

filtrate was concentrated in vacuo to afford crude **8** (mixture of syn and anti diastereoisomers, 2.48 g, 95%). The crude product was purified via recrystallization from methylene chloride-pentane mixed solvent to afford pure **8** (a single diastereoisomer of unknown configuration, 1.89 g, 76%) as a colorless microcrystalline solid, mp 104.5–105.8 °C; ¹H NMR (CDCl₃) δ -0.11 (s, 9 H), 1.42 (AB, J_{AB} = 11 Hz, 1 H), 1.75 (AB, J_{AB} = 11 Hz, 1 H), 2.11–3.04 (m, 9 H); ¹³C NMR (CDCl₃) δ -2.85 (q, 3 C), 36.80 (d), 38.38 (t), 39.40 (d), 41.35 (d), 42.01 (d), 42.71 (d), 44.55 (d), 52.08 (d), 53.92 (d), 56.79 (d), 67.63 (s), 215.74 (s); IR (film) 3055 (w), 2968 (s), 2905 (w), 1735 (s), 1426 (m), 1267 (s), 1252 (s), 1104 (w), 924 (w), 908 (m), 890 (m), 862 (m), 844 cm⁻¹ (m); mass spectrum (70 eV), *m/e* (relative intensity) 260.2 (molecular ion, 2.7), 176.1 (20.6), 155.1 (6.2), 151.2 (6.7), 129.1 (8.7), 128.1 (7.7), 115.1 (11.2), 91.1 (10.1), 77.1 (9.4), 75.1 (20.9), 74.1 (9.4), 73.1 (100.0), 45.1 (24.3), 43.0 (13.5).

Anal. Calcd for C₁₅H₂₀O₂Si: C, 69.19; H, 7.74. Found: C, 69.42; H, 7.79

8,11-Bis((trimethylsilyl)methylene)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (7). To a solution of bis(trimethylsilyl)methane (6.42 g, 0.04 mol) in 4:1 THF-HMPA mixed solvent (80 mL) under argon maintained between -90 and -78 °C was added *tert*-butyllithium (20 mL of a 2 M solution in pentane, 0.04 mol). The resulting solution was stirred (10 h) while the temperature was maintained between -60 and -50 °C. A solution of **1** (3.484 g, 0.02 mol) in dry THF (20 mL) was then added to the reaction mixture during 10 min; the temperature was maintained at -60 °C throughout the time of addition. The reaction mixture was stirred at -60 °C (2.5 h) and then allowed to warm slowly to room temperature overnight with stirring. The reaction mixture was then poured into saturated aqueous ammonium chloride solution (200 mL) and then stirred (10 min). The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with water several times to remove the last traces of HMPA. The organic layer was then dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford crude **7** (mixture of

diastereoisomers, 3.73 g, 59%). The crude product was purified by column chromatography on silica gel (pentane eluent); pure **7** (mixture of diastereoisomers, 2.61 g, 42%) was thereby obtained as a colorless oil: bp 103–106 °C (0.02 mm); ¹H NMR (CDCl₃) δ 0.06–0.11 (overlapping singlets, 9 H), 1.61 (AB, J_{AB} = 11 Hz, 1 H), 1.93 (AB, J_{AB} = 11 Hz, 1 H), 2.24–3.28 (m, 8 H), 5.06, 5.17 (singlets, total 1 H); ¹³C NMR (CDCl₃) δ 0.51 (q), 0.73 (q), 35.59 (t), 37.02 (t), 41.46 (d), 41.63 (d), 42.50 (d), 42.66 (d), 43.40 (d), 43.69 (d), 46.61 (d), 47.31 (d), 47.53 (d), 47.75 (d), 48.78 (d), 49.05 (d), 50.40 (d), 51.75 (d), 57.06 (d), 57.17 (d), 117.74 (d), 117.90 (d), 118.01 (d), 162.16 (s), 162.87 (s), 163.08 (s); IR (film) 2948 (vs), 2900 (s), 2870 (s), 1624 (vs), 1458 (m), 1405 (m), 1290 (m), 1244 (vs), 1109 (w), 868 (vs), 840 (vs), 758 (s), 692 cm⁻¹ (s); mass spectrum (70 eV), *m/e* (relative intensity) 314.2 (molecular ion, 4.4), 241.2 (15.2), 240.2 (14.1), 211.1 (7.4), 167.1 (11.9), 166.1 (10.2), 74.1 (7.6), 73.0 (100.0), 59.0 (15.4), 45.0 (19.3), 43.0 (10.1).

