $\phi_{\text{isom}}{}^{\text{dir}} \sim 0.7$, whereas considerably smaller yields arise from intermolecular sensitization by $\text{Ru(bpy)}_3{}^{2+}$ and a number of organic triplet sensitizers. This behavior provides an intriguing contrast to that of the parent diene, NBD, for which the triplet-sensitized pathway is generally more efficient than direct conversion.[28] Evidently, the incorporation of electron-donor and electron-acceptor substituents into the norbornadiene system can cause a marked change in the pattern of photoreactivity.

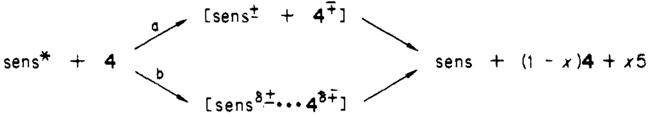
Before considering the origins and implications of this substituent effect, we need to delineate more precisely the pathways by which **4** undergoes direct and sensitized photoisomerization. In the former case, irradiation of the diene at 366 nm populates a singlet π–π* excited state, S_1, that possesses some charge-transfer character. As illustrated in Figure 4, deactivation of this state can occur via internal conversion (ic) to the ground state, intersystem crossing (isc) to the lowest triplet state, T_1, and rearrangement (isom) to the corresponding quadricyclene isomer.[29] The triplet state, in turn, may decay via pathways that include intersystem crossing (isc′) to the ground state and isomerization (isom′). The quantum yield for direct photoisomerization is defined by eq 4, where the k's denote rate constants for individual

$$\phi_{\text{isom}}{}^{\text{dir}} = \left(\frac{k_{\text{isom}}}{k_{\text{ic}} + k_{\text{isc}} + k_{\text{isom}}}\right) + \left(\frac{k_{\text{isc}}}{k_{\text{ic}} + k_{\text{isc}} + k_{\text{isom}}} \times \frac{k_{\text{isom}'}}{k_{\text{isc}'} + k_{\text{isom}'}}\right) \tag{4}$$

excited-state processes. The first term in this expression represents the efficiency of prompt reaction from S_1, while the second is the product of the efficiencies of S_1–T_1 intersystem crossing and reaction from T_1. Since $\phi_{\text{isom}}{}^{\text{dir}}$ is ~0.7, one or both of these terms must have an appreciable value.

The relative importance of singlet- vs. triplet-state reactivity in **4** can be assessed from the quantitative studies of its interactions with various triplet sensitizers. A key observation is that the sensitized production of **5** occurs with relatively low efficiency (Table II) under conditions of complete quenching of the sensitizer by **4**. In other words, only a small fraction of quenching events results in net chemical reaction.

We considered the likelihood that such behavior arises from complete (eq 5a) or partial (eq 5b) electron transfer between the photoexcited sensitizer and **4** to yield an ion pair or charge-transfer complex, respectively, which decays most of the time ($x < 0.2$)



(5)

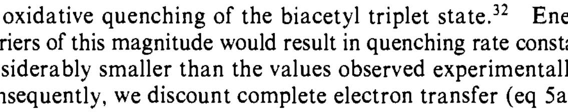
to the ground states of the reactants. The energetics of the former process can be estimated from eq 6,[30] where the redox potentials,

$$\Delta G\ (\text{kcal}) = 23.06\left(E_{1/2}{}^{\text{ox}} - E_{1/2}{}^{\text{red}} + z_1 z_2 e^2/\epsilon r\right) - \Delta E_{0,0} \tag{6}$$