Anal. Calcd for C₁₉H₃₀Si₂: C, 72.54; H, 9.61. Found: C, 72.45; H, 9.75.

Acknowledgment. Financial support of our study by the Naval Air Systems Command, The Robert A. Welch Foundation (Grant No. B-963), the Air Force Office of Scientific Research, and the North Texas State University Faculty Research Committee is gratefully acknowledged. A.D.B. acknowledges a grant from the PSC-BHE CUNY Research Award Program (Grant No. 6-63222).

Supplementary Material Available: A listing of coordinates and vibrational frequencies for **1**, **2**, and **3** and two figures showing the variations in HOMO, NHOMO, LUMO, and NLUMO energies for **1** and **3** that occur when various overlap matrix elements are deleted (7 pages). Ordering information is given on any current masthead page.

Photochemical Transformations. 46. Photophysics and Photochemistry of Some Compounds Undergoing Light-Induced Solvolysis and Wagner–Meerwein Rearrangement¹

Stanley J. Cristol,* Ellen O. Aeling, S. J. Strickler, and Robert D. Ito

Contribution from the Department of Chemistry & Biochemistry, University of Colorado, Boulder, Colorado 80309-0215. Received April 2, 1987

Abstract: Absorption maxima, fluorescence maxima, and fluorescence quantum yields are reported for a variety of 7-substituted and 7,8-disubstituted dibenzobicyclo[2.2.2]octadienes and veratrolobenzobicyclo[2.2.2]octadienes in cyclohexane and/or acetonitrile. Singlet lifetimes have been computed from these data. Those compounds that are reactive toward photosolvolysis and/or Wagner–Meerwein photorearrangement have fluorescence yields (and lifetimes) 10⁻²–10⁻⁴ times those of the corresponding compounds containing only hydrogens on the saturated bridges. Compounds that are photoinert but have an electron-attracting group on the bridge have lifetimes about one-tenth those of unsubstituted compounds. These results and the variations in fluorescence maximum wavelengths are rationalized by assumptions that there is some degree of charge transfer from aromatic ring to C–X bond in the photoexcited state and that this favors decay to the ground state. When more or less complete intramolecular electron transfer to a zwitterionic biradical intermediate is exergonic, lifetimes in the 4–80-ps range are computed.

For some time, members of our research group have been studying photosolvolysis and Wagner–Meerwein photorearrangements. Recently, we reported² results on photochemical yields of [3.2.1] products from the *cis* and *trans* isomers of 7,8-dichloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-dienes **1** and **2**,

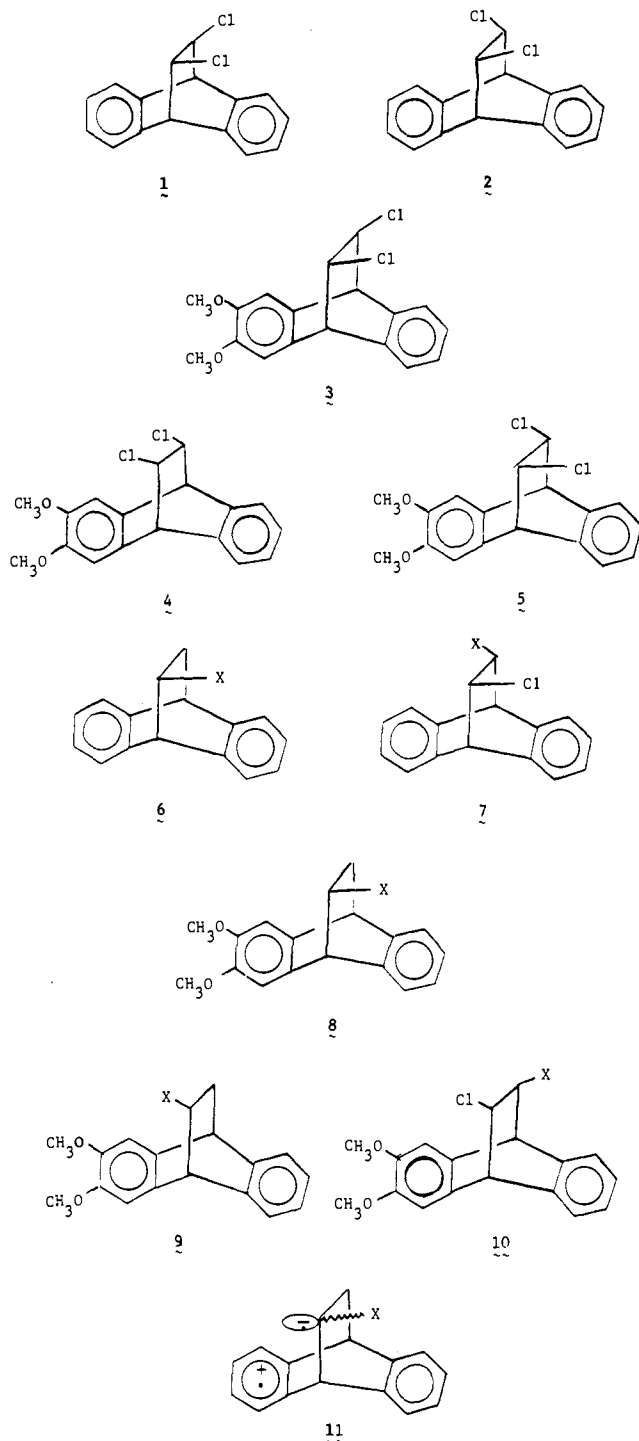
irradiated in acetonitrile or in acetic acid. Similar results were reported previously³ on the corresponding veratrol–benzo systems **3–5**, irradiated in acetic acid. In addition, results on a variety of species **6–10**, irradiated in acetic acid, have been reported.⁴ All

(1) Cristol, S. J.; Aeling, E. O. *J. Am. Chem. Soc.* **1987**, *109*, 830.

(2) Cristol, S. J.; Opitz, R. J. *J. Org. Chem.* **1985**, *50*, 4558.

(3) Cristol, S. J.; Seapy, D. G.; Aeling, E. O. *J. Am. Chem. Soc.* **1983**, *105*, 7337.

(4) Cristol, S. J.; Aeling, E. O. *J. Org. Chem.* **1985**, *50*, 2698.



of these results (where possible to determine), as well as others,³⁻⁵ showed preferential loss of nucleofugal group anti to the chromophoric ring or loss of chloride ion in preference to ions such as methanesulfonate or acetate. The anti preference was rationalized by noting the Coulombic advantage involved in electron transfer from the π^* orbital of an excited aromatic ring to the σ^* orbital of a carbon-chlorine bond, whose lobe anterior to the carbon atom would contain the greater fraction of the electron density when (partially) occupied.⁶ That lobe is significantly

closer to the electron-deficient aromatic ring than is any portion of the σ^* orbital of a syn carbon-chlorine bond. Thus, the zwitterionic biradical (π, σ^* state) **11** resulting from electron transfer to a carbon-chlorine bond anti to the excited aromatic ring should be thermodynamically more stable than that to one syn to it and thus should be more readily formed.^{2-5,7} In similar fashion, the argument has been made that electron transfer to the more readily reducible carbon-chlorine bond should occur in preference to that to the less readily reduced carbon-(methanesulfonyloxy) or carbon-acetoxy bonds.^{4,7}

If these ideas are correct, the requirement for intramolecular electron transfer is the key for reactivity. The resulting zwitterion **11** may have a variety of reaction channels available to it. It may lose X^- to give a biradical cation, either concerted with aromatic ring migration or preceding it, or it may return to the ground state of the reactant by reverse electron transfer. The π, π^* state preceding electron transfer similarly may have several reaction channels. It may fluoresce, reverting to ground state (rate constant k_F), intersystem cross to triplet (k_{ISC}), give zwitterion **11** (k_{ET}), or otherwise decay nonradiatively to ground state (k_D). In the absence of electron transfer, the lifetime of the π, π^* state ${}^1\tau_0$ is given by eq 1 and the fluorescence quantum yield by eq 2, while for reactive species, the lifetime ${}^1\tau_R$ is given by eq 3, the fluorescence yield by eq 4, and the reaction quantum yield by eq 5, if the triplet is inert to electron transfer,⁸ where F_R is the fraction of zwitterion **11** undergoing carbon-X bond cleavage.