$E_{1/2}{}^{\text{ox}}$ and $E_{1/2}{}^{\text{red}}$, refer to the electron donor and acceptor, respectively, $\Delta E_{0,0}$ is the excitation energy of the sensitizer, and the term $z_1 z_2 e^2/\epsilon r$ represents the Coulombic energy associated with bringing two ions of charges z_1 and z_2 to encounter distance r in a solvent of dielectric constant ϵ. Based upon the reported $E_{1/2}{}^{\text{red}}$ (−1.33 V vs. SCE[12]) and $\Delta E_{0,0}$ (47 kcal) values for $\text{Ru(bpy)}_3{}^{2+}$ in acetonitrile and the electrochemical data in Table I, we calculate that reductive quenching of $\text{Ru(bpy)}_3{}^{2+}{}^{*}$ by **4** should possess a ΔG of about 25 kcal. A similar calculation for the organic sensitizers 9-fluorenone and biacetyl[31] shows that reductive quenching of their triplet states would be thermodynamically unfavorable by roughly 15 and 8 kcal, respectively. Electron transfer in the opposite direction also gives rise to positive ΔG values. Oxidative quenching of $\text{Ru(bpy)}_3{}^{2+}{}^{*}$ by **4**, for example, would be uphill by some 10 kcal. Likewise, a ΔG of almost 40 kcal can be calculated for oxidative quenching of the biacetyl triplet state.[32] Energy barriers of this magnitude would result in quenching rate constants considerably smaller than the values observed experimentally.[30] Consequently, we discount complete electron transfer (eq 5a) as a significant pathway for triplet-state quenching by **4**.

Less information is available concerning the occurrence of quenching within a charge-transfer stabilized encounter complex (eq 5b). The finding that **5**, which undergoes oxidation more readily than **4** (Table I), causes little quenching of $\text{Ru(bpy)}_3{}^{2+}$ luminescence argues against a mechanism involving partial electron transfer to the photoexcited sensitizer. This conclusion is buttressed by the negligible quenching ($K_{\text{sv}} < 0.2$) observed for even relatively good electron-donor substrates such as NBD and Q.[33] While partial electron transfer in the opposite direction (i.e., photoexcited sensitizer to substrate) can explain the relative abilities of **4** and **5** to quench $\text{Ru(bpy)}_3{}^{2+}{}^{*}$ (note $E_{1/2}{}^{\text{red}}$ values in Table I), it does not accommodate the quenching behavior of biacetyl. Specifically, **4** quenches biacetyl phosphorescence at least 10 times more effectively than fluorescence despite a more favorable free energy change associated with electron transfer from the excited singlet state.[34] Overall, we feel that the case for partial electron-transfer quenching of sensitizer excited states by **4** (eq 5b) is unconvincing.

A more plausible quenching mechanism, and one which we shall adopt as a working hypothesis in the ensuing discussion, is triplet–triplet energy transfer (e.g., eq 7). This process results in



(7)

the population of the diene triplet state, T_1, which then undergoes isomerization to **5** in competition with decay to the ground state. The quantum yield for sensitized isomerization is given by eq 8,

$$\phi_{\text{isom}}{}^{\text{sen}} = \phi_{\text{T}}\phi_{\text{ET}}\left(\frac{k_{\text{isom}'}}{k_{\text{isc}'} + k_{\text{isom}'}}\right) \tag{8}$$

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[28] Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388.

[29] Since **4** does not luminesce in room-temperature fluid solution, radiative deactivation has been neglected.

[30] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[31] Half-wave reduction potentials of −1.2 and −1.0 V (vs. SCE) were measured for 9-fluorenone and biacetyl, respectively, in a buffered aqueous ethanol solution.[31b] (b) Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Smith, P. G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 1814.

[32] Biacetyl has an estimated oxidation potential of 2.8 V vs. SCE.[25e]

[33] Grutsch, P. A.; Kutal, C., unpublished results.

[34] In terms of eq 6, which can also be applied to systems in which only partial electron transfer occurs,[31b] the more favorable ΔG value arises from the higher excitation energy ($\Delta E_{0,0}$) of the excited singlet state relative to the triplet.