$${}^1\tau_0 = (k_F + k_{ISC} + k_D)^{-1} \quad (1)$$

$$\phi_F = k_F {}^1\tau_0 \quad (2)$$

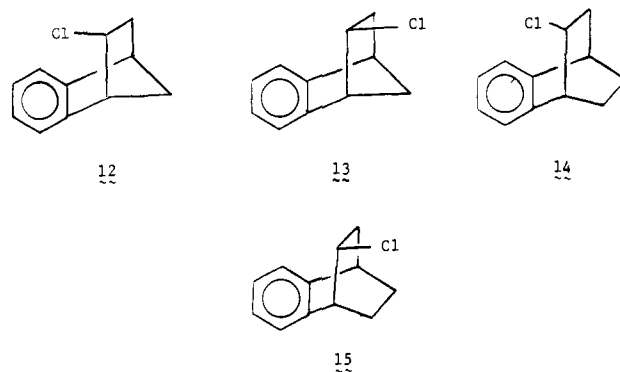
$${}^1\tau_R = (k_F + k_{ISC} + k_{ET} + k_D)^{-1} \quad (3)$$

$$\phi_F = k_F {}^1\tau_R \quad (4)$$

$$\phi_R = k_{ET} {}^1\tau_R F_R \quad (5)$$

It seems possible then to predict, with some degree of confidence, that those compounds in our system that are photoinert will have higher fluorescence quantum yields and longer lifetimes than those that are photoactive. In order to test this and, as well, to get values approximating k_{ET} (or more precisely, estimating $k_{ET}F_R$), we undertook a photophysical study of certain of the [2.2.2] compounds mentioned above.

Indeed, Morrison and co-workers have reported data consistent with these ideas on chloro derivatives of benzobicyclo[2.2.1]hept-2-ene¹⁰ and benzobicyclo[2.2.2]oct-2-ene.¹¹ *endo*-5-Chlorobenzonorborene (**12**), with chlorine syn to the aromatic chromophore, has a quantum yield for fluorescence of 0.11 in hexane (the comparable fluorescence yield for the hydrocarbon benzonorborene is 0.24) and a singlet lifetime of 12.6 ns. The ϕ_F in methanol is also 0.11, and ${}^1\tau$ was measured as 10.9 ns, with the quantum yield ϕ_R for "ionic" products¹² of 0.011.



(5) (a) Cristol, S. J.; Optiz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977. (b) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *Ibid.* **1983**, *105*, 1218. (c) Cristol, S. J.; Dickenson, W. A. *J. Org. Chem.* **1986**, *51*, 3625.

(6) (a) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic: New York, 1974; p 104. (b) Jorgensen, W. L. *J. Am. Chem. Soc.* **1978**, *100*, 1049.

(7) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 279.

(8) This is generally, but not always, the case.^{2-4,9}

(9) Cristol, S. J.; Bindel, T. H.; Hoffman, D.; Aeling, E. O. *J. Org. Chem.* **1984**, *49*, 2368.

(10) Morrison, H.; Miller, A.; Bigot, B. *J. Am. Chem. Soc.* **1983**, *105*, 2398.

(11) Morrison, H.; Muthuramu, K.; Pandey, G.; Severance, D.; Bigot, B. *J. Org. Chem.* **1986**, *51*, 3358.

Table I. Absorption and Fluorescence Data on Some 7-Substituted and 7,8-Disubstituted Dibenzobicyclo[2.2.2]octadienes (**16**) and Their Photoreactivities

substituent(s)	solvent ^a	ϵ_{\max}^b	ϕ_F^c	${}^1\tau_{\text{calcd}}^d$, ns	λ_{\max}^F , nm	ϕ_R^e
X = Y = H	CH		0.44	27		0
	AN	1650	0.51	33	286	0
X = OH, Y = H	AN	1400	0.06	4	290	0
X = OAc, Y = H	AN	1320	0.03	2	290	0
X = OMs, Y = H	AN	1230	0.06	4	290	0
X = Cl, Y = H	CH		0.05	4	290	
	AN	1250	1×10^{-3}	0.08	290	+(AN) ^f
X = Cl, Y = OAc (trans)	AN	930	4×10^{-3}	0.4	290	+(HA)
X = Y = Cl (trans)	CH		1×10^{-3}	0.1		0.03 (CH)
	AN	780	3×10^{-5}	0.004	290	0.20 (AN) 0.15 (HA)
X = Y = Cl (cis)	CH		1×10^{-3}	0.2		0.22 (AN)
	AN	550	4×10^{-5}	0.007	290	0.10 (HA)

^a CH = cyclohexane, AN = acetonitrile, HA = acetic acid. ^b All compounds had absorption maxima at 272 nm. ^c Excitation wavelength 254 nm. ^d Calculated by use of eq 6. ^e Quantum yield of ionic products in solvent indicated; ² when + indicated, the compound was reactive, but the quantum yield was not measured. ^f Data of: Opitz, R. J. Ph.D. Thesis, University of Colorado—Boulder, 1980; p 203.

Table II. Absorption and Fluorescence Data on Some 7-Substituted and 7,8-Disubstituted Derivatives of Veratrolobenzobicyclo[2.2.2]octadiene (**17**) in Acetonitrile and Their Photoreactivities in Acetic Acid

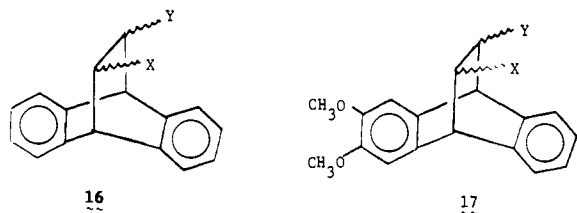
substituent(s)	ϵ_{\max}^a	ϕ_F^b	${}^1\tau_{\text{calcd}}^c$, ns	λ_{\max}^F , nm	ϕ_R^d
X = Y = H	5420	0.45	8	304	0
X = OH (syn), Y = H	5770	0.03	0.5	319	0
X = OAc (syn), Y = H	5770	0.02	0.4	318	0
X = OMs (syn), Y = H	4840	3×10^{-3}	0.06	318	+
X = Cl (syn), Y = OH (anti)	5300	2×10^{-3}	0.04	323	+
X = Cl (syn), Y = OAc (anti)	5410	2×10^{-3}	0.04	324	+
X = Cl (syn), Y = OMs (anti)	5070	2×10^{-3}	0.04	322	+
X = Y = Cl (syn-cis)	5300	7×10^{-4}	0.01	322	0.048
X = Y = Cl (anti-cis)	5270	7×10^{-4}	0.01	322	0.21
X = Y = Cl (trans)	5870	8×10^{-4}	0.01	324	0.14

^a All compounds had λ_{\max} at 286–288 nm. ^b Excitation wavelength 285 nm. ^c Calculated by use of eq 6. ^d Quantum yield of ionic products; when + indicated, compound was active but quantum yield was not measured.

The exo isomer **13** (with an anti chlorine) has a ϕ_F of 0.065 and ${}^1\tau$ of 4.8 ns in hexane, with substantial formation of products derived from homolysis of the carbon–chlorine bond. In methanol, ϕ_F was reduced to 0.007 and ${}^1\tau$ to 0.5 ns, with $\phi_R = 0.16$ for ionic products.

In like fashion, the endosyn isomer **14** has similar ϕ_F values in cyclohexane (0.12) and in methanol (0.11) and similar lifetimes (cyclohexane, 21.7 ns; methanol, 18.3 ns). The corresponding hydrocarbon benzobicyclo[2.2.2]octene has $\phi_F = 0.20$ and ${}^1\tau = 25$ ns. The exo (anti) chloride **15** had ϕ_F and ${}^1\tau$ values substantially lower in methanol (0.01₅ and 1.2 ns) than in cyclohexane (0.09₅ and 13.0 ns) with $\phi_R = 0.20$ (as compared with the endo ϕ_R of 0.002) in methanol.

Data on our compounds in the dibenzo series **16** are given on Table I and those in the veratrol–benzo system **17** are given in Table II. As the singlet lifetimes for most of the compounds



studied were too short for us to measure with the nanosecond equipment available to us, approximate values were computed from eq 6.¹³ Use of a more precise relationship¹⁴ was judged to be

$${}^1\tau = \phi_F / 10^4 \epsilon_{\max} \quad (6)$$

(12) We have selected from the products reported those plausibly derived from a cation intermediate, as Morrison and co-workers report both radical and ionic products.^{10,11}

pointless as transitions to at least two states overlapped in the absorption spectra. The use of any relationship between absorption intensity and lifetime depends on the assumption that the transition to the emitting state is responsible for a large fraction of the observed absorption in the region of the lowest band. We believe it likely that this is the case, but if emission were coming from a very weakly allowed state, the lifetimes calculated could be too short.