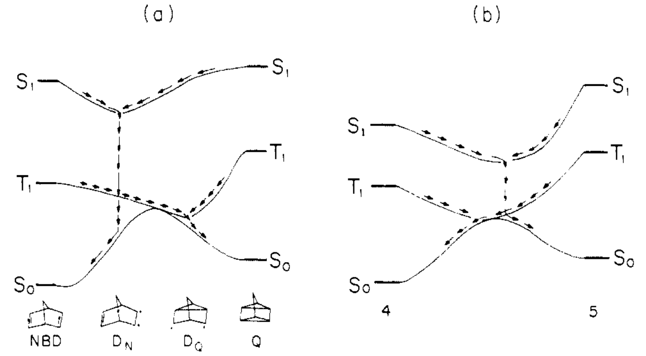


Figure 5. Postulated energy surfaces for the interconversion of (a) NBD and Q (after ref 28) and (b) 4 and 5. Energies are not drawn to scale.

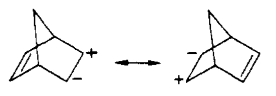
where ϕ_T is the efficiency of forming the sensitizer triplet state, ϕ_{ET} is the efficiency of energy transfer to **4**, and the other terms have been defined previously (Figure 4). Since $\phi_T \sim 1$[12] for $Ru(bpy)_3^{2+}$ and $\phi_{ET} > 0.9$ at high concentrations of **4**, the inefficiency of sensitization must reflect a *relatively low reactivity of the diene triplet state*. Moreover, the close proximity of the quenching rate constant, k_q, to the diffusion limit ($\sim 1 \times 10^{10}$ M^{-1} s^{-1}) suggests that T_1 lies no more than 2–3 kcal above the $Ru(bpy)_3^{2+}$ triplet.[35] This estimate receives support from the data compiled in Table II, where it is seen that organic sensitizers having triplet energies well above the 47-kcal value for $Ru(bpy)_3^{2+}$ cause only a modest increase in the isomerization quantum yield. Such behavior is entirely consistent with the occurrence of exoergic energy transfer from these sensitizers to a triplet state of **4** having an energy of 47–50 kcal and an intrinsic quantum efficiency (i.e., $k_{isom'}/(k_{isc'} + k_{isom'})$) of 0.1–0.2.

Returning now to the question of singlet- vs. triplet-state reactivity upon direct photolysis of **4**, we can set an upper limit of 0.1 on the value of the second term in eq 4.[36] Recall that this term defines the efficiency of isomerization proceeding through T_1. Since $\phi_{isom}{}^{dir} \sim 0.7$, it is clear that the first term, representing prompt reaction from S_1, makes the dominant contribution to the overall quantum yield. That is, direct photoisomerization of **4** occurs largely (if not entirely) via the singlet excited state.[37]

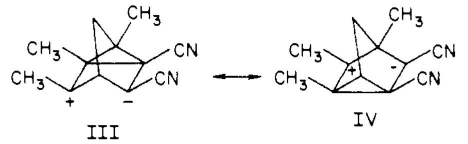
Let us summarize our findings to this point. We have presented evidence that the singlet excited state of substituted norbornadiene **4** decays to the corresponding quadricyclene structure much more efficiently than does the triplet state. This behavior, in turn, provides a ready explanation for the disparity between the quantum yields for direct (proceeding through S_1) and triplet-sensitized (proceeding through T_1) photoisomerization of the diene. As noted earlier, this pattern of excited-state reactivity contrasts sharply with that of the unsubstituted analogue, NBD, for which the triplet state is considerably more prone to rearrangement than the singlet.

Turro et al.[28] have interpreted the photochemical interconversion of NBD and Q in terms of the potential energy surfaces depicted in Figure 5.[38] The minimum on the singlet surface, starting from either isomer, occurs at a structure, D_N, that can be described as a "tight" 1,2-diradical. On the other hand, the favored geometry on the triplet surface corresponds to a structure, D_Q, which can be characterized as a "loose" 1,3-diradical. These diradicaloid geometries act as funnels[39] through which transitions to the ground-state surface are most likely to occur. Decay from the S_1 surface to S_0 with formation of a norbornadiene-type structure will be favored, since the S_1 funnel lies to the left of the maximum in the ground-state curve[40] and thus delivers singlet diradicals into the NBD well. Similar reasoning leads to the conclusion that intersystem crossing from the T_1 surface to S_0 at a geometry corresponding to D_Q favors production of a quadricyclene-type ground-state structure.

Within the framework of the Turro model, we propose that the S_1 and T_1 surfaces connecting **4** and **5** differ in one or more important respects from those of their unsubstituted analogues. Minimally, the incorporation of electron-donor and electron-acceptor substituents decreases both the S_1/ground-state and T_1/ground-state energy gaps. Moreover, the propensity of the singlet state of **4** to undergo valence isomerization most likely reflects an S_1 surface whose minimum lies closer to the quadricyclene structure (compare Figure 5, parts a and b). This shift of the minimum from the 1,2- toward the 1,3-diradicaloid geometry can be accounted for in terms of ionic contributions to the S_1 wave function.[28] For the parent hydrocarbons, the 1,2 structure is stabilized by the proximity of opposite charges in resonance forms I and II. In contrast, the 1,3 structure becomes more favorable in the substituted molecules owing to charge stabilization by the substituents in resonance forms III and IV. Decay from the S_1 surface to the ground state in the latter case should therefore favor production of **5**.



I II



III IV

Parallel arguments involving a T_1 surface whose minimum has shifted toward the 1,2-diradicaloid geometry (compare Figure 5, parts a and b) could account for the low triplet-state reactivity of **4**. Alternatively, this minimum may retain a 1,3 geometry but lie energetically below the maximum in the ground-state surface. This situation results in intersecting T_1–S_0 surfaces which, in turn, could provide a favorable relaxation pathway back to **4**. Determination of the triplet-state reactivity of **5** would be helpful in deciding between these possibilities.

In closing, we wish to make one practical observation concerning the suitability of triplet sensitization as a means of enhancing the wavelength response of energy storage systems based upon substituted norbornadienes. Although the sensitized isomerization of **4** to **5** is significantly less efficient than direct photolysis on a per-photon-absorbed basis, the former process can be driven with 546-nm irradiation. This ability to utilize a larger fraction of the available solar spectrum tends to counterbalance the lower quantum efficiency. Thus the factor of 4–6 in ϕ_{isom} favoring direct photolysis is largely offset by the gain in integrated photon flux that results upon extending the effective photoexcitation wavelength from 425 to 600 nm.[41] Consequently, in at least some norbornadiene-based energy storage cycles, triplet sensitization can give rise to rates of product formation that are competitive with or even greater than those for direct photolysis despite a seemingly unfavorable quantum efficiency of the sensitized reaction.

Acknowledgment. We are grateful to Dr. K. Takahashi for

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(35) This estimated difference in triplet-state energies is based upon the assumption that steric hindrance by the methyl and cyano substituents imposes no significant kinetic barrier to energy transfer. See: Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978, Chapter 9.

(36) The second term in eq 4 may be considerably smaller than 0.1 if S_1–T_1 intersystem crossing is inefficient.

(37) For example, let us assume that the only pathways available to S_1 are isomerization to **5** and intersystem crossing to T_1 (i.e., $k_{ic} = 0$ in eq 4). A simple calculation shows that ~88% of the product would be formed via the singlet state. An even higher percentage results if $k_{ic} \neq 0$.

(38) A molecular orbital analysis of the NBD–Q triplet surface has been reported: Raghavachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110.

(39) Michl, J. *Pure Appl. Chem.* **1975**, *41*, 507.

(40) This maximum corresponds to the transition state for thermal interconversion of NBD and Q.

(41) Robinson, N., Ed. "Solar Radiation"; Elsevier: New York, 1966; Chapter 1.

performing the electrochemical measurements, to Dr. M. Santhanam for conducting some exploratory experiments, and to a referee for some very helpful comments concerning the properties of diradicals. We thank the Science and Technology Agency, Japan, the U.S. National Science Foundation (Grants CHE-8210558 and INT-8309942), and the Oji Paper Company for financial assistance.