The data obtained are, in general, consistent with the expectations outlined above. With only hydrogen atoms present at C-7 and C-8 in either **16** or **17**, the fluorescence quantum yields ϕ_F approach 0.5 in acetonitrile and are comparable (measured only for **16**) in acetonitrile and in cyclohexane. The ϕ_F for the dibenzo compound is somewhat larger than that (0.19) reported¹⁵ for *o*-xylene, while that for **17**-H is comparable with that (0.40) we measured for veratrol. Calculated values for ${}^1\tau$ are about 30 ns for **16**-H and 8 ns for **17**-H. Monosubstitution with nonleaving groups (OH, OAc, and OMs in **16** and OH and OAc in **17**) reduces ϕ_F by about 1 order of magnitude, which we discuss below.

When **16** is monosubstituted by a chlorine atom (which is ultimately lost as chloride ion), ϕ_F is reduced to 1×10^{-3} (0.2% of that of **16**-H) in acetonitrile, with a lifetime calculated to be about 80 ps. This compound is photoactive in the polar solvent acetonitrile but not in nonpolar cyclohexane, where ϕ_F is 50 times greater than in acetonitrile.

(13) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; p 90. (b) Uses of analogous procedures have been described by Dalton and Turro^{13c} and by Zimmerman and co-workers,^{13d,e} with varying success. The problems associated with such procedures have been discussed.^{13c} (c) Dalton, J. C.; Turro, N. J. *J. Am. Chem. Soc.* **1971**, *93*, 3569. (d) Zimmerman, H. E.; Baum, A. A. *Ibid* **1971**, *93*, 3646. (e) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *Ibid* **1974**, *96*, 439.

(14) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

(15) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Compounds*, 2nd ed.; Academic: New York, 1971.

With dichloro-**16** compounds in acetonitrile, ϕ_F is reduced further ($3-4 \times 10^{-5}$), with computed singlet lifetimes below 10 ps. Here ϕ_R 's in the range of 0.1-0.2 in acetic acid or acetonitrile are observed. In cyclohexane, the value for ϕ_F is 1×10^{-3} , and the compounds are photoactive for Wagner-Meerwein rearrangement in cyclohexane, although with moderately low quantum efficiencies. Thus, both fluorescence and reactivity quantum yields show large solvent effects.

The veratrol-**benzo** compounds **17** follow a similar pattern. Monosubstitution with a nonleaving group (OH, OAc) leads to reduction of ϕ_F and ${}^1\tau$ by a factor of 15-20. In **17**, unlike **16**, methanesulfonate is a nucleofuge, and this substitution reduces ϕ_F and ${}^1\tau$ to values similar to those produced by chlorine substitution. Like dichloro-**16**, dichloro-**17** isomers have ϕ_F and ${}^1\tau$ values lower than monochlorinated species.

In addition to the effect of substitution on fluorescence intensity, we note an effect on the wavelengths of the fluorescence maxima (the fluorescence spectra are broad and structureless). In the dibenzo (**16**) system, both mono- and disubstitution lead to a 4-nm increase. The increase is considerably greater in the veratrol-**benzo** systems (**17**), where monosubstitution leads to a 14- to 15-nm red shift and disubstitution to an 18- to 20-nm shift. These results may be rationalized by the assumption that the S_1 states of the substituted compounds have some degree of charge transfer, greater in the veratrol-**benzo** compounds, which have lower excited-state oxidation potentials,³ than in the benzo compounds, without a similar degree of charge transfer in the ground state.

As mentioned above, compounds **16** with monohydroxy, -acetoxy, and -(methanesulfonyl)oxy groups and **17** with monohydroxy and -acetoxy groups have moderately (ca. 10-fold) reduced ϕ_F and ${}^1\tau$ values, compared with the hydrocarbons, although they are not photoactive, within the limits of our measurements. These data and those on emission wavelengths suggest that charge transfer promotes decay modes of S_1 to S_0 , although the manner in which this is accomplished remains to be elucidated. In this regard, corresponding data¹⁵ on toluene, benzyl alcohol, and benzyl acetate in cyclohexane may be of interest. The latter two compounds have ϕ_F 's of 0.08 and 0.07, values somewhat less than 50% of that of toluene, 0.17, and the (measured) singlet lifetimes are 29 and 17 ns, as compared with that of toluene of 34 ns. It has also been shown¹⁶ that the decrease in quantum yields (measured