Registry No. 4, 84352-42-1; **5**, 87340-59-8; [Ru(bpy)$_3$]Cl$_2$, 14323-06-9; 9-fluorenone, 486-25-9; thioxanthone, 492-22-8; biacetyl, 431-03-8.

Carbon-13 and Oxygen-18 Kinetic Isotope Effects on Methanolysis of *p*-Nitrostyrene Oxide

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Abstract: Kinetic isotope effects for the acid- and base-catalyzed methanolysis of [*epoxide*-^{18}O]- and [8-^{13}C]-*p*-nitrostyrene oxide have been measured at 30.0°. In acid 94.7% of the reaction occurs at the benzylic carbon, while in base 83.5% occurs at the primary carbon (C(8)). In base the isotope effects k_{16}/k_{18} and k_{12}/k_{13} were 1.035 ± 0.013 and 1.082 ± 0.012, while in acid they were 1.012 ± 0.011 and 0.995 ± 0.012, respectively. These data complement previously determined deuterium isotope effects for the reaction in base. They suggest a late transition state in base with considerable ring opening via an S$_N$2 mechanism. However, in acid, the data suggest a somewhat earlier transition state with less ring opening and weaker bonding to the nucleophile than in base.

Epoxides are important intermediates in many synthetic and biosynthetic pathways, and they are potentially toxic intermediates in the biotransformation of aromatic and olefinic compounds. The chemical reactivity of epoxides arises from the strained three-membered ring. Because of their chemical reactivity and widespread involvement, epoxides and their reactions have been the subject of considerable interest.

The mechanisms of ring-opening reactions of epoxides with nucleophiles have been widely studied.[1,2] Many previous studies of epoxide ring-opening reactions have centered on the questions of degree of carbonium ion formation vs. requirement for nucleophilic participation under acidic conditions. These considerations are also relevant to current interest in the relationship between the chemical properties and the biological effects of epoxides.

Recently we utilized secondary kinetic deuterium isotope effects to characterize transition-state structures for the acid- and base-catalyzed methanolysis of *p*-nitrosytrene oxide (PNSO, **1**).[3a] We now report complementary ^{13}C and ^{18}O kinetic isotope effects which define further the transition states for these reactions.

Experimental Section

A. Instrumentation. Melting points were determined in open capillary tubes with a Thomas-Hoover Uni-melt melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained on Varian FT-80, T-60, or EM-360 spectrometers with tetramethylsilane as an internal standard. Mass spectra and selected ion monitoring data were obtained on a Nermag R10-10 quadrupole mass spectrometer by electron impact. HPLC analyses were performed with a Waters liquid chromatograph with an Altex 153 UV detector at 254 nm and a Varian CDS 111 digital electronic integrator. Kinetic studies were performed on a Cary 118C UV/vis recording spectrophotometer interfaced to a Cromemco Z-2 microcomputer for data collection.

B. Synthesis. *p*-Nitrostyrene (2a). (*p*-Nitrobenzyl)triphenylphosphonium bromide (50.3 g, 0.105 mol)[4] was dissolved in a mixture of 100 mL of ethanol and 100 mL of aqueous formaldehyde (37%, 2.77 mol). Aqueous sodium carbonate (30%, 100 mL) was added in 2-mL portions over a 2-h, period when the intermediate phosphorane (red color) faded to yellow. The solution was stirred for an additional 60 min and the white precipitate (triphenylphosphine oxide) which formed was filtered off. The product was extracted with twelve 50-mL portions of hexane. The crude product (21 g) was chromatographed on 350 g of silica gel with 10% ether in hexane, which yielded 13.5 g (86%) of pure **2a** as a yellow oil. ^{1}H NMR (CDCl$_3$) δ 5.44 (d, 1, J = 11 Hz, trans C8–H), 5.85 (d, 1, J = 18 Hz, cis C8–H), 6.78 (dd, J = 11, 18 Hz, C7–H), 7.50 (d, 2, J = 9 Hz, Ar), 8.18 (d, 2, J = 9 Hz, Ar).