in cyclohexane) for benzyl alcohol ($\phi_F = 0.074$) compared with toluene ($\phi_F = 0.23$) was greater than that for β -phenylethyl alcohol ($\phi_F = 0.094$) and that γ -phenylpropyl alcohol ($\phi_F = 0.16$) had a still greater fluorescence yield. All of these are photoinert.¹⁷ While these reductions are not as dramatic as those we report, they are qualitatively similar. They show that the radiationless decay modes are markedly dependent upon the distance between the aromatic ring and the carbon-X bond. The fixation of bond distances and bond angles in the rigid bicyclooctane system compared with these acyclic systems appears to be reflected in the enhanced effects we observe.

We conclude that ideas regarding electron transfer¹⁻⁵ as the key step in photosolvolysis and Wagner-Meerwein photorearrangements in these bridged systems are consistent with and confirmed by results described in this paper.

Experimental Section

All of the compounds used, except the veratrol-**benzo** "hydrocarbon" **17** ($X = Y = H$), have been previously reported.¹⁻⁵ **17** ($X = Y = H$) was prepared from *trans*-**17** ($X = Y = Cl$) by Dr. M. Z. Ali by azobis(isobutyronitrile)-promoted reduction with tri-*n*-butyltin hydride.

Samples were purified by repeated recrystallization (filtered through and collected on sintered-glass funnels). Solutions were generally prepared at about 10^{-3} - 10^{-4} M in spectrograde solvents, placed in fluorescence cells, covered with septa and deoxygenated in a stream of nitrogen.

Fluorescence spectra were measured on a Perkin-Elmer Model MPF-2A fluorimeter using an excitation bandwidth of 10 nm. Fluorescence quantum yields were determined relative to that of anisole in cyclohexane, whose yield was taken as 0.29.¹⁵ Relative integrated fluorescence intensities of deoxygenated solutions were corrected for differences in light absorption by the samples and the standard over the excitation bandwidth and for the refractive index of the solvent. It was assumed that all fluorescences were similar enough that corrections for wavelength-dependent instrumental response were not necessary.

Acknowledgment. The authors are indebted to the National Science Foundation (Grant CHE 85-03422 and predecessor grants) for partial support of this work.

(16) Berenfeld, V. M.; Kronganz, V. A. *Dokl. Akad. Nauk SSSR* **1965**, *162*, 1300.

(17) Interestingly, benzyl chloride, which is photoactive,¹⁸ has a quantum yield of about one-tenth of that of the alcohol.

(18) Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327.

Reactions of Triazolinediones with Alkoxy-Substituted 1,3-Butadienes. Rearrangements of 2 + 2 to 4 + 2 Cycloadducts

Edward L. Clennan* and Arthur D. Earlywine

Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071. Received April 10, 1987

Abstract: The reactions of *N*-methyl- and *N*-phenyltriazolinedione with electron-rich 1,3-butadienes are reported. Reaction with (*Z,Z*)-1,4-di-*tert*-butoxy-1,3-butadiene in acetone produced two acetone insertion products and two 4 + 2 adducts. The major 4 + 2 adduct was the unanticipated *cis*-2,5-di-*tert*-butoxy compound. At low temperatures two intermediates were observed by NMR that rearranged and reacted with acetone at temperatures higher than -50 °C to give the four products. These intermediates were identified spectroscopically as 2 + 2 adducts. Potential mechanisms for these reactions are discussed.

Triazolinediones **1** are singlet oxygen mimics,¹ undergoing 2 + 2, 4 + 2, and ene reactions. They also undergo reactions with

azines² and sulfides³ that mirror singlet oxygen reactivity. The recent focus of interest in triazolinedione chemistry, stimulated by this similarity to singlet oxygen,^{1a} has revolved around the

(1) (a) Greene, F. D. In *Stereochemistry and Reactivity of Systems Containing π Electrons*; Watson, W. H., Ed.; Verlag Chemie: New York, 1983. (b) Cheng, C.-C.; Seymour, C. A.; Petti, M. A.; Greene, F. D. *J. Org. Chem.* **1984**, *49*, 2910.

(2) Sato, R.; Sonobe, H.; Akasaka, T.; Ando, W. *Tetrahedron* **1986**, *42*, 5273.

(3) Ando, W.; Ito, K.; Takata, T. *Tetrahedron Lett.* **1982**, 3209.