[8-^{13}C]-*p*-Nitrostyrene (2b). (*p*-Nitrobenzyl)triphenylphosphonium bromide (7.96 g, 16.7 mmol) was dissolved in a mixture of 30 mL of ethanol and 10 mL of water. ^{13}C-Enriched formaldehyde (200 mg, 6.47 mmol, 90% ^{13}C, KOR Isotopes Lot DM-1-123) was added to the solution. Aqueous sodium carbonate (30%, 16 mL) was added dropwise over a 3-day period. The white precipitate which formed (triphenylphosphine oxide) was filtered off, and the product was extracted with three 30-mL portions of hexane. The hexane was removed, and the crude product (2.39 g) was chromatographed on 30 g of silica gel with 6% ether in hexane which yielded 1.77 g of a mixture consisting of ca. 55% *p*-nitrostyrene (100% yield) and 45% *p*-nitrotoluene; this mixture was used directly for bromohydrin formation.

2-Bromo-1-(4-nitrophenyl)ethanol (3a). The styrene **2a** (4.85 g, 32.5 mmol) was dissolved in 75 mL of acetonitrile, 50 mL of water and 6.27 g of *N*-bromosuccinimide (35.2 mmol) were added, and the mixture was stirred for 90 min. The acetonitrile was removed under reduced pressure, and the product was extracted with four 40-mL portions of ether. The ether was dried over Na$_2$SO$_4$, filtered, and evaporated to obtain the crude product (8.68 g). The latter was purified on 175 g of silica gel with 30–40% ether in hexane, yielding 7.25 g (91%) of pure product. Mp 83–84 °C; ^{1}H NMR (CDCl$_3$) δ 2.84 (d, 1, J = 4 Hz, OH), 3.53 (d, 1, J = 8 Hz, CH$_2$Br), 3.57 (d, 1, J = 4 Hz, CH$_2$Br), 5.00 (m, 1, C7–H), 7.54 (d, 2, J = 9 Hz, Ar), 8.21 (d, 2, J = 9 Hz, Ar).

[2-^{13}C]-2-Bromo-1-(4-nitrophenyl)ethanol (3b). This bromohydrin was prepared as described for **3a** with crude **2b** (contaminated with *p*-nitrotoluene, see above). From 1.06 g of crude **2b** (corresponding to *ca.* 596 mg of pure **2b**) a total of 997 mg of pure **3b** (102%) was obtained. ^{1}H NMR (CDCl$_3$) δ 2.28 (d, 0.5, J = 8 Hz, $J(^{13}$C–H) = 76 Hz, CH$_2$Br), 2.33 (d, 0.5, J = 4 Hz, $J(^{13}$C–H) = 76 Hz, CH$_2$Br), 3.17 (br s, 1, OH), 5.00 (m, 2, CH$_2$Br, C7–H), 7.54 (d, 2, J = 9 Hz, Ar), 8.19 (d, 2, J = 9 Hz, Ar).

[^{18}O]-2-Bromo-1-(4-nitrophenyl)ethanol (3c). The styrene **2a** (304 mg, 2.01 mmol) was dissolved in 6 mL of dry acetonitrile, 450 mg of *N*-bromosuccinimide (2.53 mmol) and 1 mL of [^{18}O]-enriched water (97 atom %, KOR Isotopes Lot YE-I-11) were added, and the mixture was stirred for 6 h. The acetonitrile and [^{18}O]-water were removed by

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(1) For leading references see: Dansette, P. M.; Makedonska, V. B.; Jerina, D. M. *Arch. Biochem. Biophys.* **1978**, *187*, 290 and also ref 3.

(2) Lynas-Gray, J. I.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 483.

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